ELSEVIER

Inorganica Chimica Acta 225 (1994) 323–326

Inorganica Chimica Acta

Note

Electron transfer properties of ReO(ECD)

J.E. Anderson[a,b,*], C.M. Murphy[b], S.M. Sawtelle[b], D.S. Edwards[a,*]

[a] *Du Pont Merck Pharmaceutical Company, Radiopharmaceutical Division, 331 Treble Cove Road, N. Billerica, MA, 01862, USA*
[b] *Department of Chemistry, Merkert Chemistry Center, Boston College, 2609 Beacon Street, Chestnut Hill, MA 02167-3860, USA*

Received 25 November 1993

Abstract

The electron transfer properties of the complex, ReO(ECD), where H_2ECD is *N,N'*-1,2-ethylenediylbis-L-cysteine, diethyl ester, are reported. The results of this study will demonstrate that ReO(ECD) has an unusual reductive electron transfer mechanism, in that the addition of one electron to this complex results in the loss of H˙ from the ligand. This corresponds to the net loss of a proton (H^+) from the complex and hence the product of the reduction is the same as that obtained by the reaction of a base with ReO(ECD) to form $[ReO(ECD)]^-$.

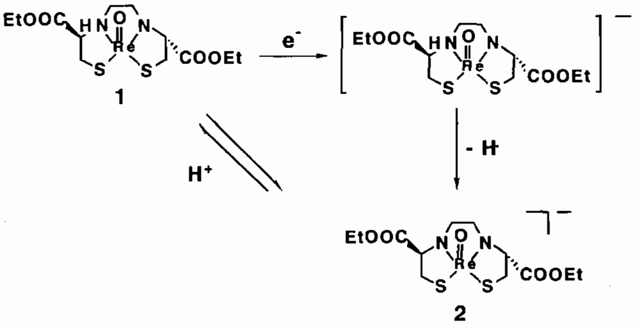
Keywords: Electron transfer; Rhenium complexes; Oxo complexes; Multidentate ligand complexes; Chelate complexes

---

1. Introduction

We recently reported electrochemical data for tin(II) and tin(IV) complexes of H_2ECD [1], where H_2ECD is *N,N'*-1,2-ethylenediylbis-L-cysteine, diethyl ester. H_2ECD is a multidentate ligand with an N_2S_2 coordination site which can incorporate several different metals. For example, the radiopharmaceutical Neurolite®, which is designed to image the brain, is based on the Tc(V) complex TcO(ECD) [2][1]. We wish to report the reductive electron transfer properties of the Re(V) complex ReO(ECD) (**1**), which is analogous to TcO(ECD), and is shown diagrammatically in Scheme 1. The aim of this study was to further examine how the electronic properties of this ligand influence the redox properties of transition metal species.

The results of this study are of general interest, however. It will be demonstrated that ReO(ECD) has a reductive electron transfer mechanism that involves the addition of one electron to **1** followed by the loss of H˙ from the ligand as a coupled chemical reaction, as shown in Scheme 1. This corresponds to the net loss of a proton (H^+) from the complex and hence the product of the reduction is the same as that obtained by the reaction of a base with ReO(ECD) to form $[ReO(ECD)]^-$ (**2**). This is an unusual reductive mechanism for transition metal complexes.



Scheme 1.

2. Experimental

2.1. Equipment and techniques

Electrochemical experiments were performed with a BAS-100A. A platinum button working electrode, approximate area 0.004 cm², a platinum wire counter

---

*Corresponding authors.

[1] The trianion, ECD^{3-}, form of H_2ECD is coordinated to Tc in TcO(ECD), due to deprotonation of the two SH and one of the NH groups.

SSDI 0020-1693(94)04020-V

electrode and an SCE reference electrode separated from the solution with a bridge were the three electrode system. All potentials are reported versus the SCE electrode and, in addition, ferrocene was used as an internal standard. The concentration of the supporting electrolyte was 0.2 M unless otherwise stated.

Electronic spectroelectrochemical data were recorded with a Perkin-Elmer Lambda 3B UV–Vis spectrometer, interfaced to an IBM PS/2 model 50 computer with PECSS software, using a BAS CV-27 potentiostat coupled to an IBM 7427 MT X-Y-T recorder. The electrodes in the spectroelectrochemical cell were a large platinum minigrid working electrode, a platinum wire counter electrode and a Pt wire pseudo-reference electrode. The supporting electrolyte concentration was 0.2 M unless otherwise stated.

The electrochemical cells were all home built and were designed for analysis of air sensitive species [3,4]. All solid and solution transfers were carried out by standard Schlenk methodologies [5]. Conventional UV–Vis measurements were performed with cells designed for inert atmosphere measurements.

Conductivity experiments were performed on a YSI model 31A conductivity bridge. NMR spectra were obtained with a GE QE-300 NMR spectrometer and FT-IR measurements were made with a Nicolet 510 FT-IR spectrometer.

2.2. Materials

The acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) used for electroanalysis were purchased (Aldrich) as spectroscopic grade, purified and dried by standard methods [6] and stored over calcium hydride (CH_3CN), phosphorous pentoxide (CH_2Cl_2) or sodium/benzophenone (THF) under an inert atmosphere and distilled just prior to use. Tetrabutylammonium perchlorate (TBAP) was purchased from Fluka, doubly recrystallized from ethanol and dried in a vacuum oven at 50 °C.

3. Results and discussion

Fig. 1(a) is the UV–Vis spectrum of ReO(ECD) in CH_3CN which indicates an absorption band at 350 nm for this complex. Upon the addition of 1 equiv. of NaOH in ethanol to **1** in acetonitrile, the original absorption band decreases and new bands are found at 260 and 305 nm with a shoulder at 350 nm, as shown in Fig. 1(b). The product is $[Re(O)ECD]^-$ (**2**)[2] as shown in Scheme 1. The ^1H NMR of ReO(ECD) has a resonance at 6.58 ppm due to the N–H proton which is absent after the neutralization reaction. (Complete analytical characterization of ReO(ECD) is reported in Ref. [2].) Consequently, addition of base results in the loss of the N–H proton from ReO(ECD). The neutralization reaction is reversible and can be cycled multiple times between **1** and **2**.

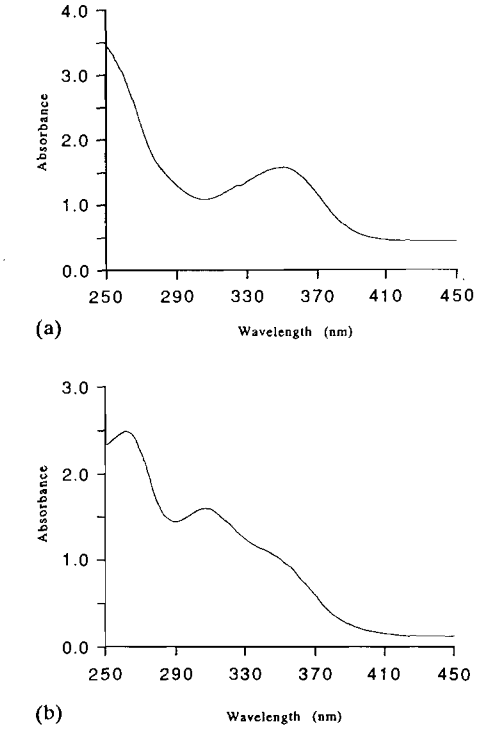


Fig. 1. UV–Vis data for: (a) a solution of ReO(ECD) in CH_3CN; (b) a solution of ReO(ECD) in CH_3CN titrated with 1.0 equiv. of NaOH in ethanol.

Fig. 2(a) shows the cyclic voltammetric data obtained when the potential is scanned from -0.30 to -2.0 V versus SCE for **1** dissolved in CH_3CN with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. As shown in Fig. 2(a), one reduction wave (wave 1a, Fig. 2(a)) is found at $E_{pc} = -1.20$ V versus SCE at a scan rate of 100 mV/s. Wave 1 is characterized by a value of $E_p - E_{p/2}$ of 100 mV[3], a constant ratio

---

[2] $[ReO(ECD)]^-$ can be isolated as the salt $[Ph_4As][ReO(ECD)]$ by the addition of 1 equiv. of 1.0 N NaOH to an aqueous acetonitrile solution of ReO(ECD), followed by the addition of 1 equiv. of $[Ph_4As][Cl]$. ^1H NMR ($CDCl_3$, 270 MHz): δ 7.85 – 7.70 (12H, m), 7.70 – 7.65 (8H, m), 4.33 – 4.31 (1H, dd), 4.19 – 4.06 (3H, m), 3.99 – 3.79 (3H, m), 3.66 – 3.60 (1H, m), 3.49 – 3.43 (1H, m), 3.31 – 3.21 (3H, m), 3.11 – 3.04 (1H, m), 2.89 – 2.80 (1H, m), 1.22 (3H, t), 1.07 (3H, t). ^{13}C NMR ($CDCl_3$, 68 MHz, ppm): 176.30 (CO_2), 175.77 (CO_2), 83.37 (CH), 78.94 (CH), 66.74 (CH_2), 65.87 (CH_2), 59.75 (CH_2), 59.72 (CH_2), 46.74 (CH_2), 46.28 (CH_2), 14.39 (CH_3), 14.19 (CH_3). FT-IR (KBr, cm^{-1}): 1723 (C=O), 919 (Re=O). *Anal.* Calc. for $C_{36}H_{40}AsN_2O_5ReS_2$: C, 47.73; H, 4.45; N, 3.09; S, 7.08. Found C, 47.67; H, 4.38; N, 3.02; S. 7.45%.

[3] Ferrocene under identical solution conditions has an $E_{1/2}$ value of 0.40 V versus SCE and an $E_p - E_{p/2}$ value of 62 mV.

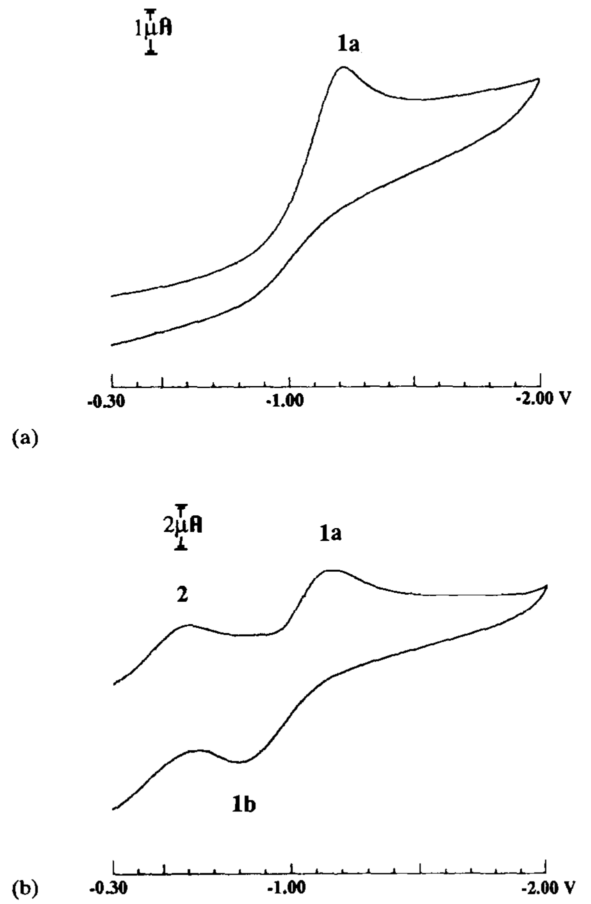


Fig. 2. Cyclic voltammogramms of: (a) a 2.0 mM solution of ReO(ECD) in CH_3CN, 0.2 M in TBAP; (b) a 2.0 mM solution of ReO(ECD) in CH_3CN, 0.2 M in TBAP in the presence of H^+. Potential range of −0.30 to −2.00 V at a scan rate of 100 mV/s.

of the peak current to the square of the scan rate ($i_p/v^{1/2}$), and a negative shift in E_p with increasing scan rate. A coupled re-oxidation wave is not observed for wave 1a at scan rates up to 1000 mV/s or upon multiple scans with cyclic voltammetry. These electrochemical properties are characteristic of a diffusion controlled, one electron $E_{rev}C$ or an E_{irr} electron transfer [7,8]. In agreement, bulk electrolysis of **1** at potentials negative of wave 1 give a value of n of 1.12 ± 0.11. Similar results are found when either THF or CH_2Cl_2 are used as the solvent.

Spectroelectrochemical data for **1** upon reduction at potentials negative of wave 1 show that the band at 350 nm decreases upon reduction while new bands are formed at 260 and 305 with a shoulder at 350 nm. The final spectrum is identical to that obtained upon the addition of base to **1** and hence the product of the reduction is $[ReO(ECD)]^-$ (**2**). Large scale generation of **2** from **1** by bulk electrolysis at $E_{app} = -1.50$ V was accomplished and confirmed by spectroscopic methods. Upon addition of an acid to the bulk electrolysis product, formation of **1** was observed by spectroscopic and electrochemical methods.

Although the site of electron transfer (metal or ligand) is unknown, the product of the reduction is clearly $[ReO(ECD)]^-$. At least two possible pathways exist for the formation of $[ReO(ECD)]^-$ from ReO(ECD) by the addition of one electron. If H^+ dissociated from complex **1** in solution wave 1 could be simply due to proton reduction, as opposed to wave 1 being the one-electron reduction of complex **1** followed by or coinciding with chemical reaction involving loss of an $H^\cdot$. In the latter case, electron transfer could be either metal or ligand centered.

Solution conductivity studies were performed on ReO(ECD) in CH_3CN and there was no indication of a dissociation reaction suggesting that wave 1 could be due to the reduction of H^+. (Conductivity measurements were made relative to TBAP, CH_3CN solutions.) This is in agreement with the electrochemical properties of ReO(ECD) as a function of solvent. Given nearly identical behavior in CH_3CN, THF and CH_2Cl_2 a mechanism involving the loss of proton prior to reduction is unlikely. Furthermore, the addition of H^+ (as HCl) to solutions of ReO(ECD) in CH_3CN was monitored by cyclic voltammetric techniques and typical results are shown in Fig. 2(b). Under these conditions a new reduction wave is found at $E_{pc} = -0.60$ V versus SCE (wave 2, Fig. 2(b)), due to the reduction of the free proton. This was confirmed by analysis of HCl in CH_3CN, TBAP. Hence, wave 1a is clearly not due to the reduction of the free proton.

The data in Fig. 2(b) also reveal that a new oxidation wave is found at $E_{pa} = -0.80$ V versus SCE at a scan rate of 100 mV/s (wave 1b, Fig. 2(b)) when added H^+ is present in the bulk solution. Wave 1b is characterized by an $E_p - E_{p/2}$ of 175 mV and a constant value of $i_p/v^{1/2}$ suggesting it is a diffusion controlled, irreversible electron transfer process. Although ΔE_p for wave 1a and 1b is 400 mV, wave 1b is found only after scanning negative of wave 1a and hence wave 1b is coupled to wave 1a. In addition, only waves 1a and 1b are found (as well as the proton reduction process) in multiple scan experiments suggesting regeneration of **1** from **2** by the oxidation process. Given the relative reduction potentials of ReO(ECD) and H^+, the presence of H^+ in the bulk solution would effectively result in the presence of excess $H^\cdot$ at or on the electrode surface when ReO(ECD) is reduced [9,10]. The presence of a return wave under these conditions further supports that the chemical reaction coupled to the reduction is loss of $H^\cdot$. Hence, the mechanism for the reduction of ReO(ECD) is that shown in Scheme 1.

Acknowledgement

J.E.A. acknowledges DuPont-Merck for support of this research.

References

[1] J.E. Anderson, S.M. Sawtelle, J.S. Thompson, S.A. Kretchmar Nguyen and J. Calabrese, *Inorg. Chem., 31* (1992) 2778.

[2] D.S. Edwards, E.H. Cheesman, M.W. Watson, L.J. Maheu, S.A. Nguyen, L. Dimitre, T. Nason, A.D. Watson and R. Walovitch, *Technetium and Rhenium in Chemistry and Nuclear Medicine,* Vol. 3, Cortina International, Verona, Italy, 1990, p. 433.

[3] J.E. Anderson and T.P. Gregory, *Inorg. Chem., 28* (1989) 3905.

[4] J.E. Anderson, S.M. Sawtelle and C.E. McAndrews, *Inorg. Chem., 29* (1990) 2627.

[5] D. Shriver and M.A. Drezdzon, *The Manipulation of Air Sensitive Compounds,* Wiley, New York, 2nd edn., 1986.

[6] J.A. Riddick, W.B. Bunger and T.K. Sakano, *Organic Solvents,* Wiley-Interscience, New York, 4th edn., 1986.

[7] A.J. Bard and L.R. Faulkner, *Electrochemical Methods Fundamentals and Applications,* Wiley, New York, 1980.

[8] R.S. Nicholsen and I. Shain, *Anal. Chem., 36* (1964) 706.

[9] P.H. Rieger, *Electrochemistry,* Prentice-Hall, Englewood Cliffs, NJ, 1987, pp. 293–296.

[10] P.T. Kissinger and W.R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry,* Marcel Dekker, New York, 1984, pp. 657–658.