

Electron-transfer behaviour of oxorhenium(V), nitridorhenium(V) and rhenium(III) diethyldithiocarbamate complexes

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Abstract

The voltammetric behaviour of $\text{ReN}(\text{S}_2\text{CN}(\text{Et})_2)_4$, $\text{Re}(\text{S}_2\text{CN}(\text{Et})_2)_3$, $\text{ReOX}(\text{S}_2\text{CN}(\text{Et})_2)_2$, where $\text{X}=\text{Cl}$ or Br , and $\text{Re}_2\text{O}_3(\text{S}_2\text{CN}(\text{Et})_2)_4$, were examined in five non-aqueous solvents. The nitridorhenium(V) complex underwent a non-reversible one-electron reduction followed by a chemical reaction. The rhenium(III) complex underwent a reversible one-electron oxidation to form the Re(IV) species; a second one-electron oxidation was followed by decomposition. The oxorhenium(V) monomers exhibit an equilibrium in solution between $\text{ReOX}(\text{S}_2\text{CN}(\text{Et})_2)_2$ and $[\text{ReO}(\text{S}_2\text{CN}(\text{Et})_2)]^+ + \text{X}^-$. Reduction of the latter caused severe electrodeposition which could be observed with the naked eye; the deposited material was non-conducting. The position of the equilibrium depended strongly on the identity of X^- . The potentials were strongly solvent dependent, with deposition of $\text{ReO}(\text{S}_2\text{CN}(\text{Et})_2)_2$ greatly reduced in the presence of electron-donating solvents. The anodic behaviour of $\text{Re}_2\text{O}_3(\text{S}_2\text{CN}(\text{Et})_2)_4$ consisted of a one-electron process which was followed rapidly by cleavage of the μ -oxo bridge to form $[\text{ReO}(\text{S}_2\text{CN}(\text{Et})_2)_2]^+$ and $\text{ReO}_2(\text{S}_2\text{CN}(\text{Et})_2)_2$.

Introduction

Transition metal complexes containing the dialkyldithiocarbamate ligand are well known for a number of metals, such as rhenium, niobium, mercury, molybdenum, vanadium and technetium [1]. These ligands are generally bidentate, though monodentate coordination is known [2]. Molybdenum species containing sulfur donor ligands have been studied extensively because of the biological import of the Mo–S moiety and the potential catalytic applications of oxo-atom transfer reactions which many dialkyldithiocarbamate formulations of Mo exhibit [3–5]. Technetium complexes have been of interest because of their widespread utility in radiopharmaceutical protocols. Rhenium complexes can be useful models for analogous complexes, due to the similarity in chemical and redox reactivity [4]. Further, rhenium complexes of dialkyldithiocarbamates also show oxo-atom transfer capability, though these compounds have received far less scrutiny in this regard than their molybdenum counterparts [3]. One compound which has received marked attention is the μ -oxo oxorhenium(V) dimer $\text{Re}_2\text{O}_3(\text{S}_2\text{CN}(\text{Et})_2)_4$, a species containing a linear $\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}$ backbone, in contrast to the *cis*-oxo structure of the analogous molybdenum complex [6]. We have been interested for

some time in the electrochemical behaviour of rhenium(III) and oxorhenium(V) complexes, especially those of potential catalytic application. The number of electrochemical investigations of dithiocarbamate complexes in general is quite large; the subject has been extensively studied [7]. Almost all involve complex electron-transfer mechanisms, which is to be expected when both metal and ligand are redox active [8]. A good example is the molybdenum complex $\text{Mo}_2\text{O}_3(\text{S}_2\text{CN}(\text{Et})_2)_4$, which is known to involve a series of electron transfers and coupled chemical reactions following an initial disproportionation in solution [9]. While the partial electron-transfer mechanism of the corresponding rhenium dimer has been published, no complete mechanism has emerged which accounts for the observed voltammetric behaviour of this complex [10]. In addition, to our knowledge, no interest has been displayed in the electron-transfer behaviour of other dialkyldithiocarbamate formulations of rhenium. This work has centred on the voltammetric behaviour of dialkyldithiocarbamate formulations of oxorhenium(V), nitridorhenium(V) and rhenium(III), a study undertaken to determine the effect of structure, oxidation state and solvent on their electron-transfer behaviour. We have observed, particularly in the monomeric and dimeric oxorhenium(V) case, a complex electron-transfer mechanism involving coupled chemical reactions and electrodeposition onto the electrode surface.

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Experimental

Reagents

The sodium salt of diethyldithiocarbamate and tetraethylthiuramdisulfide were purchased from Fisher Chemicals and Aldrich and used as received. The rhenium(II), nitridorhenium(V) and oxorhenium(V) diethyldithiocarbamate complexes $\text{Re}(\text{S}_2\text{CN}(\text{Et})_2)_3$, $\text{ReN}(\text{S}_2\text{CN}(\text{Et})_2)_2$, $\text{Re}_2\text{O}_3(\text{S}_2\text{CN}(\text{Et})_2)_4$ and $\text{ReOX}(\text{S}_2\text{CN}(\text{Et})_2)_2$, ($\text{X} = \text{Cl}^-$ and Br^-) were synthesized as described by Rowbottom and Wilkinson [11]. All received satisfactory elemental analyses before being used in electrochemical experiments.

All electrochemical solvents were purified and dried according to literature methods [12], with the exception of propylene carbonate, which was used as received from Fisher. The supporting electrolyte was $[\text{n-Bu}_4\text{N}][\text{ClO}_4]$ purchased from Fisher Chemical or $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ prepared from $[\text{n-Bu}_4\text{N}][\text{Br}]$ and KPF_6 . All were recrystallized three times from EtOH , dried *in vacuo*, and kept in an oven at 110°C prior to use.

Instrumentation

Cyclic voltammetric experiments and differential pulse polarographic measurements were carried out on an IBM instruments model 225A Polarographic System or an EG&G model 264A Polarographic analyser. Coulometric measurements were performed on an EG&G PARC model 273 potentiostat/galvanostat in order to verify the number of electrons transferred for each of the compounds described herein. Voltammograms obtained at potential sweep rates between 0.020 and 0.500 V s^{-1} were recorded on a Houston Omnigraphic 2000 X-Y recorder or EG&G model RE0089 X-Y recorder. High scan rate voltammograms were obtained on a Tektronix model 564 Storage Oscilloscope equipped with two type 3472 dual trace amplifiers, and were recorded on Polaroid type 667 black-and-white Land film. Infrared spectra were recorded on a Beckman model 4240 IR spectrophotometer or a Perkin-Elmer 1330 spectrophotometer. ^1H NMR spectra were obtained on a Varian EM360A 60 MHz spectrometer or a Bruker WM-300 instrument, using CDCl_3 with Me_4Si as internal reference.

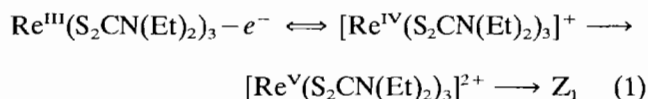
Voltammetric experiments were performed at 25°C in 0.1 M supporting electrolyte with a platinum button working electrode, platinum foil counter electrode and saturated calomel reference. Reported potentials were not corrected for liquid junction, but were calibrated daily against an internal reference (ferrocene). All electrochemical experiments were performed under nitrogen atmosphere. Elemental analyses were by Atlantic

MicroLab, Atlanta, GA, USA and Galbraith Laboratories of Knoxville, TN, USA.

Results and discussion

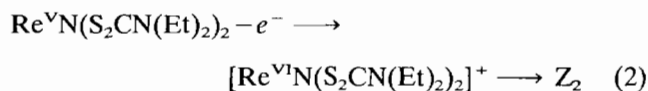
Voltammetry of tris(diethyldithiocarbamato)rhenium(III)

The cyclic voltammetric behaviour of this complex consisted of two oxidations, at $E_{1/2} = 0.656 \text{ V}$ and at $E_{p,a} = 1.25 \text{ V}$. For the first process, $i_p/v^{1/2}$ was independent of scan rate between 0.010 and 9.900 V s^{-1} , $i_{p,c}/i_{p,a}$ was unity at all scan rates, and the separation of anodic and cathodic peak potentials was invariant with scan rate at 0.062 V . For the second oxidation, no reverse wave or shift in peak potential with scan rate was observed, and $i_p/v^{1/2}$ decreased with increasing scan rate. Based on this information, the first oxidation can be characterized as a reversible one-electron oxidation. The second oxidation appears to be a one-electron transfer followed by a chemical reaction, the product of which (Z_1) was not identified. A postulated mechanism based on observations is given in eqn. (1).



Voltammetry of bis(diethyldithiocarbamato)-nitridorhenium(V)

This complex exhibited an oxidation, $E_{p,a} = 0.88 \text{ V}$, complicated by a following chemical reaction. No reverse wave was observed at any scan rate. The peak at $E_{p,a} = 0.88 \text{ V}$ shifts anodically with increasing scan rate, and $i_p/v^{1/2}$ decreases with increasing scan rate. Following this process, two additional oxidations of very low amplitude were observed at 1.23 and 1.38 V . Two low-amplitude reductions coupled to the oxidation at 0.88 V appear at 0.31 and -0.51 V . These were very small in magnitude and did not appear until after scanning to potentials positive of 0.88 V . These four processes appear to be coupled to this oxidation. The diagnostic criteria given above indicate that this is an electron transfer followed by a chemical reaction. The product of the following reaction was not identified. A postulated mechanism is given in eqn. (2).



Voltammetry of oxohalo(X)bis(diethyldithiocarbamato)-rhenium(V)

$\text{X} = \text{Cl}^-$. The observed voltammetric behaviour consisted of a single oxidation at $E_{p,a} = 1.30 \text{ V}$, with no reverse wave at any scan rate. A reduction appears at

$E_{p,c} = -0.50$ V, and a smaller one at $E_{p,c} = -0.79$ V. At high scan rates only one broad wave appeared which shifted anodically with increasing scan rate. A reverse wave appeared at -0.251 V. The current magnitude was much larger than the forward process, and 'spiked', suggesting adsorption onto the electrode surface [13]. The magnitude of this adsorption wave varied with switching potential, as is observed in Fig. 1. Upon reversal of sweep direction following the first reduction (-0.50 V), the magnitude of the spiked wave is very large. On reversal of sweep direction following the second reduction (-0.79 V), the adsorption splits into a pair of waves. If scan is reversed at the solvent limit, the spiked wave is lower in amplitude than in the previous cases, and appears as a single process. The 'spike' often appears as two distinct waves, typically separated by approximately 0.190 V. In 1,2-dichloroethane the wave generally appears as a single wave although the potential at which the adsorption wave appears shifts by 0.136 V depending on E_{sw} ; reversal at $E_{sw} = -0.65$ V gives $E_{p,ads} = -0.08$ V; reversal at $E_{sw} = -1.00$ V gives $E_{p,ads} = -0.134$ V; reversal at the solvent limit gives the steady-state value of $E_{p,ads} = -0.251$ V. It is evident from Fig. 1 that more than one species is being adsorbed, and that the most strongly adsorbed species is being formed initially.

In continuous cathodic sweep mode, a red mass was observed to collect on the surface of the electrode; on repetitive sweep for 3 h, this material grew to lengths of 2–4 mm from the electrode surface. The material could be stripped from the electrode by continuous anodic scans. The current magnitude of all waves was severely reduced during continuous cathodic scans, indicating that the red material is non-conducting.

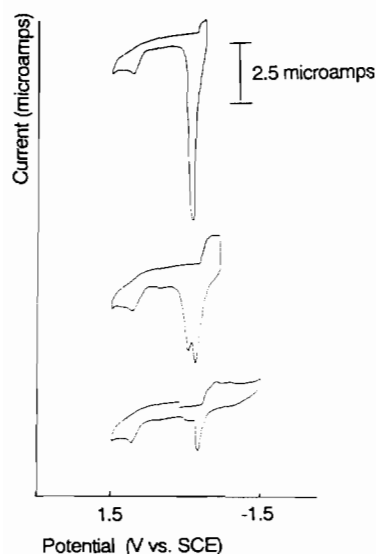


Fig. 1. Cyclic voltammetric behaviour of $\text{ReOCl}(\text{S}_2\text{CN}(\text{Et})_2)_2$ in 1,2-dichloroethane/0.1 M TBAP. Upper trace: $E_{sw} = -0.60$ V. Middle trace: $E_{sw} = -0.90$ V. Lower trace: $E_{sw} = -1.50$ V.

TABLE 1. Peak potentials of the first reduction of $\text{ReOX}(\text{S}_2\text{CN}(\text{Et})_2)_2$ with solvent

Complex	Solvent	$E_{p,c}$	$E_{p,ads(1)}$	$E_{p,ads(2)}$
$\text{ReOCl}(\text{S}_2\text{CN}(\text{Et})_2)_2$	MeCN	-0.39	-0.21	-0.02
	THF	-0.50	-0.33	-0.04
	DMF	-0.62	-0.36	-0.04
	1,2-dichloroethane	-0.50	-0.25	-0.08
	propylene carbonate	-0.54	-0.25	-0.14
$\text{ReOBr}(\text{S}_2\text{CN}(\text{Et})_2)_2$	MeCN	-0.38	-0.26	-0.13
	THF	-0.45	-0.11	n.o.
	DMF	-0.68	-0.39	n.o.
	1,2-dichloroethane	-0.51	-0.25	-0.09

n.o. = not observed.

The current magnitude of the spike varied greatly with solvent. In DMF no adsorption wave was observed. In MeCN, some enhanced current was observed but was not as pronounced as that in 1,2-dichloroethane. The potential of the first reduction varied with solvent; these potentials are listed for all X^- in Table 1.

A change in the voltammetric behaviour was observed upon the titration of free Cl^- into the cell (as $[\text{n-Bu}_4\text{N}][\text{Cl}^-]$). The addition resulted in a decrease in the current magnitude of the 'spike' wave. Further, the wave at -0.50 V disappeared; the process at -0.79 V remained as the only reduction. Addition of excess sodium salt of diethyldithiocarbamate caused the solution to turn dark brown from the original pale green. The resulting voltammogram consisted of two non-reversible oxidations, at $E_p = 0.80$ and 1.14 V, and a reduction at $E_{1/2} = -1.37$ V. The first reduction remained at -0.50 V with the adsorption spike, now of greatly reduced magnitude, at -0.25 V. This darkening of solution was also exhibited during coulometric experiments; the cyclic voltammetric behaviour of the product was identical with that just described.

$\text{X} = \text{Br}^-$. The voltammetry of the oxo-bromo species was similar to that of the oxo-chloro. An initial reduction appeared at $E_p = -0.46$ V, and the return wave, a spike of greatly enhanced magnitude indicating electrodeposition, appeared at $E_p = -0.04$ V. Exact potentials depended on solvent. Scan rate dependences of the reduction and 'spike' potentials were similar to those of the oxo-chloro species. In contrast to the oxo-chloro case, this wave does not show any doubling dependent on E_{sw} . A shoulder appears at -0.251 V only in the presence of excess Br^- , added as $[\text{n-Bu}_4\text{N}][\text{Br}]$. The wave at -0.46 V is a single wave, with a small-amplitude process (less than 10% of the initial reduction current at all scan rates) appearing at -1.00 V that exhibits a small coupled wave at -0.58 V. The oxo-bromo species exhibits two oxidative waves at 0.83 and 1.08 V. The first shows no return wave on reversing scan

direction 0.090 V past $E_{p,a}$. The second does exhibit a small return wave at 0.95 V. Both of these waves are greatly enhanced by added Br^- .

On repetitive cathodic scan, the same growth of red material with time on the electrode was observed when $\text{X}=\text{Cl}^-$. It was especially tenacious in this case; the electrode had to be cleaned with acetone to fully remove the film. Continuous scan also resulted in the appearance of the spike being split into four peaks. Removal of the electrode from the solution followed by mechanical wiping and reinsertion resulted in the disappearance of two of these waves, indicating that these resulted from electrodeposited decomposition products.

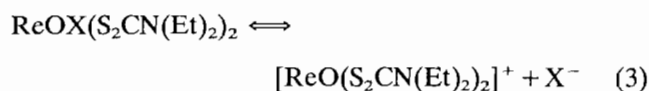
When Cl^- was added in 1,2-dichloroethane, the most extreme oxidation shifted from 1.08 to 1.30 V. Also, a shoulder at -0.26 V appeared on the spike and the first reduction became broader, with a distinct wave appearing at -0.78 V. The amplitude of the Br^- reduction was unchanged. With added SCN^- , a large wave appeared at -0.90 V, with a return at -0.435 V. Addition of free sodium diethyldithiocarbamate caused the solution immediately to darken to brown, as was described for the oxo-chloro case. Identical voltammetric behaviour was observed, with peak and half-wave potentials corresponding to the oxo-chloro experiment.

In MeCN, repetitive reductive scan gave rise to the voltammetric behaviour observed in Fig. 2. Initial reduction at -0.36 V gave rise to two waves, one initially at -0.541 V, which gradually moved cathodically to -0.70 V with time, and one at -0.77 V, which moved to -0.87 V. It is evident from exaggerated current magnitudes that pronounced adsorption is taking place following the initial reduction. The spikes are present at -0.253 and -0.129 V, the latter appearing initially

as a separate wave, degenerating with time to a shoulder on the more cathodic process. This behaviour was not observed when $\text{X}=\text{Cl}^-$. Also shown in Fig. 2 is the effect of adding 1 equiv. of Cl^- (as $[\text{n-Bu}_4\text{N}][\text{Cl}]$) to the cell, resulting in the attainment of the steady-state voltammogram identical to the one obtained for the oxo-chloro derivative. This behaviour is unique to the oxo-bromo derivative.

Electron-transfer mechanism of oxohalobis(diethyldithiocarbamato)rhenium(V)

It is apparent from the coincidence of potentials for the first reduction for each of the complexes that the same species is being reduced in each case. Further, the change in voltammetric behaviour brought on by the addition of excess X^- indicates an initial dissociation of halide ligand from the complex, setting up the following equilibrium in solution (eqn. (3)).



This assertion stems from the observation that (i) the potential of the first reduction was independent of the identity of X^- ; (ii) excess X^- eliminated the wave at -0.50 V, and (iii) addition of excess dissimilar X^- altered the peak potentials to those characteristic of the oxorhenium(V) species bearing the added X ligand. The position of this equilibrium appeared to depend on the identity of X^- . The amount of $[\text{ReO}(\text{S}_2\text{CN}(\text{Et})_2)_2]^+$ present depends on the basicity of leaving group X. Added Br^- had little effect on the reduction, indicating the position of the equilibrium described above lies far to the right. In addition, the oxidation of Cl^- has a much lower current magnitude than the oxidation of Br^- at the same concentration and in the same solvent, indicating that less free Cl^- is present.

Ichimura *et al.* state that the tetra-n-butyl diethyldithiocarbamate species is oxidized with adsorption at -0.2 V; therefore it is probable that one of the spike waves observed is due to adsorbed $[\text{S}_2\text{CN}(\text{Et})_2]_2$ [10]. More than one adsorption wave is usually observed in this region in some solvents, indicating that the ligand, generated upon dissociation, is not the only adsorbing species present in solution.

The position of equilibrium (3) when $\text{X}=\text{Cl}^-$ lies to the left of the $\text{X}=\text{Br}^-$ case, since the oxo-chloro derivative has an oxidation of low current magnitude when compared with the reduction. This indicates that less free Cl^- is present. The reduction, as seen in Fig. 1, results from more than one process. Each wave has a corresponding spike; the potential at which the scan is reversed determines which species predominates. The product of the first reduction appears to be more strongly adsorbed than that following the second reduction.

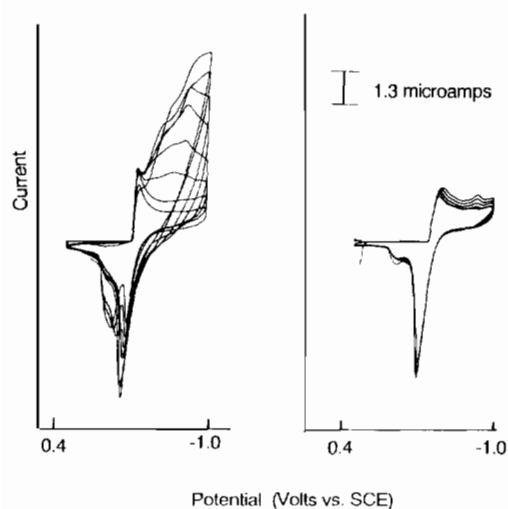


Fig. 2. Left trace: repetitive cathodic scans of $\text{ReOBr}(\text{S}_2\text{CN}(\text{Et})_2)_2$ in 1,2-dichloroethane/0.1 M TBAP. Right trace: same, following addition of 1 equiv. Cl^- .

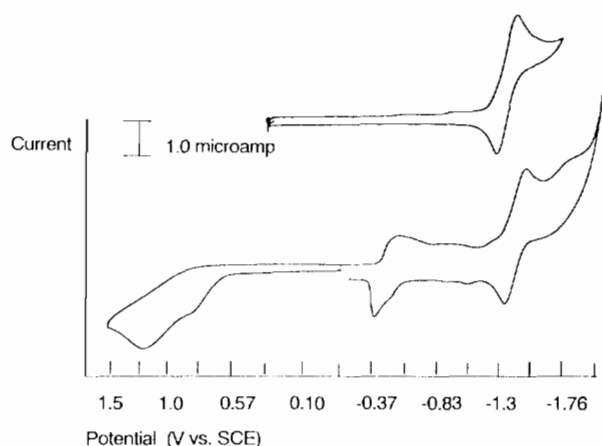


Fig. 3. Cyclic voltammetric behaviour of $O[ReO(S_2CN(Et)_2)_2]_2$ in 1,2-dichloroethane/0.1 M TBAP. Upper trace: initial cathodic scan. Lower trace: initial anodic scan.

between anodic and cathodic processes increased with scan rate from 0.059 V at 0.050 V s^{-1} to 0.085 V at 9.900 V s^{-1} . A small peak was observed at $E_p = -1.72$, but only after scanning through the oxidations.

When the initial scan direction is anodic (lower trace), no indication of the process at $E_{p,a} = -0.53 \text{ V}$ was observed until $E_{sw} = 0.90 \text{ V}$, indicating that this first reduction is coupled to this oxidative process. For the oxidation, $i_p/v^{1/2}$ remained independent of scan rate. For the first reduction, $i_{p,c}/v^{1/2}$ increased slightly with scan rate; the anodic and cathodic peak separation increases with scan rate, from 0.113 to 0.262 V. The value of $i_{p,a}/v$ for the spike did not vary with scan rate.

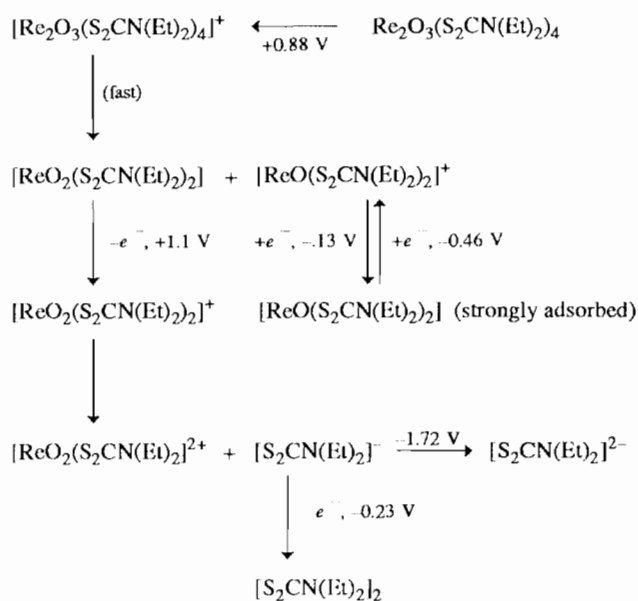
Variation of solvent did not have a pronounced change on the electrochemical behaviour, with the exception that in better donating solvents, such as DMF, no sharp spike was seen at $E_p = -0.25 \text{ V}$. Some changes in peak potentials were noted for the first reduction. The peak potentials for the reductions were shifted cathodically in more donating solvents, such as nitriles and DMF in a manner similar to that described by Ichimura *et al.* for the reduction at -1.2 V . In this case, the shifts were particularly extreme, varying from $E_p = -0.33 \text{ V}$ in propylene carbonate to $E_p = -0.60 \text{ V}$ in DMF. However, the trend does not depend on the donor number of the solvent. Current magnitudes also varied significantly with solvent, especially that of the spike, indicating an intimate involvement by the solvent in the electron-transfer mechanism.

On continuous cathodic scan, the growth of a red mass was observed on the electrode surface similar to that observed with $ReOX(S_2CN(Et)_2)_2$. However, the amount of material deposited was very small compared to the oxo-chloro or oxo-bromo species.

When starting at the point of zero charge and scanning anodically, no reversibility was seen for either the first or the second oxidation, even at temperatures of -77

$^{\circ}\text{C}$. Reversal of scan after the first oxidation indicates that the products which are reduced at -0.49 V are formed following this step; therefore the mixed valence $[Re(V)-O-Re(VI)]^+$ dimer (ligands omitted for clarity) is formed and immediately undergoes a fast decomposition to form the intermediates $[(S_2CN(Et)_2)_2Re=O]^+$ and $(S_2CN(Et)_2)_2ReO_2$. The former is postulated because of the identical match of redox potentials and appearance with the oxo-X species formed in reaction (1), which is reduced with concomitant adsorption onto the electrode surface. The neutral *trans*-dioxo species is oxidized at $+1.10 \text{ V}$, forming $[(S_2CN(Et)_2)_2ReO_2]^+$, which loses $S_2CN(Et)_2^-$. The peak at $E_p = -1.72 \text{ V}$, which appears following oxidation but not following repetitive reduction, occurs at the same potential as the reduction of diethyldithiocarbamate anion alone.

A postulated mechanism in the case of initial anodic scan is given below:



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