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Voltammetry of monomeric and dimeric oxorhenium(V) complexes of Schiff base ligands *N,N′*-ethylenebis(acetylacetone)diimine, *N,N′*-ethylene(salicylidene)diimine and *N,N′*-phenylenebis(salicylidene)diimine

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Abstract

The electrochemical study of six Schiff base complexes of oxorhenium(V) of the general formula $Re_2O_3L_2$ and ReOClL (L = *N,N′*-ethylenebis(acetylacetone)diimine (acacen), *N,N′*-ethylene(salicylidene)diimine (salen) and *N,N′*-phenylenebis(salicylidene)diimine (salphen)) was undertaken. In non-aqueous media the oxorhenium(V) monomers exhibit an equilibrium in solution (between forms ReOClL and $[ReOL]^+ + Cl^-$), the position of the equilibrium dependent on L. A one-electron reduction and one-electron oxidation are observed, followed by a fast chemical reaction, resulting in decomposition of the complex. The μ-oxo dimeric complexes underwent a two-electron reduction followed by decomposition to an electroinactive product. Successive one-electron oxidations of each rhenium in $Re_2O_3L_2$ were observed. Each electron-transfer step was coupled to a chemical reaction; the generation of $[Re_2O_3L_2]^+$ was followed by the cleavage of the μ-oxo bond and formation of mono-oxo species. This reaction was much slower than the decomposition which followed generation of $[Re_2O_3L_2]^{2+}$.

Keywords: Electrochemistry; Rhenium complexes; Oxo complexes; Schiff base complexes

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1. Introduction

Oxorhenium(V) complexes have been known for 4 decades. Recent interest in these complexes stems from their utility as intermediates in the synthesis of a large number of neutral and ionic compounds as well as their catalytic activity [1]. Some rhenium complexes show oxo-atom transfer capability, although rhenium complexes have received only minor scrutiny in this regard [2]. Oxorhenium complexes are also useful in the design of new radiopharmaceuticals. The redox behavior of the Re and Tc complexes are quite similar, and the redox behavior is correlated to the bioactivity of ^{99m}Tc radioimaging agents [3]. Thus, many workers evaluate the reactivity of the rhenium complex prior to evaluation and testing of the corresponding technetium complex.

Schiff base complexes containing the oxorhenium(V) moiety are known; these relatively polarizable ligands stabilize the rather acidic $[ReO]^{3+}$ core, as do complexes of pyridines [4], phosphines [5] and dithiocarbamates [6]. Several studies of oxorhenium(V) Schiff base ligands have appeared [7], undoubtedly prompted by the influence of ligand identity on the thermodynamic and kinetic stability of the similar $[TcO]^{3+}$ core toward ligand substitution reactions, an important consideration for an in vivo radioimaging agent, the action of which depends on its formulation.

2. Experimental

2.1. Materials

Ammonium perrhenate (Aesar Chemicals) was used as received. The precursor $ReOCl_3(P(C_6H_5)_3)_2$ was prepared and characterized according to the method of Chatt and Rowe [8]. Ethylenediamine and salicylaldehyde were obtained from Aldrich and used without further purification. Acetylacetone was obtained from Eastman Chemicals and distilled under air prior to use. The fraction boiling at 137°C was collected and redistilled until examination by NMR yielded

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only resonances characteristic of the β-diketone. All Schiff base ligands were prepared by condensation of either ethylenediamine or *o*-phenylenediamine and either acetylacetone or salicylaldehyde, according to the method of McCarthy [9]. Recrystallization was from absolute ethanol and characterization was by NMR and IR spectroscopy. All reactions were carried out under dry N_2 atmosphere.

The electrochemical solvent, Aldrich Gold Label HPLC grade 1,2-dichloroethane, was used as received. The supporting electrolyte used was $[n\text{-}Bu_4N][ClO_4]$ purchased from Fisher Chemical, which was subsequently recrystallized three times from EtOH, dried in vacuo and kept in an oven at 110°C prior to use.

Infrared spectra were obtained with a Nicolet 5DXB Fourier transform IR spectrometer. All NMR spectra were obtained using a Bruker WM-300 Fourier transform spectrometer using deuterated solvents obtained from Aldrich. Cyclic voltammetry/differential pulse voltammetry was performed using an IBM model EC-225 Voltammetric Analyzer. Output was obtained on a Houston Instruments Omnigraphic 2000 X–Y Recorder (for scan rates ≤ 0.500 V s^{-1}) or a Tektronix model 564 storage oscilloscope equipped with a type 2A60 amplifier in the X-channel and a type 3A72 dual trace amplifier in the Y-channel. A model C-12 oscilloscope camera was used to record data on Polaroid type 667 (ASA 3000) black and white film. Coulometric and conductometric instruments were designed and built by the electronics shop in the School of Chemistry. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA, USA.

2.2. Syntheses

2.2.1. $Re_2O_3(salphen)_2$

Repeated attempts to synthesize this complex according to literature procedure gave dramatically lower yields than originally reported [10]. The procedure presented here gave the highest yields and purities and required the simultaneous addition of triethylamine and ligand. Into a solution of 1.0 g (1.2 mmol) $ReOCl_3(P(C_6H_5)_3)_2$ in 100 ml of reagent grade toluene, 0.38 g (1.2 mmol) of H_2salphen and 1.0 ml (7.2 mmol) of triethylamine were added simultaneously with vigorous stirring. The yellow color of the solution darkened to brown as the mixture was then brought to reflux for 90 min. The reaction mixture was cooled to r.t. and filtered. The brown product was collected and washed with three 10 ml aliquots of toluene, five 10 ml aliquots of deionized distilled water and five 10 ml portions of diethyl ether.

The compound was purified on a Sephadex LH-20 column. Elution of $Re_2O_3(salphen)_2$ with a 1:1 (vol./vol.) CH_2Cl_2/Me_2CO mobile phase produced a faint yellow band which was eluted prior to the dark brown band containing the product. Yield after chromatography was 62% based on $ReOCl_3(P(C_6H_5)_3)_2$. *Anal.* Calc. for $C_{40}H_{28}N_4O_7Re_2$: C, 40.47; H, 2.62; N, 4.44. Found: C, 40.50; H, 2.77; N, 4.42%. IR stretches at 700(s) and 962(w) cm^{-1} confirm the presence of the O=Re–O–Re=O structural backbone. There was no evidence for the formation of a *trans*-dioxo species (m–s absorption ~860 cm^{-1}).

2.2.2. $Re_2O_3(salen)_2$

Two methods of synthesis were employed to obtain this complex.

Method A: The synthesis of Middleton et al. [10] as modified above for $Re_2O_3(salphen)_2$.

Method B: Preparation of ReOCl(salen) followed by μ-oxo dimerization on activated basic alumina in 7:3 (vol./vol.) CH_2Cl_2/Me_2CO. The dimerization yield was always in excess of 80% based on the amount of monomer loaded onto the column and the eluted product required no further purification. *Anal.* Calc. for $C_{32}H_{28}N_4O_7Re_2$: C, 40.34; H, 3.94; N, 5.87. Found (Method B): C, 40.81; H, 3.98; N, 5.95%. The IR stretch at 690(s) cm^{-1} confirmed the presence of the μ-oxo bridge and an absorption at 965(w) cm^{-1} verified existence of the $(ReO)^{3+}$ moiety. There were no absorptions in the 860 cm^{-1} range corresponding to the formation of a monomeric *trans*-dioxo species.

2.2.3. $Re_2O_3(acacen)_2$

The conditions described for the analogous salphen complex apply except that the reaction is not complete until after 2 h of reflux. Yields decrease as the time of reflux exceeded this limit; best yield obtained was 40%. Purification was accomplished by chromatography on basic alumina using 1:1 (vol./vol.) CH_2Cl_2/MeOH mobile phase. The final, dark green band was collected. *Anal.* Calc. for $C_{24}H_{36}N_4O_7Re_2$: C, 33.30; H, 4.20; N, 6.50. Found: C, 33.39; H, 4.27; N, 6.19%. IR absorptions at 720(s) and 975(w) cm^{-1} confirmed the presence of the O=Re–O–Re=O structure. IR absorptions characteristic of monomeric *trans*-dioxo species were absent. The preparation of this complex from the monomer was also successfully demonstrated on basic alumina in CH_2Cl_2. This is not a useful approach to $Re_2O_3(acacen)_2$, however, as synthesis of the pure monomer is difficult.

2.2.4. ReOCl(salphen)

This complex proved very elusive due to a tendency for this complex to form the μ-oxo dimer, $Re_2O_3(salphen)_2$, even under conditions of rigorous exclusion of atmospheric moisture and oxygen. The following procedure provided the highest yield of ReOCl(salphen). In an oven dried flask containing 1.0 g of $ReOCl_3(P(C_6H_5)_3)_2$, toluene which had been dried over pellitized Na for 36 h was introduced with vigorous stirring. An amount of 0.38 g (1.2 mmol) of dry, degassed H_2salphen and 0.33 ml (2.4 mmol) of triethylamine were added simultaneously. No significant color change was observed until the reaction was brought to reflux. After 60 min a dark brown color appeared and an insoluble material formed. If allowed to reflux beyond 90 min, a dark oil formed and yield dropped significantly. Optimum yield was obtained following 60 ± 5 min of reflux.

Purification was on a Sephadex LH-20 column, as basic alumina caused the compound to form the μ-oxo dimer. A

7:3 (vol./vol.) CH_2Cl_2/Me_2CO solution was used as mobile phase, the system again eluting a faint yellow band before the dark brown product. *Anal.* Calc. for $C_{20}H_{14}ClN_2O_3Re$: C, 42.11; H, 2.80; N, 4.91; Cl, 6.22. Found: C, 42.30; H, 2.84; N, 4.90; Cl, 6.24%. IR absorption at 948(m) cm^{-1} indicated the presence of the Re=O stretch. There were no IR absorptions characteristic of a μ-oxo dimer ($\sim 700\ cm^{-1}$) or a *trans*-dioxo monomer ($\sim 860\ cm^{-1}$). Yield of purified product was 58% after chromatography.

2.2.5. ReOCl(salen)

This complex was successfully prepared in 50.5% yield using the procedures outlined for ReOCl(salphen) with carefully prepared solvent. Purification was accomplished on Sephadex LH-20 in 7:3 (vol./vol.) CH_2Cl_2/Me_2CO as previously outlined. *Anal.* Calc. for $C_{16}H_{14}ClN_2O_3$: C, 38.14; H, 2.78; Cl, 7.05; N, 5.56. Found: C, 37.95; H, 3.05; Cl, 6.80; N, 5.35%. IR absorption at 958(m) cm^{-1} indicates the Re=O stretch. Bands consistent with either a μ-oxo dimer or *trans*-dioxo monomer were absent.

2.2.6. ReOCl(acacen)

This complex was prepared according to the method previously described for the salphen complex; however, even meticulously dried solvents and reagents produced a mixture of monomer and μ-oxo dimer under all conditions. Pure monomer was obtained by dissolving the washed but unchromatographed product in methylene chloride and then bubbling dry HCl gas through the solution at a moderate rate for 3 min. The solution was then degassed with dry N_2 for 15 min. Treatment of the reaction product in this manner quantitatively yielded acacen monomer which was then successfully chromatographed on Sephadex LH-20 in 7:3 (vol./vol.) solution of CH_2Cl_2/Me_2CO, yielding a single slow moving dark brown band, which was collected. *Anal.* Calc. for $C_{12}H_{18}N_2O_3Re$: C, 31.35; H, 3.91; Cl, 7.71; N, 6.09. Found: C, 31.23; H, 3.85; Cl, 7.55; N, 6.00%. The presence of a medium strength absorption at 973 cm^{-1} confirms the presence of the Re=O moiety. The presence of either the O=Re–O–Re=O structure or the O=Re=O moiety was discounted due to the absence of characteristic IR absorption bands.

3. Results and discussion

3.1. Voltammetric behavior of $Re_2O_3L_2$ complexes

3.1.1. $Re_2O_3(salphen)_2$

Data that typifies cyclic voltammetric and differential pulse voltammetric behavior of the μ-oxo dimeric compounds are shown in Fig. 1. On initial sweep to positive potentials, two one-electron oxidations were observed at $E_{1/2} = +0.610$ V (e1) and $+1.058$ V (e2) versus SCE. The return scan revealed a single reduction at $E_p = -0.300$ V (e3). Subsequent cathodic scans did not show the (e3) reduction but revealed a reduction of comparatively greater current at $E_p = -0.925$ V (e4). For the first oxidation (e1), the separation of anodic and cathodic peak potentials was invariant with a scan rate at 0.060 V. The ratio of cathodic and anodic peak currents (i_{pc}/i_{pa}) increases with scan rate (ν) to 0.500 V s^{-1}, above which it levels off to unity. The current parameter $i_{pa}/\nu^{1/2}$ increases only slightly over the scan rate observed (0.050–9.900 V s^{-1}). These criteria correspond to a reversible single electron-transfer followed by a slow chemical reaction [11]. Repeated scans indicate the product of the following chemical reaction was electroinactive within the potential window of the solvent system.

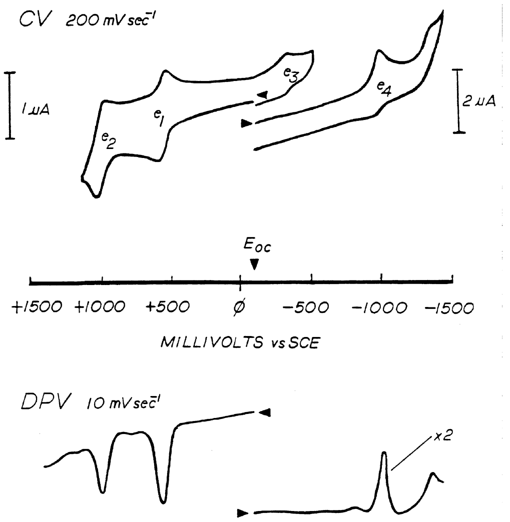


Fig. 1. Initial cyclic voltammetric (CV) and differential pulse voltammetric (DPV) scans of $Re_2O_3(salphen)_2$ in 0.10 M TBAP/1,2-dichloroethane.

Examination of the diagnostic criteria corresponding to the second oxidation (e2) shows a peak potential difference (ΔE_p) of 0.083 V; the anodic peak potential demonstrated a 0.030 V anodic shift for each ten-fold increase in scan rate above 0.500 V s^{-1}. Peak current ratio increases with scan rate while the current parameter increases slightly for scan rates above 1.000 V s^{-1}. These trends constitute evidence for an irreversible chemical reaction following electron transfer [11]. Since repetitive scan following the first oxidation indicate that the product of the chemical reaction following (e1) is electroinactive, the reduction observed at -0.300 V (e3) must be an electroactive product formed following the second oxidation (e2); current parameters indicate the reaction following (e2) is faster than that following (e1). That the processes (e2) and (e3) are interrelated are evident by examining the ratio of the two anodic peak currents ($i_{pa,e2}$ and $i_{pa,e3}$), which is unity at all scan rates, a relationship that serves as an indication of two successive and related electron transfers [11c].

At scan rates (ν) between 0.100 and 0.500 V s^{-1}, both oxidations (e1 and e2) exhibit evidence of electrochemical irreversibility, and the reduction at -0.300 V (e3) is observed. However, when $\nu > 0.500$ V s^{-1}, the reductive process (e3) is *not* observed and the reversibility of the second oxidation (e2) (as indicated by current ratios) increases substantially, additional evidence that (e3) is coupled to the second oxidation.

The most extreme reduction (e4) showed only partial reversibility over accessible scan rates. The value of the cathodic peak potential (E_{pc}) was found to shift cathodically 0.016 V per ten-fold increase in scan rate while the anodic peak potential (E_{pa}) was invariant at 0.0867 V. Peak current ratio increased with increasing scan rate to a maximum of 0.40 at 9.900 V s^{-1}; $i_{pc}/\nu^{1/2}$ (current function) increased slightly with scan rate. Taken together, these criteria are indicative of an electron transfer followed by irreversible chemical reaction for both processes [11a,c]. Consistent 1:2 relationships between the current magnitude of either oxidation (e1 or e2) and the reduction (e4) over the entire range of scan rates observed indicate a two-electron process. As H_2salphen is not electroactive within the accessible electrochemical window, the reduction (e4) must be related to the oxo–rhenium center and represents either (a) concurrent reduction of both oxo–metal moieties to Re(IV) or (b) two-electron reduction of one of the two oxo groups. The scenario (a) is considered more likely because (i) it is known that Re(V) species are generally readily reducible [12], and (ii) very similar electrochemical behaviors (successive one-electron oxidations, two-electron reductions) have been observed for other μ-oxo rhenium dimers carrying anionic ligands [6].

3.2. Voltammetric behavior of ReOClL complexes

3.2.1. Re_2O_3(salen)$_2$

An initial anodic scan revealed two successive one-electron oxidations at $E_p = +0.521$ V (e5) and $E_p = +1.051$ V (e6). On reversing direction, a single reduction appeared at +0.272 V (e7). On initial cathodic scan, a wave at $E_{1/2} = -1.060$ V (e8) was observed.

For the first oxidation (e5), E_{pa} shifts 0.017 V anodically per ten-fold increase in scan rate. The current ratio is unity and $i_{pa}/\nu^{1/2}$ is independent of ν when $\nu > 0.040$ V s^{-1}. For the second oxidation (e6), E_{pa} shifts anodically by 0.025 V per ten-fold increase in ν, i_{pc}/i_{pa} rises to unity for $\nu \geq 0.300$ V s^{-1}, and $i_{pa}/\nu^{1/2}$ is independent of scan rate. These diagnostic criteria strongly indicate irreversible chemical reaction following charge transfer for both processes (e5) and (e6). As was the case with the μ-oxo salphen dimer, reversing scan direction between (e5) and (e6) and examining voltammetric behavior on repetitive scans for both processes indicates the reduction at $E_p = +0.272$ V (e7) was coupled to the second oxidation (e6).

The most extreme reduction (e8) also exhibits characteristics previously encountered in Re_2O_3(salphen)$_2$. Peak reductive current is approximately twice that of either oxidative wave (e5 or e6) at identical scan rates and concentrations. The value of E_{pc} shifts 0.036 V per ten-fold increase in scan rate, while i_{pa}/i_{pc} is relatively constant with ν, and the value of $i_{pc}/\nu^{1/2}$ slowly decreases with scan rate. The aforementioned criteria are evidence for a very fast chemical reaction following a two-electron reduction. As H_2salen exhibits no electroactivity within the observed potential window, these electron-transfers are metal-centered.

3.2.2. Re_2O_3(acacen)$_2$

Two one-electron oxidations were observed at $E_p = +0.490$ V (e9) and $E_p = +0.925$ V (e10), respectively. A single reduction (e11) was observed at $E_p = +0.130$ V on reversal of scan direction following (e10). This reduction is observed only for $\nu \leq 0.500$ V s^{-1}. Initial cathodic scan revealed a reduction at $E_{1/2} = -1.302$ V (e12).

The reduction at +0.130 V (e11) is observed only for $\nu \leq 0.500$ V s^{-1}. At $\nu \geq 0.500$ V s^{-1}, the midpoint potential was found to be +0.450 V. For $\nu < 0.500$ V s^{-1}, E_{pa} shifted 0.015 V per ten-fold increase in scan rate. The ratio i_{pc}/i_{pa} increased to unity with increasing ν, and $i_{pa}/\nu^{1/2}$ was independent of scan rate. These findings indicate a slow and irreversible chemical reaction following the reversible charge transfer [11,13]. The product of the reaction following the first oxidation is reduced at +0.130 V. The reaction was found to be first order with $k_f = 0.2$ s^{-1} using the single scan method of Nicholson and Shain [11a]. Examination of the first oxidation by differential pulse voltammetry revealed a single peak having a width at half height of 0.090 V, corroborating the reversibility of the charge transfer [14].

A corresponding anodic component of the wave observed at +0.130 V (e11) was not observed at any scan rate. The value of E_{pc} (e11) was dependent on scan rate, shifting cathodically by 0.028 V over 0.050 V $s^{-1} < \nu < 0.500$ V s^{-1}, strongly suggesting the presence of a fast chemical reaction immediately following the reduction.

For the second oxidative wave (e10), E_{pa} shifted cathodically by 0.030 V between 0.050 V and 0.500 V s^{-1}. Peak current ratio approached unity only at 9.900 V s^{-1} while $i_{pa}/\nu^{1/2}$ was independent of scan rate. This diagnostic criteria is also strongly indicative of an irreversible chemical reaction following the charge transfer. As H_2acacen is electroinactive over the potential window observed, these charge transfers are assigned to the $[ReO]^{3+}$ core, in the manner of the other μ-oxo dimers previously discussed.

The two-electron reduction at $E_{1/2} = -1.302$ V (e12) shows some evidence of a following chemical reaction when $\nu < 0.500$ V s^{-1}. The value of E_{pc} shifts cathodically by 0.015 V between 0.050 V and 0.500 V s^{-1}; the peak current ratio increases rapidly to unity. The current parameter remains independent of scan rate. The return sweep of a scan with $\nu < -0.500$ V s^{-1} exhibits an oxidation at -1.050 V of low current relative to the forward sweep, a process which is not observed at fast scan rates and is linked to a chemical reaction following the reduction (e12).

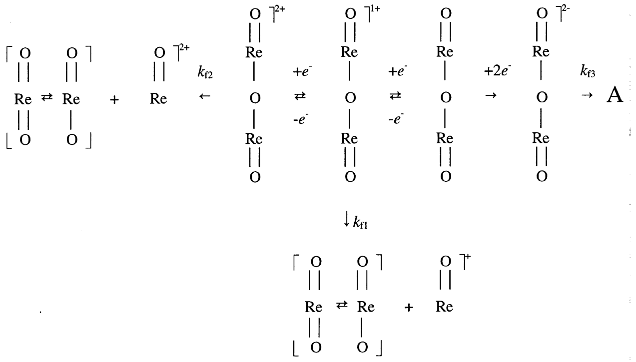
3.3. Electron-transfer behavior of $Re_2O_3L_2$ complexes

In an attempt to discern the chemically coupled $Re_2O_3L_2$ oxidation products, electrolysis products were characterized in situ using FT-IR to compute difference spectra. This was necessary due to interference from the supporting electrolyte.

As an example, electrolysis of Re_2O_3(salphen) was carried out at +0.750 V, that is, between first and second oxidations. Comparison of the spectra obtained from this solution with that of an unelectrolyzed complex acquired in the same manner indicated (i) the μ-oxo bridge is cleaved following the first oxidation, as the characteristic stretch at 706 cm^{-1} is not present; (ii) there is no evidence of a *trans*-dioxo species, as evidenced by the absence of a strong absorbance at 800 ± 30 cm^{-1} and (iii) the presence of an absorption at 963 cm^{-1} that can be assigned to the Re=O stretch [15]. The presence and/or identity of any *trans*-ligand could not be established unambiguously from this data. Electrolyses of salen and acacen dimers gave similar results.

A cyclic voltammogram taken on the product of the electrolysis of Re_2O_3(salphen) gave a wave-for-wave match of the corresponding mono-oxo species ReOCl(salphen). An identical experiment was carried out for the salen and acacen species with comparable results. On the voltammetric time scale, voltammetric and coulometric data indicate successive oxidations of the μ-oxo bridged dimer forming a $[O{=}Re^{V}{-}O{-}Re^{VI}{=}O]^{+}$ mixed-valent (first oxidation), followed by the formation of the dicationic complex $[O{=}Re^{VI}{-}O{-}Re^{VI}{=}O]^{2+}$ (second oxidation). Reduction involved a single two-electron process, which was only observed on an initial cathodic scan.

Both oxidations are coupled to chemical reactions which follow charge transfer, with the reaction that followed the second oxidation being much faster than the reaction following the first oxidation (e.g. for L = salphen, $k_{f2} = 1.5$ and $k_{f1} = 0.35\ s^{-1}$). This chemical coupling impeded characterization of the initial electron transfer products. Analysis of the reaction products following electrolysis at potentials sufficient to generate the dication indicated mono-oxo species formation. Exhaustive electrolysis at cathodic potentials resulted in an electroinactive solution, regardless of L. The half-wave potential for the rhenium V/VI couple of the corresponding mono-oxo species is anodic of the first and second oxidation potentials of $Re_2O_3L_2$. Thus, any mono-oxo Re(VI) species formed would be immediately reduced back to Re(V). Further, *trans*-dioxo species with dianionic ligands are presently unknown. Satisfaction of the high charge requirements of Re(V) by an oxo group and an anionic ligand with good π-donor characteristics normally results in a mono-oxo complex, none of which has ever been converted into a *trans*-dioxo species [16]. The presence of the mono-oxo Re(V) species in the product mixture was confirmed by both voltammetric and IR results. Our inability to detect a *trans*-dioxo Re(VI) species is probably due to proton transfer from adventitious water present in the medium to one of the oxo groups. One resonance form of a possible product of this oxidation, the $[O{=}Re^{VI}{-}OA]^{+}$ species, has the d^2 cation bonded to an oxo radical; this has been shown on numerous occasions to abstract hydrogen atoms efficiently [17]. The $[O{=}Re^{V}{-}OH]^{+}$ species is not stable in the medium, and decomposes rapidly to form the mono-oxo species. This is one possible explanation for the lack of the characteristic $\nu[O{=}Re^{V}{=}O]^{+}$ absorption among the electrolysis products. Nearly identical redox pathways involving these intermediates are quite well-known for μ-oxo rhenium dimers and extrapolation to the aforementioned Schiff base complexes seems appropriate in view of their nearly identical electron-transfer behavior [1c,6,18], although direct evidence for the existence of a *trans*-dioxo or oxo–hydroxo species remains elusive.



Scheme 1. Electron transfer pathway proposed for $Re_2O_3L_2$ complexes, long time scale. Products of reactions coupled to electron-transfers (k_{f1}, k_{f2}) are postulated.

On the basis of this information, we postulate that electrooxidation of the dimer to the dication product produces the species shown in Scheme 1. The Schiff base ligands are omitted for clarity. The second oxidation is well anodic of the V/VI couple. Thus, during exhaustive electrolysis, the dimeric cation dissociates with spontaneous reduction of the mono-oxo Re(VI) species.

3.4. Voltammetric behavior of ReOCl(L) complexes

The monomeric oxorhenium Schiff base complexes were studied under the same conditions as the μ-oxo dimers. For the acacen complex, two oxidations are observed, one at +0.950 V and one at +1.185 V. The more extreme wave is irreversible electrochemically, and is located at a potential corresponding to the oxidation of free Cl^{-}. The +0.950 process corresponds to the oxidation of the $[ReO]^{3+}$ core. In the salphen (Fig. 2) and salen monomers, the extreme nature of the overlap of the two oxidations complicated the analysis of the metal-centered oxidative wave, showing both E_{pa} and E_{pc} to be independent of scan rate, and i_{pc}/i_{pa} to be constant with scan rate, a situation which would not normally be associated with an isolated EC wave.

Cathodic sweeps of the salphen monomer revealed a complex wave with $E_p = -0.320$ and -0.635 V. The more extreme wave was dependent on scan rate, shifting cathodically 0.025 V per ten-fold scan rate increase. The peak potential of the first wave shifted very slightly with ν, and is similar to the wave observed in the corresponding μ-oxo dimer in that it is only observed following anodic scan. Significantly, this wave disappeared on the addition of free chloride (as $[n\text{-}Pr_4N][Cl]$) to solutions of any of the ReOClL complexes, regardless of oxidation state. Conductivity measurements rel-

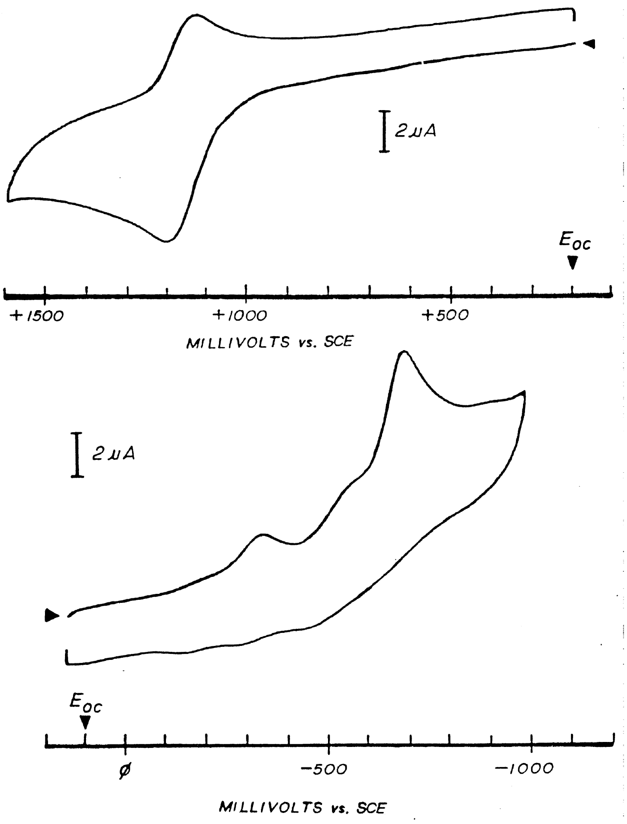


Fig. 2. Cyclic voltammetric scans of ReOCl(salphen) in 0.10 M TBAP/ 1,2-dichloroethane. Upper trace: initial anodic scan; lower trace: initial cathodic scan. E_{oc}: point of zero charge.

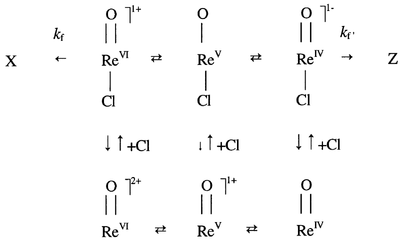
ative to neat ethylene chloride indicated at least partial dissociation of the coordinated chloride in solution in the manner $\mathrm{ReOClL} \rightleftarrows [\mathrm{ReOL}]^{+} + \mathrm{Cl}^{-}$. This is not surprising in that similar *trans*-oxo/halo technetium and rhenium(V) complexes have displayed analogous dissociative behavior [6,3d]. The position of the equilibrium appears to depend somewhat on the identity of L, as salen and salphen complexes have irresolvable metal-centered and chloride oxidations, while those of the acacen complex are readily distinguishable. This would seem to suggest that the equilibrium described lies further toward the dissociated form in the latter complex and toward the coordinated chloride form in the former. For the salen/salphen complexes, the Re(V) → Re(VI) oxidation has an i_{pa} value twice that of i_{pc}, and a midpoint potential almost identical to that of free Cl^{-}. Thus it appears that both halide and the $[\mathrm{ReO}]^{3+}$ core are oxidized during anodic scan. The acacen complex displays two separate oxidation steps, with E_{p} for chloride at +1.185 V and the complex E_{p} at +0.950 V. Displacement of chloride by perchlorate is not anticipated due to the non-coordinating nature of the latter anion. Redox potentials for all complexes described in this study are given in Table 1.

The voltammetric, conductometric and coulometric observations described above are in agreement with the electron-transfer mechanism proposed in Scheme 2. Once again, the Schiff base ligands L have been omitted for clarity.

Table 1
Redox potentials for $\mathrm{Re_2O_3L_2}$ and ReOClL complexes (0.200 V $\mathrm{s^{-1}}$)

Complex	V/VI		V/IV	
	$E_{1/2,1}$ (V)	$E_{1/2,2}$ (V)	$E_{1/2,1}$ (V)	$E_{1/2,2}$ (V)
$\mathrm{Re_2O_3(salphen)_2}$	+0.610	$^{a}{}_{1}$	−0.920 [b]	[c]
$\mathrm{Re_2O_3(salen)_2}$	+0.490	$^{a}{}_{2}$	−1.060 [b]	[c]
$\mathrm{Re_2O_3(acacen)_2}$	+0.450	+0.915	−1.302	[c]
ReOCl(salphen)	+1.197	[c]	−0.320	−0.635
ReOCl(salen)	+1.150	[c]	−0.185	−0.840
ReOCl(acacen)	+0.950	[c]	+0.125	−0.995

[a] Chloride oxidations: $^{a}{}_{1} = 1.058$ V, $^{a}{}_{2} = 0.988$ V.
[b] Peak potentials.
[c] Not observed.



Scheme 2. Electron transfer pathway proposed for ReOClL complexes.

4. Summary

Electrochemically, the compounds described above are very similar to those based on *N*,*N*-diethyldithiocarbamate [6]. This is not surprising in view of the fact that both ligand systems are anionic. Their voltammetric behavior varies radically from $\mathrm{Re_2O_3Cl_4(pyridine)_4}$, which exhibits reversible oxidations and distinct one-electron reductions, the first of which is reversible [19]. Unlike the diethyldithiocarbamate formulations, however, the Schiff bases showed no severe adsorption of anionic and/or cationic intermediate forms. The differences between voltammetric behavior of the μ-oxo diethyldithiocarbamate or aforementioned μ-oxo Schiff base complexes and $\mathrm{Re_2O_3Cl_4(pyridine)_4}$ cannot be explained by differences in π-backbonding; this would seem to indicate that the ligand plays a critical role in the electron-transfer mechanism. Further, it is intriguing that while the synthesis of the compound $\mathrm{ReOCl(S_2CN(C_2H_5)_2)_2}$ is relatively simple, synthesis of the corresponding Schiff base mono-oxo complexes is done only with difficulty, and $\mathrm{ReOCl_3(py)_2}$ is unknown. Interesting also is the fact that in both diethyldithiocarbamates and these Schiff base complexes, the chloride in the ReOClL complex is so weakly bound that both are partially dissociated in solution before oxidation or reduction. On oxidation to Re(VI), the anionic ligands would seem to be unable to stabilize a rhenium–oxo moiety; the moeity is so electropositive that it has been shown on numerous occasions to abstract hydrogen atoms [1]. Similarly, Re(IV) species formed on reduction do not have the high charge requirement of the Re(VI); the anionic ligand over-satisfies the requirement, and decomposition after the reduction is the result. This pattern seems to dominate the behavior of large, anionic bases like dithiocarbamate and the Schiff bases reported herein. The chloride ligands of $Re_2O_3Cl_4(pyridine)_4$ do not appear to interact as closely with the rhenium metals, possibly because they are such poor bases.

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