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Electrochemistry of arylimido rhenium(V) dithiocarbamate complexes [{$Re(NR)(S_2CNR'_2)_2$}$_2O$] in *N,N*-dimethylformamide

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Abstract

The electrochemistry of tetrakis(*N,N*-diethyl- and *N,N*-diphenyldithiocarbamato)bis(arylimido)-μ-oxo-dirhenium complexes, [{$Re(NR)(S_2CNR'_2)_2$}$_2O$], where R = phenyl, *p*-tolyl, *p*-chlorophenyl and *p*-methoxyphenyl, has been studied in *N,N*-dimethylformamide. The [{$Re(NR)(S_2CNR'_2)_2$}$_2O$] complexes undergo a quasireversible one-electron reduction followed by the cleavage of the μ-oxo bond (Re–O–Re) including the release of one dithiocarbamate ligand from the complex. The redox potential for the [{$Re(NR)(S_2CNR'_2)_2$}$_2O$]$^{0/-}$ couple and the stability of the reduction products depend on R and R′. Linear correlations have been obtained between the redox potential of the diethyl- and diphenyldithiocarbamate complexes and the Hammett p-substituent constant of the aryl moiety. The diphenyldithiocarbamate complexes are easier to reduce by 170 mV than the corresponding diethyldithiocarbamate complexes. The weaker π-bonding of RN=Re causes the imido complexes to be more difficult to reduce than the corresponding oxo analogues [{$ReO(S_2CNR'_2)_2$}$_2O$]. The oxidation of [{$Re(NR)(S_2CNR'_2)_2$}$_2O$] is an irreversible one-electron process but the oxo analogues exhibit ill-defined voltammograms.

Introduction

The existence of accessible oxidation states VII to −I is an important feature of rhenium chemistry leading to various electrochemical studies. Electrochemical studies of technetium complexes have been applied to characterize the ^{99m}Tc radiopharamaceuticals for imaging organ systems in the diagnosis of disease. Recently, analogous complexes of a radioactive isotope ^{186}Re to ^{99m}Tc have been investigated with regard to the potential use in nuclear medicine and the electrochemistry of rhenium complexes has been extended to estimate the imaging efficiency of ^{186}Re complexes [1]. To better understand technetium and rhenium in terms of chemical periodicity, the electrochemical behavior of rhenium complexes has been compared to those of technetium complexes [2–5]. The rhenium(V) complexes having a rhenium–imido (sometimes called nitrene) bond (Re=NR) and a rhenium–oxo bond (Re=O) are isoelectronic [6, 7] and isostructural [8], and the Re=NR bond [9] as well as the Re=O bond [10] possesses a triple bond character. Moreover, the similarity between oxygen transfer reactions of imido and oxo complexes of molybdenum(VI), [$MoO(NTo)(S_2CNEt)_2$] and [$MoO_2(S_2CNEt_2)_2$], has been reported [11, 12]. A diagonal relationship between molybdenum and rhenium in the Periodic Table suggests that similarities can be expected in reaction chemistry and electrochemistry of the imido and oxo rhenium(V) complexes. Therefore, we focus on the study of the electrochemical characterization of rhenium(V) dithiocarbamate complexes with an imido or oxo bond to better understand the redox chemistry of sulfur-coordinating rhenium complexes. In this paper, the comparison of the electrochemistry of [{$Re(NR)(S_2CNR'_2)_2$}$_2O$] complexes having a linear RN=Re−O−Re=NR geometry [13] and [{$ReO(S_2CNR'_2)_2$}$_2O$] having a linear O=Re−O−Re=O geometry [14, 15] is reported. The effect of R′ of the dithiocarbamate ligand and the solvent effect on the electrochemical reduction for the [{$ReO(S_2CNR'_2)_2$}$_2O$] complexes have already been studied [16].

Experimental

Reagents

Unless otherwise noted, all reagents were of reagent grade. Aryliminophosphoranes ($RN{=}PPh_3$, R = phenyl (Ph), *p*-tolyl (To)) were prepared from the corresponding azides [17] by the literature method [18]. Reaction of the aryliminophosphorane with [$ReOCl_3(PPh_3)_2$] [19]

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gave $[Re(NR)Cl_3(PPh_3)_2]$. The *N*,*N*-diethyldithiocarbamate complex, $[\{Re(NR)(S_2CNEt_2)_2\}_2O]$ [13], was obtained by the reaction of $[Re(NR)Cl_3(PPh_3)_2]$ with *N*,*N*,*N*′,*N*′-tetraethylthiuram disulfide (Wako Pure Chemicals) followed by the base hydrolysis in acetone.

The preparation of $[\{Re(NPh)(S_2CNPh_2)_2\}_2O]$ was according to the following procedure. The reflux of $[Re(NPh)Cl_3(PPh_3)_2]$ with sodium *N*,*N*-diphenyldithiocarbamate [20] in acetone containing 1 vol.% water gave a brown precipitate, which was purified by column chromatography with silica gel (70–230 mesh, Merck) using dichloromethane as an eluent and then dried under vacuum. IR (KBr): 1489 (C–N), 1001 (C–S), 712 (Re–O–Re) cm^{-1}. *Anal.* Found: C, 49.65; H, 3.21; N, 5.48. Calc. for $C_{64}H_{50}N_6ORe_2S_8$: C, 49.69; H, 3.26; N, 5.43%. The tolylimido complex, $[\{Re(NTo)(S_2CNPh_2)_2\}_2O]$, was prepared by a similar procedure. IR (KBr): 1485 (C–N), 999 (C–S), 710 (Re–O–Re) cm^{-1}. *Anal.* Found: C, 51.89; H, 3.55; N, 5.48. Calc. for $C_{66}H_{54}N_6ORe_2S_8$: C, 51.90; H, 3.53; N, 5.43%.

The reflux of *p*-chloroaniline or *p*-anisidine with $[ReOCl_3(PPh_3)_2]$ in benzene gave $[Re(NC_6H_4Cl)Cl_3(PPh_3)_2]$ or $[Re(NC_6H_4OCH_3)Cl_3(PPh_3)_2]$. In acetone $[Re(NC_6H_4Cl)Cl_3(PPh_3)_2]$ was refluxed with sodium *N*,*N*-diethyldithiocarbamate to give $[\{Re(NC_6H_4Cl)(S_2CNEt_2)_2\}_2O]$. IR (KBr): 1489 (C–N), 998 (C–S), 710 (Re–O–Re) cm^{-1}. *Anal.* Found: C, 30.57; H, 3.82; N, 6.78. Calc. for $C_{32}H_{48}Cl_2N_6ORe_2S_8$: C, 31.19; H, 3.93; N, 6.82%. The *p*-methoxyphenylimido complex, $[\{Re(NC_6H_4OCH_3)(S_2CNEt_2)_2\}_2O]$, was prepared by the reaction of $[Re(NC_6H_4OCH_3)Cl_3(PPh_3)_2]$ with *N*,*N*,*N*′,*N*′-tetraethylthiuram disulfide followed by base hydrolysis. IR (KBr): 1491 (C–N), 990 (C–S), 710 (Re–O–Re) cm^{-1}. *Anal.* Found: C, 30.57; H, 3.82; N, 6.78. Calc. for $C_{58}H_{54}N_6O_3Re_2S_8$: C, 31.19; H, 3.93; N, 6.78%.

N,*N*-Dimethylformamide (DMF) was dried over molecular sieves 4A and anhydrous copper sulfate to remove water and amines, distilled at a reduced pressure under a nitrogen atmosphere, and stored under argon. The preparations of tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium *N*,*N*-diethyldithiocarbamate have already been described [16]. Cryptand 22 was purchased from Merck.

Instrumentation and methods

IR spectra were obtained on a Jasco DS-701G infrared spectrometer. A Nichia potentiostat NP-IR1000 and a Huso potential sweep unit HECS-321B were used for the conventional and thin-layer cyclic voltammetric measurements. For the steady state voltammetry, a Huso microelectrode potentiostat HECS-972W was used instead. Voltammograms were recorded on a Graphtech x-y recorder WVX-2400. Conventional cyclic voltammetry and thin-layer cyclic voltammetry were performed, respectively, at a platinum disk electrode (diameter = 2 mm) and a gold minigrid thin-layer electrode [21] in which two quartz slides were held with ceramic cement instead of epoxy for the use in non-aqueous solvent. A 30-μm diameter platinum microdisk electrode served as the working electrode for the steady-state voltammetry [22]. The reference electrode, $Ag/AgClO_4$ (0.005 M), cryptand 22 (0.01 M), TBAP (0.1 M) ||, was same as the previous one [16] and it was connected to the sample solution through a 0.1 M TBAP–DMF salt bridge. The formal redox potential ($E^{\circ\prime}$) of the ferrocenium/ferrocene couple (Fc^+/Fc) as an internal standard was measured with this reference electrode and the $E^{\circ\prime}(Fc^+/Fc)$ value was found to be 0.462 V.

Electrochemical measurements were made at 25 ± 1 °C in DMF. Sample solutions containing about 1 mM complex and 0.1 M TBAP as a supporting electrolyte were deoxygenated by passing dried argon through the sample solution before measurements. All the potentials reported here are referred to $E^{\circ\prime}(Fc^+/Fc)$.

Results and discussion

Electrochemistry of $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ complexes

All of the $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ complexes, where R is phenyl, *p*-tolyl, *p*-chlorophenyl or *p*-methoxyphenyl and R′ is ethyl or phenyl, undergo a quasireversible one-electron reduction in 0.1 M TBAP–DMF. Here, we report on the reduction of $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$ as a representative. We chose DMF as a solvent because DMF provides adequate solubility for $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ and the use of DMF allows the facile comparison of an electrochemical study of the imido complexes with that of the oxo analogues which has been conducted in the same medium [16]. Curve a in Fig. 1 is a typical cyclic voltammogram of 1 mM $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$ in 0.1 M TBAP–DMF

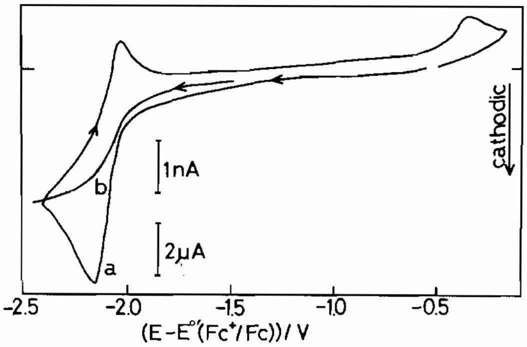

Fig. 1. Voltammograms for the reduction of 1 mM $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$ in 0.1 M TBAP–DMF. Curve a: cyclic voltammetry at a platinum disk electrode with a scan rate of 0.1 V/s. Curve b: steady state voltammetry at a platinum microdisk electrode with a scan rate of 1 mV/s.

at a platinum disk electrode. The negative scan initiated at −0.61 V yielded a reduction peak with $E_{p,c} = -2.16$ V coupled with the reoxidation peak of $E_{p,a} = -2.08$ V on the reverse scan. On the further positive reverse scan an additional oxidation peak with $E_{p,a} = -0.406$ V was observed. The proportionality of cathodic peak current to the square root of scan rate within 0.05–0.4 V/s suggests that the reduction process is diffusion controlled. The peak-to-peak separation is 75 mV at 0.1 V/s, indicating that the process is an electrochemically quasireversible one-electron transfer. In thin-layer cyclic voltammetry of the $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$ complex with a scan rate of 1 mV/s, one reduction peak with $E_{p,a} = -2.17$ V was observed. The reduction process is identical with that in conventional cyclic voltammetry. Thin-layer coulometry, by integrating the area under the reduction peak in thin-layer cyclic voltammetry with respect to time, gave 0.99 as the number of electron transferred per one molecule of $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$, confirming that the reduction is a one-electron process.

In conventional cyclic voltammetry, the ratio of anodic peak to cathodic peak currents for the scan rates ranging from 0.05 to 0.4 V/s was less than unity and decreased from 0.78 to 0.50 with decreasing scan rate. The peak potential of $E_{p,a} = -0.406$ V and the peak shape of the additional oxidation peak are consistent with those for the oxidation process of tetrabutylammonium *N,N*-diethyldithiocarbamate which was separately examined in the same media. These facts imply that the reduction is followed by a chemical reaction in which the μ-oxo bond in the complex is broken and one dithiocarbamate ligand is released. If the release of dithiocarbamate ligand took place before the cleavage of the μ-oxo bond, the addition of diethyldithiocarbamate ligand would cause a change in the voltammogram such as an increase in the anodic peak current. In fact, the voltammogram remained unchanged in the presence of a ten-fold excess of tetrabutylammonium *N,N*-diethyldithiocarbamate. Therefore, the release of dithiocarbamate ligand takes place after the cleavage of the μ-oxo bond, and the reduction mechanism is similar to that of the oxo analogues $[\{ReO(S_2CNR'_2)_2\}_2O]$ [16] and may be expressed as

$$[\{Re(NPh)(S_2CNEt_2)_2\}_2O] + e^- \rightleftharpoons [\{Re(NPh)(S_2CNEt_2)_2\}_2O]^- \quad (1)$$

$$[\{Re(NPh)(S_2CNEt_2)_2\}_2O]^- \longrightarrow [Re(NPh)(S_2CNEt_2)_2] + [ReO(NPh)(S_2CNEt_2)] + Et_2NCS_2^- \quad (2)$$

although the rhenium products have not been identified.

Curve a in Fig. 2 is the conventional cyclic voltammogram for the oxidation process of $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$. The other $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ complexes showed similar voltammograms. The voltammogram for the $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$ complex exhibits an oxidation peak with $E_{p,a} = 0.11$ V and there is no coupled peak on the reverse scan. Thus, the oxidation process is a chemically irreversible process. The number of electron transferred for the oxidation process should be one because the limiting current of the steady-state voltammogram at the platinum microdisk electrode of this process (curve b in Fig. 2) is nearly equal to that for the reduction process (curve b in Fig. 1).

Comparison of $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ complexes

The redox potential of the $[\{Re(NC_6H_4X)(S_2CNEt_2)_2\}_2O]^{0/-}$ couple (X = Cl, H, CH_3, OCH_3) is largely dependent upon X of the imido ligand. Table 1 summarizes the formal redox potential, $E^{\circ\prime}$, determined by averaging the cathodic and anodic peak potentials and the ratio of anodic to cathodic peak currents, $-I_{p,a}/I_{p,c}$, which is a measure of the stability of the reduction product. As shown in Fig. 3 there is a linear correlation between $E^{\circ\prime}$ and Hammett p-substituent constants, σ_p [23], of X with a slope of $\rho = 533$ mV and a correlation coefficient of 0.990. The more electron-withdrawing ability of X the more positive is the $E^{\circ\prime}$ and vice versa. A similar relationship is observed in the case of the diphenyldithiocarbamate complexes, but $E^{\circ\prime}$ for the $[\{Re(NR)(S_2CNEt_2)_2\}_2O]^{0/-}$ couple is 170 mV more negative than that for the $[\{Re(NR)(S_2CNPh_2)_2\}_2O]^{0/-}$ couple on average. It was 177 mV in the case of the oxo analogues [16]. The difference in $E^{\circ\prime}$ between the diphenyl- and diethyldithiocarbamate complexes is independent of the *trans* ligand in the case of the imido complexes and also in the case of the oxo complexes. This difference is explained in terms of the π-acceptance property of the

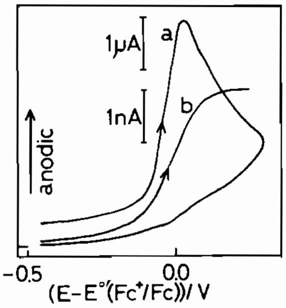

Fig. 2. Voltammograms for the oxidation of 1 mM $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$ in 0.1 M TBAP–DMF. Curve a: cyclic voltammetry at a platinum disk electrode with a scan rate of 0.1 V/s. Curve b: steady state voltammetry at a platinum microdisk electrode with a scan rate of 1 mV/s.

TABLE 1. Voltammetric data for the reduction of $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ in DMF at 25 °C

Complex	R′ = ethyl			R′ = phenyl		
	$E^{\circ\prime}$ (V)[a]	$-I_{p,a}/I_{p,c}$[b]	ν(Re–O–Re) (cm^{-1})	$E^{\circ\prime}$ (V)[a]	$-I_{p,a}/I_{p,c}$[b]	ν(Re–O–Re) (cm^{-1})
$[\{Re(NC_6H_4Cl)(S_2CNR'_2)_2\}_2O]$	−2.022	0.73	700			
$[\{Re(NC_6H_5)(S_2CNR'_2)_2\}_2O]$	−2.132	0.69	710	−1.971	0.63	712
$[\{Re(NC_6H_4CH_3)(S_2CNR'_2)_2\}_2O]$	−2.208	0.63	712	−2.042	0.60	712
$[\{Re(NC_6H_4OCH_3)(S_2CNR'_2)_2\}_2O]$	−2.300	0.60	710			
$[\{ReO(S_2CNR'_2)_2\}_2O]$[c]	−1.845	0.89	672	−1.668	0.77	675

[a] $E^{\circ\prime}=(E_{p,a}+E_{p,c})/2$. [b] At a scan rate of 0.1 V/s. [c] Ref. 16.

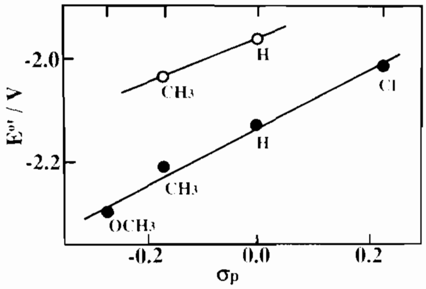

Fig. 3. Hammett plots of $E^{\circ\prime}$ for the reduction against σ_p of X of $[\{Re(NC_6H_4X)(S_2CNR'_2)_2\}_2O]$, where R′ = Et (●), Ph (○).

phenyl group through the C–N bond, reducing the electron density on the rhenium atom. The stability of the reduction product, $[\{Re(NR)(S_2CNR'_2)_2\}_2O]^-$, estimated by the $-I_{p,a}/I_{p,c}$ value is also dependent upon the R and R′ substituents. The reduction product becomes more stable to the cleavage of the μ-oxo bond as the complex becomes harder to reduce.

In the imido complexes, it is important that the *trans* influence of the imido ligand is probably associated with its geometry. On the basis of the structural postulation, Nugent and Haymore have suggested that the octahedral complexes with the maximum electron count (MEC), which is an electron count if all ligands donate the maximum number to the metal, of 18 electrons possess the linear C–N–M geometry while the imido ligands are bound in a bent geometry in the complexes having an MEC of 20 electrons [8]. The absence of the *trans* influence has been observed in the octahedrally coordinated rhenium(V) imido complexes, $[ReCl_3(NPh)(PPh_3)_2]$ [24–26], with a linear C–N–Re geometry. Thus, in the $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$ complex having an MEC of 18 and a linear Ph–N=Re–O–Re=N–Ph geometry [13], the imido ligand appears to exert no *trans* influence. The IR absorption bands attributable to ν(Re–O–Re) of all the imido complexes are found in the narrow region of 710–712 cm^{-1} (Table 1), showing that there is no *trans* influence. The cleavage of the μ-oxo bond upon electroreduction suggests that the reduction can take place at the μ-oxo bond. The strength of the μ-oxo bond from the IR data, however, is independent of the *trans* arylimido group which is capable of changing $E^{\circ\prime}$. Therefore, the reduction center may be the rhenium atom in the light of the difference in $E^{\circ\prime}$ between the diethyl- and diphenyldithiocarbamate complexes, although the imido ligand is a possible center.

Table 2 lists the anodic peak potentials, $E_{p,a}$, in conventional cyclic voltammetry for the irreversible oxidation process of $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$. The oxo analogues exhibit an ill-defined voltammogram and reliable $E_{p,a}$ values could not be obtained. The electron-withdrawing or electron-donating effect of X governs the $E_{p,a}$ value for the oxidation of $[\{Re(NC_6H_4X)(S_2CNR'_2)_2\}_2O]$. The $E_{p,a}$ value of the oxidation process, however, is less sensitive to X than the E° value of the reduction process. Generally, the complexes which are easier to reduce are more difficult to oxidize. The diphenyldithiocarbamate complexes are more difficult to oxidize by 105 mV than the diethyldithiocarbamate complexes; the difference is smaller than that of the reduction process.

Comparison of $[\{Re(NR)(S_2CNR'_2)_2\}_2O]$ and $[\{ReO(S_2CNR'_2)_2\}_2O]$

The $E^{\circ\prime}$ values for the $[\{Re(NR)(S_2CNR'_2)_2\}_2O]^{0/-}$ couples are significantly different from that of the $[\{ReO(S_2CNR'_2)_2\}_2O]^{0/-}$ couples. According to the estimation of the relative bond strengths of O=M and

TABLE 2. Peak potentials for the oxidation of $[\{Re(NC_6H_4X)(S_2CNR'_2)_2\}_2O]$ in DMF at 25 °C

X	$E_{p,a}$ (V)[a]	
	R′ = ethyl	R′ = phenyl
Cl	0.211	
H	0.196	0.226
CH_3	0.145	0.182
OCH_3	0.094	

[a] At a scan rate of 0.1 V/s.

RN=M from the structural data, the former is stronger than the latter [8]. Our IR data, ν(Re−O)=960 and ν(Re−O−Re)=672 cm^{-1} in $[\{ReO(S_2CNEt_2)_2\}_2O]$; ν(Re−N)=760 and ν(Re−O−Re)=710 cm^{-1} in $[\{Re(NPh)(S_2CNEt_2)_2\}_2O]$, support the difference in bond strengths. Moreover, π-backdonation occurs in the oxo complexes [27]. Thus, the potential difference is ascribed to the difference in bond character. The strong bonding of Re−O shifts the $E^{\circ\prime}$ for the oxo complex to a more positive potential.

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