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Electrochemical Reduction of Rhenium(V) Dithiocarbamate Complexes *trans*-$Re_2O_3(S_2CNR_2)_4$ in Nonaqueous Media

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Abstract

The electrochemistry for the reduction of tetrakis(dialkyl- and diphenyldithiocarbamato)-μ-oxodioxodirhenium complexes *trans*-$Re_2O_3(S_2CNR_2)_4$ (R = methyl, ethyl, propyl, butyl and phenyl) was investigated in seven nonaqueous solvents. The complexes underwent a reversible reduction involving one-electron at a platinum electrode to $[Re_2O_3(S_2CNR_2)_4]^-$, which decomposed with the cleavage of the μ-oxo bridge to form $ReO(S_2CNR_2)_2$, $R_2CNS_2^-$ and other rhenium complexes. The redox potential $E^{\circ\prime}$ of $[Re_2O_3(S_2CNR_2)_4]^{0/-}$ couples and the stability of the reduction product $[Re_2O_3(S_2CNR_2)_4]^-$ depend on the R group. The $E^{\circ\prime}$ are appreciably solvent-dependent. The difference in $E^{\circ\prime}$ with solvents could be interpreted in terms of the solubility parameters.

Introduction

The chemistry of rhenium has been investigated for synthetic and catalytic reasons and compared with that of manganese and technetium [1–3]. The electrochemistry of rhenium and technetium has not been developed although the complexes of these group VII B elements have a rich redox chemistry, the oxidation state of them ranging from VII to –I. Technetium complexes have been widely used as radiopharmaceuticals in nuclear medicine. Recently, the utility of some rhenium complexes as radiopharmaceuticals has been compared with that of the technetium analogues from the viewpoint of periodic relationship, in which the redox potential of these complexes affects the imaging efficiency [4].

In this paper, we report on the electrochemical reaction of rhenium(V) dithiocarbamate complexes *trans*-$Re_2O_3(S_2CNR_2)_4$ in nonaqueous media in order to understand the rhenium–sulfur redox chemistry. $Re_2O_3(S_2CNEt_2)_4$ has been structurally characterized and found to contain the linear O=Re–O–Re=O moiety [5, 6]. The rhenium complexes are stable and do not undergo disproportionation in nonaqueous media, which appeared in the *cis*-$Mo_2O_3(S_2CNEt_2)_4$ complex [7], a model compound for molybdenum-containing enzymes. The tetramethylenedithiocarbamate complexes of manganese, iron and copper are oxidized and reduced with one-electron in nonaqueous media. We have found that the redox potentials of these complexes are appreciably dependent on the solvent [8]. We also report the solvent effect on the reduction of $Re_2O_3(S_2CNR_2)_4$.

Experimental

Reagents

Unless otherwise noted, all chemicals were of reagent grade. Rhenium oxide (Re_2O_7) was purchased from Mitsuwa Chemicals. Sodium dimethyl- and diethyldithiocarbamates from Wako Pure Chemicals were used as received. Sodium dipropyl- [9], dibutyl- [9] and diphenyldithiocarbamates [10] were synthesized according to literature procedures. Tetrabutylammonium diethyldithiocarbamate was prepared as follows. An aqueous solution of sodium diethyldithiocarbamate was loaded on a column of cation exchanger with tetrabutylammonium form, which had been changed from H form (Dowex 50WX8) by loading an aqueous solution of tetrabutylammonium hydroxide. The eluate was cooled to precipitate tetrabutylammonium diethyldithiocarbamate. The white precipitate was filtered off and dried under vacuum. The rhenium(V) dithiocarbamate complexes, tetrakis(dialkyl- and diphenyldithiocarbamato)-μ-oxodioxodirhenium(V) ($Re_2O_3(S_2CNR_2)_4$ R = methyl, ethyl, propyl, butyl or phenyl) were prepared by a method similar to that of Rowbottom and Wilkinson [11] from respective sodium dialkyl- or diphenyldithiocarbamate and $ReOCl_3(PPh_3)_2$ which had been prepared from Re_2O_7 [12].

Dichloromethane, acetone, and acetonitrile were dried over molecular sieves type 4 Å and distilled

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under nitrogen. *N,N*-Dimethylformamide (DMF), dimethyl sulfoxide and propylene carbonate were dried over molecular sieves type 4 Å and distilled under nitrogen at reduced pressure. 1,2-Dimethoxyethane was distilled under argon from a mixture of sodium and benzophenone. All solvents were freshly distilled before use and stored over molecular sieves 4 Å under argon. Tetrabutylammonium perchlorate (TBAP) was prepared by metathesis from an aqueous solution of sodium perchlorate and tetrabutylammonium bromide, thoroughly washed with water until no bromide was detected, recrystallized twice from ethanol, and dried at 80 °C under vacuum. Cryptand(2,2) was purchased from Merck.

Instrumentation and Methods

IR spectra were obtained on a Jusco DS-701G infrared spectrometer. Voltammetric measurements were performed with a Yanaco P-1000 voltammetric analyzer, and voltammograms were recorded on a Riken Denshi F-43 x-y recorder. The working electrode for conventional cyclic voltammetry was a platinum disk electrode with a surface area of 0.0451 cm^2 as determined by chronoamperometry of a standard potassium ferrocyanide solution. The thin-layer cell [13] was conventionally constructed with 150 mesh platinum minigrid and the cell volume was 15 μl as calibrated by coulometry of a standard potassium ferrocyanide solution. Bulk controlled-potential electrolysis was made with a Nichia IR-1000 potentiostat using a platinum gauze electrode. The $Ag/Ag(cryptand(2,2))^+$ reference electrode [14] was constructed as $Ag/0.005$ M $AgClO_4$, 0.01 M cryptand(2,2), 0.1 M TBAP (DMF)// and isolated from the sample solution with porous ceramics.

Electrochemical measurements were performed at 25 ± 1 °C. The sample solution (1–2 mM) containing 0.1 M TBAP as supporting electrolyte in a volumetric flask was deoxygenated with a stream of argon and transferred to the electrochemical cell via Teflon tubing and argon pressure. The cell was placed in a dry box filled with dry argon. Potential scan rates were 20–200 mV/s and 1–2 mV/s for conventional and thin-layer cyclic voltammetry, respectively. Potentials were measured *versus* the $Ag/Ag(cryptand(2,2))^+$ and against the ferrocenium/ferrocene couple as an internal standard. Here all potentials are reported with respect to the ferrocenium/ferrocene couple.

Results and Discussion

Reduction of $Re_2O_3(S_2CNEt_2)_4$ Complex in DMF

Electrochemical reduction of the $Re_2O_3(S_2CNEt_2)_4$ complex is described here as a representative one of $Re_2O_3(S_2CNR_2)_4$. DMF was chosen as solvent for these electrochemical studies except the solvent effects, primarily because it provides sufficient solubility for $Re_2O_3(S_2CNR_2)_4$ complexes. In the case of a hanging mercury drop electrode as the working electrode the reduction process is accompanied by the strong adsorption [15] of the $Re_2O_3(S_2CNEt_2)_4$ complex and the reduction product on the electrode. Hereafter platinum electrodes were used for electrochemical measurements. Figure 1 shows typical cyclic voltammograms on the platinum disk electrode for the $Re_2O_3(S_2CNEt_2)_4$ complex at 25 and –25 °C in DMF. A negative potential scan initiated at –0.2 V gives a single reduction peak with $E_{pc} = -1.89$ V. The proportionality of peak current to the square root of scan rate within the range of 20–200 mV/s indicates that the reduction process is diffusion-controlled. A reoxidation peak corresponding to the reduction peak appears on the reverse scan. The separation of peak potentials at a scan rate of 100 mV/s is 63 mV, which is close to that of the reversible one-electron process. At 25 °C the ratio of oxidation to reduction peak currents is less than unity in the range of scan rate from 20 to 200 mV/s. The further positive scan gives another small oxidation peak at –0.4 V. The current ratio approaches unity with decreasing temperature and no significant peak is observed around –0.4 V at –25 °C. These observations suggest the presence of the chemical reaction following the reduction process.

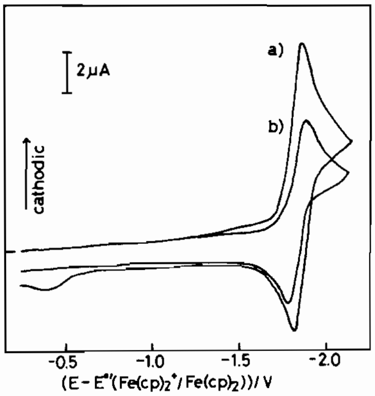

Fig. 1. Cyclic voltammograms of 1 mM $Re_2O_3(S_2CNEt_2)_4$ in DMF containing 0.1 M TBAP at a platinum disk electrode with a scan rate of 100 mV/s. (a) 25 °C, (b) –25 °C.

Figure 2 illustrates a thin-layer cyclic voltammogram of the $Re_2O_3(S_2CNEt_2)_4$ complex with a scan rate of 1 mV/s in the same potential range as in Fig. 1. One reduction and one oxidation peak are observed on the negative potential scan initiated at –0.2 V and on the reverse positive scan from –2.2 V, respectively. The reduction process is identical with that in the conventional cyclic voltammetry; the more negative shift of peak potential is due to the solution resistance of nonaqueous solvent in the thin-layer arrangement. No appreciable peak for the reoxidation to $Re_2O_3(S_2CNEt_2)_4$ around –1.8 V on

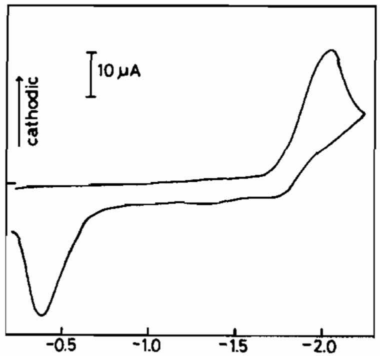

Fig. 2. Thin-layer cyclic voltammogram of 2 mM $Re_2O_3(S_2CNEt_2)_4$ in DMF containing 0.1 M TBAP with a scan rate of 1 mV/s at 25 °C.

the reverse scan indicates again that the electrode reaction is coupled with a following chemical reaction and the reaction product gives the oxidation peak at a more positive potential. The thin-layer coulometry, which was performed by integrating the area under peak in thin-layer cyclic voltammetry with respect to time, gave the number of electron transferred as 0.97 for the reduction process and 0.98 for the oxidation process per one molecule of the starting $Re_2O_3(S_2CNEt_2)_4$ complex. The oxidation process at −0.2 V is completely consistent with that of tetrabutylammonium diethyldithiocarbamate. An electrode reaction of a dithiocarbamate in non-aqueous solvents [16] is

$$2Et_2NCS_2^- \longrightarrow Et_2NC(S)SSC(S)NEt_2 + 2e^- \qquad (1)$$

Thus the reduction of the $Re_2O_3(S_2CNEt_2)_4$ complex is the reversible one-electron process followed by the chemical reaction including the release of one of the diethyldithiocarbamate ligands from the reduction product $[Re_2O_3(S_2CNEt_2)_4]^-$.

$$Re_2O_3(S_2CNEt_2)_4 + e^- \rightleftharpoons [Re_2O_3(S_2CNEt_2)_4]^- \qquad (2)$$

$$[Re_2O_3(S_2CNEt_2)_4]^- \longrightarrow Et_2NCS_2^- + \text{Re product(s)} \qquad (3)$$

The released diethyldithiocarbamate is oxidized at −0.2 V on the reverse scan to the dimeric thiuram disulfide according to eqn. (1). The rhenium products are not electroactive in the potential range of interest.

Product Analysis

In order to elucidate the electrode reaction (eqns. (2) and (3)) of $Re_2O_3(S_2CNEt_2)_4$ complex more clearly, the controlled-potential electrolysis was carried out with a platinum gauze electrode in acetonitrile as solvent with 0.1 M tetraethylammonium perchlorate as supporting electrolyte. After electrolysis at −2.2 V the sample solution was evaporated. The products containing rhenium were easily separated from the other components which were soluble in water. IR spectra of the rhenium product mixture do not show any absorption band of Re–O–Re, indicating the cleavage of the μ-oxo bridge in the course of chemical reaction (3). Chromatographic separation of the rhenium products on a silica gel column gave at least three mononuclear rhenium complexes. The green complex, the first eluate with chloroform as eluent, is identified as the $Re^{IV}O(S_2CNEt_2)_2$ complex from the elemental analysis and IR spectra (ν(CN) = 1505 cm^{-1}, ν(Re=O) = 985 cm^{-1}). Though the other complexes have not been identified, it is thought that they are the decomposition products of the $Re^{V}O_2(S_2CNEt_2)$ complex. These results suggest that the Re^{IV}–O–Re^{V} bridge formed by one-electron reduction from the Re^{V}–O–Re^{V} complex cleaves at the Re^{IV}–O bond rather than Re^{V}–O. Thus eqn. (3) can be expressed as follows

$$[Re_2O_3(S_2CNEt_2)_4]^- \longrightarrow ReO(S_2CNEt_2)_2 + ReO_2(S_2CNEt_2) + Et_2NCS_2^- \qquad (4)$$

$$ReO_2(S_2CNEt_2) \longrightarrow \text{products} \qquad (5)$$

Comparison of $Re_2O_3(S_2CNR_2)_4$ Complexes

Bulk and thin-layer cyclic voltammetric behaviors for the reduction of $Re_2O_3(S_2CNR_2)_4$ are similar to those of $Re_2O_3(S_2CNEt_2)_4$. Table I summarizes the voltammetric data in DMF corresponding to eqns. (2) and (4). The formal redox potential $E^{\circ\prime}$ for the reduction of $Re_2O_3(S_2CNR_2)_4$ depends on the R group; there is a linear relation between $E^{\circ\prime}$ and Taft's σ^* constant of the R group. Among the dialkyldithiocarbamate complexes the $E^{\circ\prime}$ shifts to a more negative potential with the increase in sigma-donor character of the alkyl group. The $Re_2O_3(S_2CNPh_2)_4$ complex is more easily reduced by 177 mV than is

TABLE I. Voltammetric Data for the Reduction of $Re_2O_3(S_2CNR_2)_4$ in DMF at 25 °C

R	$E^{\circ\prime}$ (V)[a]	I_{pa}/I_{pc} [b]	σ^* of R[c]
Methyl	−1.794[d, e]	[e]	0
Ethyl	−1.849	0.89	−0.10
Propyl	−1.852	0.83	−0.115
Butyl	−1.860	0.80	−0.13
Phenyl	−1.672	0.77	0.60

[a] $E^{\circ\prime} = (E_{pa} + E_{pc})/2$. [b] At scan rate of 50 mV/s. [c] Taken from ref. 17. [d] Peak potential in differential pulse voltammetry. [e] Solubility is too small to measure the parameters in cyclic voltammetry.

TABLE II. Solvent Effect on $E^{\circ\prime}$ for the Reduction of $Re_2O_3(S_2CNR_2)_4$

No.	Solvent	$E^{\circ\prime}$ (V)[a]		ϵ_r [b]	AN [c]	δ_s ((cal cm^{-3})$^{1/2}$)[d]
		R = ethyl	R = phenyl			
1	propylene carbonate	−1.709	−1.556	65.0	18.3	13.50
2	dimethyl sulfoxide	−1.744	−1.595	46.68	19.3	13.00
3	acetonitrile	−1.774	−1.639	36.02	18.9	11.73
4	*N,N*-dimethylformamide	−1.845	−1.667	36.71	16.0	11.79
5	dichloromethane	−1.869	−1.752	8.93	20.4	9.83
6	acetone	−1.904	−1.752	20.70	12.5	9.64
7	1,2-dimethoxyethane	−1.929	−1.832	7.20	10.2	8.81

[a] *vs.* $E^{\circ\prime}$ of ferrocenium/ferrocene couple. [b] Taken from ref. 18. [c] Taken from ref. 19. [d] Calculated from $\delta_s = ((\Delta H_v - RT)/V_s)^{1/2}$. ΔH_v and V_s are taken from ref. 18.

the $Re_2O_3(S_2CNEt_2)_4$ complex. This trend is interpreted in terms of pi-acceptance of the phenyl group through the C–N bond. The stability of the reduction product $[Re_2O_3(S_2CNR_2)_4]^-$ also depends on the R group. The ratio of anodic to cathodic peak currents at a scan rate decreases in the order of R = ethyl > propyl > butyl > phenyl. This implies that the rate of Re^{IV}–O bond cleavage of $[Re_2O_3(S_2CNR_2)_4]^-$ represented by eqn. (4) increases with the above order.

Solvent Effect on the Redox Potential for the Reduction of $Re_2O_3(S_2CNR_2)_4$

The redox potentials $E^{\circ\prime}$ for the $[Re_2O_3(S_2CNR_2)_4]^{0/-}$ couples are appreciably solvent-dependent. Table II lists the $E^{\circ\prime}$ for $[Re_2O_3(S_2CNEt_2)_4]^{0/-}$ and $[Re_2O_3(S_2CNPh_2)_4]^{0/-}$ couples, together with relative dielectric constants (ϵ_r), acceptor numbers (AN) [19], and solubility parameters (δ_s) of solvents. By applying the Born–Harber cycle to the reduction, the $E^{\circ\prime}$ for the M/M$^-$ couple can be expressed as follows.

$$-FE^{\circ\prime} = -E_A + \Delta G^s{}_{M^-} - \Delta G^s{}_M + k \qquad (6)$$

where E_A is the electron affinity of the neutral complex M, and $\Delta G^s{}_M$ and $\Delta G^s{}_{M^-}$ are the solvation energy for the neutral and the anionic complex M$^-$, respectively. The value of k is the potential of reference electrode employed. In order to understand the solvent effect we use the internal standard of the ferrocenium/ferrocene couple, which is a solvent-independent redox couple and recommended for reporting electrode potentials in nonaqueous solvents [20]. Thus k is considered to be constant in all solvents studied. The $\Delta G^s{}_M$ and $\Delta G^S{}_{M^-}$ on the right-hand side of eqn. (6) may vary with different solvents. The solvation energy of an ion is predominantly electrostatic in nature and is, then, expressed by the Born equation. The variation in $\Delta G^s{}_{M^-}$ with different solvents evaluated from the Born equation is too small to explain the differences in $E^{\circ\prime}$. Gritzner *et al.* found a correlation between $E^{\circ\prime}$ for anionic complexes and the acceptor number of solvents [21, 22], which is a measure of the solvent acceptor properties. However, there is no correlation between the $E^{\circ\prime}$ of $[Re_2O_2(S_2CNR_2)_4]^{0/-}$ couples and the acceptor number. This observation indicates no specific interaction of the anionic complex $[Re_2O_3(S_2CNR_2)_4]^-$ with the solvent molecule, that is, the solvent independence of $\Delta G^s{}_{M^-}$. Consequently, the remaining term, that is, the solvation energy of the neutral complex, must be largely responsible for the difference in $E^{\circ\prime}$ values. When the complex with a solubility parameter, δ_M, is transferred from the gas phase to the polar solvent of the molar volume, V_s and solubility parameter, δ_s, $\Delta G^s{}_M$ is approximately expressed by [8]

$$\Delta G^s{}_M = V_s\delta_s(\delta_s - \delta_M) \qquad (7)$$

Since E_A on the right-hand side of eqn. (6) is inherent in the complexes, the $E^{\circ\prime}$ is almost dependent on $\Delta G^s{}_M$ and then eqn. (6) can be written as

$$-FE^{\circ\prime} = -V_s\delta_s(\delta_s - \delta_M) + k' \qquad (8)$$

or

$$-FE^{\circ\prime} + V_s\delta_s{}^2 = V_s\delta_s\delta_M + k' \qquad (9)$$

A plot of the value of left-hand side of eqn. (9) against $V_s\delta_s$ gives a straight line with a slope of δ_M. The δ_M values can be obtained from the plot and are 11.79 (cal cm^{-3})$^{1/2}$ for $Re_2O_3(S_2CNEt_2)_4$ and 10.91 (cal cm^{-3})$^{1/2}$ for $Re_2O_3(S_2CNPh_2)_4$. These δ_M values are comparable to the value of other dithiocarbamate complexes [8]. Using the evaluated δ_M values, the $-FE^{\circ\prime}$ are plotted against $V_s\delta_s(\delta_s - \delta_M)$. The plots are shown in Fig. 3, which gives two straight lines with a slope of −1. This linear relationship supports that eqn. (8) is a valid expression of the solvent effect. In conclusion the variation in the redox potential of the rhenium dithiocarbamate complexes with different solvents represented by eqn. (1) is not dependent on the solvation energy of the ions formed by reduction, but is dependent on the solvation energy of the neutral complexes.

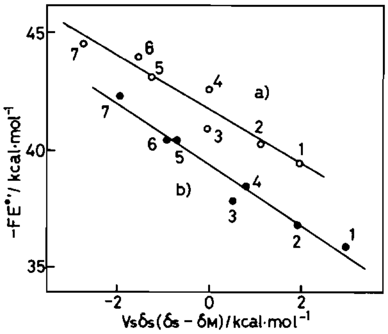

Fig. 3. Plots of $-FE^{\circ\prime}$ *vs.* $V_s\delta_s(\delta_s - \delta_M)$ for the reduction of $Re_2O_3(S_2CNEt_2)_4$ (a) and $Re_2O_3(S_2CNPh_2)_4$ (b) in non-aqueous solvent with molar volume of V_s and solubility parameter of δ_s. Solubility parameters of $Re_2O_3(S_2CNEt_2)_4$ and $Re_2O_3(S_2CNPh_2)_4$, δ_M, are 11.79 and 10.91 (cal cm^{-3})$^{1/2}$, respectively. Numbers correspond to those in Table II.

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