

with a bisc process. The associated activation energy while it is relatively large (59 kJ mol⁻¹) is commensurate with the 0-0 energy gap of ca. 50 kJ mol⁻¹ for the spacing between the doublet and quartet states that has been estimated by the procedure given by Fleischauer and co-workers.^{29,30}

In the photoreaction of *cis*-[Cr(cyclam)(NH₃)₂]³⁺ to yield *cis*-[Cr(cyclam)(NH₃)(H₂O)]³⁺ as the eventual product, an intervening chemically reactive species is found. This intermediate is clearly derived from the decay of the doublet state, and furthermore, its formation appears to be associated with the incorporation of a water molecule. This process would not involve a change in overall electrostatic charge on the complex, and thus a contribution to the volume change due to electrostriction effects is anticipated to be quite small. In this circumstance, one anticipates that the incorporation of water may be attendant by a negative volume change and that if this process involves strong-coupled surface crossing directly from the doublet state to that the ground-state intermediate, then this negative volume change will contribute to the observed volume of activation. This consideration may account for the observed volume of activation (+2.9 cm³ mol⁻¹) being smaller than that of +6.6 cm³ mol⁻¹ for the *trans* case; however, the overall algebraic sign for the observed volume of activation of the *cis* complex is positive, indicating in the general

sense that dissociative contributions prevail over associative ones and thus at least one further pathway having a positive volume change must contribute.³¹ It is notable in this context that the results found for the decay of the doublet-state emission in the *solid* phase where at 20 °C there is no detectable photochemistry suggest the influence of a strong-coupled relaxation process (other than direct decay to the ground state).⁹ Consequently the possibility exists that in the thermally activated region, the decay of the doublet state for the *cis* complex may follow several strongly coupled pathways in solution although they may not all lead to the generation of the intermediate, and Lessard and co-workers have recently discussed in some detail this type of situation.²⁷

Acknowledgment. The support of the Natural Sciences and Engineering Research Council of Canada in the form of Operating and Equipment Grants and of a postgraduate scholarship to D.A.F. and that of the University of Saskatchewan for awards to S.H.L. of G. Herzberg and University Scholarships is very much appreciated.

Supplementary Material Available: Tables listing the features of the absorption and emission bands for the transitions between the doublet state and the ground state for *cis*- and *trans*-[Cr(cyclam)(NH₃)₂]³⁺ in aqueous media (2 pages). Ordering information is given on any current masthead page.

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(30) Lessard and co-workers, employing the same procedure as used by us, report a somewhat larger energy gap of ca. 60 kJ mol⁻¹.^{27,29}

(31) The contribution here from a bisc process seems problematical at least from the viewpoint that the observed activation energy (36 kJ mol⁻¹) is less than the estimated energy gap between the quartet and doublet states of ca. 43 kJ mol⁻¹.²⁹

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Electrochemical Parametrization of Rhenium Redox Couples

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Received August 10, 1990

The observed rhenium potentials for Re^{IV/III}, Re^{III/II}, and Re^{II/I} reversible couples, for mononuclear species, are analyzed in terms of the electrochemical parametrization scheme based upon the Ru^{III/II} couples. Two independent sets of Re^{II/I} potentials are observed, which, if extended, would cross the Re^{III/II} correlation line. The possible significance of these sets is explored. The Re^{IV/III} couple correlation is roughly parallel to one of the Re^{II/I} correlation lines. The analysis leads to some interesting avenues for future synthetic studies.

General Introduction

Recently¹ a ligand electrochemical series based upon the Ru^{III/II} couple as an electrochemical standard was introduced. From this series of $E_L(L)$ values, it was shown that many redox couples would fit a linear correlation:

$$E(\text{obs}) = S_M[\sum E_L(L)] + I_M \quad (1)$$

where for a given metal and oxidation state, S_M and I_M were constant for all derivatives of given coordination number, stereochemistry, and spin state. The sum $[\sum E_L(L)]$ is the sum of the $E_L(L)$ values for all ligands binding to the metal ion. Thus, a series of linear correlations was presented for various couples, $M^{n+1/n}$, depending on the spin states and relative stereochemistries of M^{n+1} and M^n .

It was noted that, for a very limited data set, pairs of redox couples for the same metal ion had essentially parallel slopes. Thus, the S_M values for the couples Nb^{V/IV} and Nb^{IV/III} were identical. Clarke et al.² have demonstrated that the correlation lines for Tc^{IV/III}, Tc^{III/II}, and Tc^{II/I} are also essentially parallel (Figure 1). However Cr^{III/II} (low-spin Cr^{II}) is not parallel to¹ Cr^{I/0} and some early work with closely related tris(dithiocarbamato)iron complexes showed that the Fe^{III/II} and

Fe^{IV/III} couples were not parallel.³ Thus the issue is unclear.

This report deals with data for Re^{IV/III}, Re^{III/II}, and Re^{II/I} in order, in part to explore this issue in more detail, but also to obtain fresh insights into rhenium synthetic chemistry. The rhenium system is more complex than that observed for technetium. Two independent lines are observed for the Re^{II/I} couples, and lines for Re^{III/II} and Re^{II/I}, if extended, would cross, leading to some interesting synthetic and electrochemical predictions. The Re^{IV/III} line is seen to be approximately parallel to one of the Re^{II/I} lines.

All data are taken from the literature as referenced and are listed versus NHE. Standard corrections were used where other electrodes were involved.⁴ Scatter in the figures may reflect some errors arising from poor reference electrodes, wet solvents, poor electrode design, etc., though scatter may also be a consequence of other factors discussed below.

Stereochemistry and Spin State in Rhenium Complexes

The complexes containing the rhenium(I) oxidation state, d⁶, are almost invariably low spin and octahedral, but five-coordination is possible.⁵ Rhenium(II) may exist in low-spin, d⁵, paramagnetic,

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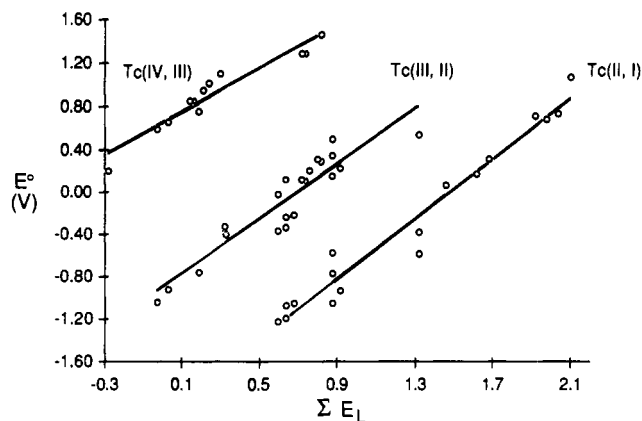


Figure 1. Correlation lines for $Tc^{IV/III}$, $Tc^{III/II}$, and $Tc^{II/I}$ (reproduced from ref 2).

six-coordinate, mononuclear species or in some dinuclear or cluster species. Rhenium(III), low spin d^4 , may be mononuclear six-coordinate or seven-coordinate⁶⁻¹⁰ or may exist in a range of polynuclear species. Finally rhenium(IV), d^3 , is commonly six-coordinate octahedral,¹¹ though seven-coordinate species are known.^{6-8,12-14}

Data Analysis

The literature was explored to find a representatively large selection of $Re^{IV/III}$, $Re^{III/II}$, and $Re^{II/I}$ electrochemically reversible or quasi-reversible couples, recorded in organic solvents (mostly CH_3CN and CH_2Cl_2) and restricted solely to the mononuclear species of these various oxidation states. Oxo species are omitted, as are species involving ligands for which well-defined E_L values are not available. All species obtained from the literature and meeting the above requirements are included in the analysis that follows. These data are collected in Table I and displayed in Figure 2.

A mononuclear rhenium(I) species may give rise to one to three reversible oxidation couples, while a mononuclear rhenium(IV) species may generate one to three reversible reduction couples. It is entirely possible, for example, that the successive oxidations of a mononuclear rhenium(I) species could lead to a polynuclear rhenium(III) species formed by a following chemical reaction at the electrode. The assumption is made that where a mononuclear species is being investigated, the appearance of *electrochemically reversible* couples precludes the possible generation of polynuclear species at that couple, on the electrochemical time scale.

The data are treated in the fashion described earlier¹ to discover the appropriate slope and intercept to describe each couple. From the above discussion, separate linear correlations might be required to describe couples involving six- or seven-coordinate rhenium(III) (and perhaps rhenium(IV)). If a six-coordinate rhenium(II) species oxidizes to six-coordinate rhenium(III) and then binds, for example, a supporting electrolyte anion to form a seven-coordinate species, this may occur sufficiently slowly on the electrochemical time scale that electrochemical reversibility is observed. In such circumstances the observed potential should fit the correlation for six-coordinate species. A six-coordinate rhenium(III) species may also rapidly bind a solvent molecule or

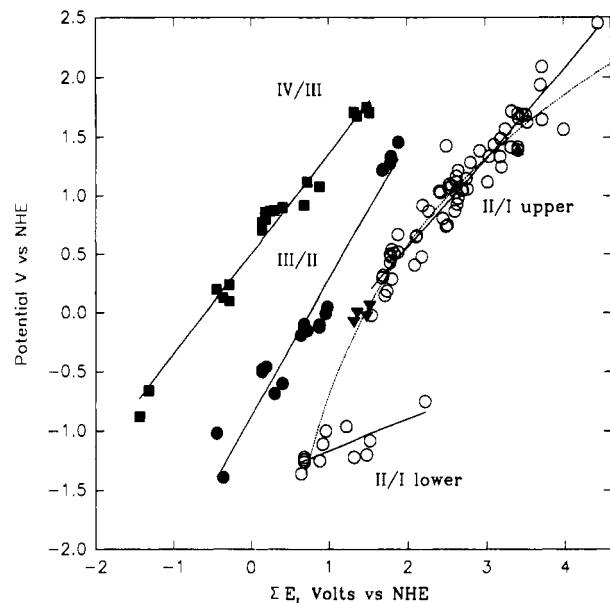


Figure 2. Correlations lines for upper and lower $Re^{II/I}$ couples, the $Re^{III/II}$ couple (the four closed triangles refer to the four poorly behaved complexes discussed in the text), and the $Re^{IV/III}$ couple. The point designated by a reversed closed triangle corresponds with the 2-electron oxidation of $m-ReCl(CO)_3(PMe_2Ph)_2$. All data are given in volts vs. NHE. See Table I for the observed and calculated data.

supporting electrolyte anion to form a seven-coordinate rhenium(III) complex. Such a system would fit a different correlation from the standard six-coordinate $Re^{III/II}$ correlation (vide infra).

No additional corrections are made in this analysis, except for isocyanide ligands as described below. In general, standard deviations from the best line fits are comparable to those noted for other redox couples in the previous study.¹

Results

Rhenium(II)/Rhenium(I). There is a large body of data available for this couple. Some 72 complexes (meeting the above criteria) are included in Table I. However, to improve the statistics for this correlation, it was necessary to increase the E_L contributions for isocyanide ligands beyond their normal (uncorrected) values.¹ Isocyanide ligands may bind to metal ions either in a linear or bent manner. When the binding mode is bent, there is an increased back electron donation toward the isocyanide ligand, resulting in increased metal-carbon double-bond character, and an effective increase in E_L value.^{1,15} In the previous publication, this correction was achieved by adding a term to eq 1 reflecting the number of isocyanide ligands interacting with the HOMO orbital involved in the redox process. In principle, this number might vary for every type of isocyanide and depend upon the degree of bend. However, in practice, it was found acceptable, within the accuracy of the study, only to consider two corrections, one for aromatic isocyanides and one for aliphatic isocyanides (defined for a given metal ion and redox couple).

X-ray data available for some rhenium isocyanide species do indeed demonstrate that some complexes contain bent isocyanide residues.¹⁶⁻²¹ However, since X-ray data are not available for

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Table I. Data Presentation for Figure 2: Comparison of Observed and Calculated Potentials (V vs NHE)^a

ref	complex	potential			ref	complex	potential		
		obs	calc	ΣE_L			obs	calc	ΣE_L
Rhenium(II)/Rhenium(I) (Lower Line)									
34, 36	Re(dmpe) ₂ Cl ₂ ⁺	-1.36	-1.26	0.64	34	Re(dppe) ₂ Cl ₂ ⁺	-1.00	-1.18	0.96
23	Re(NCS) ₃ (PEt ₂ Ph)(bpy)	-1.26	-1.25	0.68	6	ReCl ₂ (CN ⁱ Pr) ₂ (PMePh) ₂	-0.96	-1.11	1.22
23	Re(NCS) ₃ (PEt ₂ Ph)(phen)	-1.24	-1.25	0.68	39	Re(<i>o</i> -phen(PPh ₂) ₂) ₂ Cl ₂	-1.22	-1.08	1.32
34	Re(dmpe) ₂ Br ₂ ⁺	-1.22	-1.25	0.68	40	Re(dppee) ₂ Cl ₂ ⁺	-1.20	-1.03	1.48
34	Re(diars) ₂ Cl ₂ ⁺	-1.25	-1.20	0.88	40	Re(dppee) ₂ Br ₂ ⁺	-1.08	-1.02	1.52
23	Re(NCS) ₃ (PEt ₂ Ph)(dppe)	-1.11	-1.19	0.92	22	ReCl ₂ (CO) ₂ (P ^{<i>i</i>} Pr) ₃	-0.75	-0.84	2.22
Rhenium(II)/Rhenium(I) (Upper Line)									
41	<i>t</i> -Re(N ₂)(dtc)(PMe ₂ Ph) ₃	-0.02	0.21	1.54	44	Re(dppe) ₂ (CNPh-4-Me) ₂	1.17	1.03	2.62
15	Re(CNCMe) ₃ (dppe) ₂ Cl	0.30	0.32	1.68	44	Re(dppe) ₂ (CNPh-4-MeO) ₂	1.12	1.03	2.62
15	Re(CNMe)(dppe) ₂ Cl	0.32	0.33	1.69	43	Re(N ₂)Cl(CO)(P(OMe) ₃)(PPh ₃) ₂	0.93	1.04	2.63
41	<i>t</i> -Re(N ₂)Cl(Py)(PMe ₂ Ph) ₃	0.15	0.34	1.71	16	Re(CNCMe) ₃ ⁺	0.98	1.04	2.64
41	Re(N ₂)Br(Py)(PMe ₂ Ph) ₃	0.19	0.36	1.74	44	Re(dppe) ₂ (CNPh-4-Cl) ₂	1.22	1.04	2.64
15	Re(CNPh-4-OMe)(dppe) ₂ Cl	0.43	0.39	1.78	43	Re(N ₂)Cl(CO)(P(OMe) ₃) ₃	1.05	1.08	2.69
15	Re(CNPh-2-Me)(dppe) ₂ Cl	0.50	0.39	1.78	16	Re(CNCMe) ₃ (PPh ₃) ₂ ⁺	1.05	1.09	2.70
15	Re(CNPh-4-Me)(dppe) ₂ Cl	0.48	0.40	1.79	43	Re(N ₂)(NCPH)(dppe) ₂ ⁺	1.15	1.13	2.75
15	Re(CNPh-4-Cl)(dppe) ₂ Cl	0.54	0.41	1.80	14	ReCl(CO) ₂ (PMe ₂ Ph) ₃	1.06	1.13	2.76
41	<i>t</i> -Re(N ₂)Cl(PMe ₂ Ph) ₄	0.29	0.41	1.80	44	Re(dppe) ₂ (CNPh-2,6-Cl ₂) ₂	1.29	1.16	2.80
42	Re(dppe) ₂ Cl(CNPh)	0.51	0.43	1.83	15	Re(CNMe)(CO)(dppe) ₂ ⁺	1.39	1.26	2.92
15	Re(CNPh-2,6-Cl ₂)(dppe) ₂ Cl	0.67	0.47	1.88	47	<i>c</i> -Re(bpy) ₂ (CO) ₂ ⁺	1.12	1.33	3.02
15, 43	Re(N ₂)(dppe) ₂ Cl	0.52	0.47	1.88	46	Re(CNPh-4-OMe) ₆ ⁺	1.34	1.35	3.04
21	Re(CNCMe) ₃ (Py)(NCMe)(PPh ₃) ₂	0.41	0.63	2.09	46	Re(CNPh-4-Me) ₆ ⁺	1.44	1.39	3.10
41	Re(CO)Cl(PMe ₂ Ph) ₄	0.65	0.64	2.11	47	<i>t</i> , <i>c</i> -Re(bpy)(PMe ₂ Ph) ₂ (CO) ₂ ⁺	1.34	1.45	3.18
43	<i>t</i> -Re(N ₂)Cl(P(OMe) ₃) ₄	0.66	0.65	2.12	48	Re(4,4'-Me ₂ bpy)(CO) ₃ Cl	1.49	1.46	3.19
21	Re(CNCMe) ₃ (NCMe) ₂ (PPh ₃) ₂	0.48	0.70	2.18	49	Re(N ₂)Cl(CO) ₂ (PPh ₃) ₂	1.25	1.47	3.20
42	Re(dppe) ₂ Cl(CO)	0.92	0.70	2.19	50	<i>f</i> -Re(phen)(CO) ₃ Cl	1.57	1.51	3.25
15	Re(CNMe)(NCMe)(dppe) ₂ ⁺	0.87	0.76	2.27	46	Re(CO)(CNMe) ₃ ⁺	1.42	1.56	3.32
44	Re(CNCMe) ₃ (dppe) ₂ ⁺	1.04	0.86	2.40	45	Re(4,4'-(NO ₂) ₂ bpy)(CO) ₃ Cl	1.72	1.57	3.33
42	Re(CNMe)(CNCMe) ₂ (dppe) ₂ ⁺	1.03	0.87	2.41	22	<i>t</i> -ReCl(CO) ₃ (PMe ₂ Ph) ₂	1.42	1.63	3.41
15	Re(CNMe) ₂ (dppe) ₂ ⁺	1.03	0.88	2.42	51	Re(Cl)(CO) ₃ (NCMe) ₂	1.70	1.63	3.41
41	Re(N ₂)Cl(CO)(PMe ₂ Ph) ₃	0.81	0.90	2.45	44	Re(CO) ₂ (dppe) ₂ ⁺	1.66	1.63	3.42
45	Re(terpy)(CO) ₂ Cl [†]	1.43	0.93	2.49	52	<i>m</i> -Re(CO) ₃ (P ^{<i>m</i>} Tol) ₃ Cl	1.69	1.67	3.47
46	Re(CNPh-4-Me) ₃ Cl	0.74	0.93	2.49	52	<i>m</i> -Re(CO) ₃ (PPh ₃) ₂ Cl	1.69	1.70	3.51
46	Re(CNPh-4-Me) ₃ Br	0.75	0.95	2.51	52	<i>m</i> -Re(CO) ₃ (P ^{<i>m</i>} Tol) ₃ Br	1.63	1.72	3.53
15	Re(CNMe)(CNPh-4-Me)(dppe) ₂ ⁺	1.07	0.95	2.52	46	<i>c</i> -Re(CO) ₂ (MeNC) ₃ [†]	1.94	1.85	3.70
15	Re(CNMe)(CNPh-4-Cl)(dppe) ₂ [†]	1.10	0.96	2.53	48	Re(bpy)(CO) ₃ (4-EtPy) ⁺	2.09	1.86	3.72
15	Re(CNMe)(CNPh)(dppe) ₂ [†]	1.09	0.98	2.56	46	Re(CNPh-4-Me) ₅ (CO) ⁺	1.65	1.86	3.72
16	Re(CNCMe) ₃ (PEt ₂) ₂ ⁺	0.87	1.01	2.60	46	<i>m</i> -Re(CO) ₃ (CNMe) ₃ (irreversible) ^b	2.45	2.41	4.44
43	Re(N ₂)(NCMe)(dppe) ₂ [†]	1.03	1.02	2.61	51	<i>f</i> -Re(CO) ₃ (NCMe) ₃ [†]	1.57	2.06	3.99
Rhenium(III)/Rhenium(II)									
23	Re(NCS) ₆ ³⁻	-1.39	-1.30	-0.36	23	Re(NCS) ₃ (PEt ₂ Ph)(dppe)	-0.10	0.15	0.88
47	Re(bpy)Cl ₄	-1.02	-1.39	-0.44	34	Re(dppe) ₂ Cl ₂ ⁺	-0.01	0.25	0.96
53	ReCl ₄ (CNPh) ₂ ⁻	-0.48	-0.71	0.14	6	ReCl ₂ (CN ^{<i>i</i>} Pr) ₂ (PMePh) ₂ ⁺	0.05	0.27	0.98
47	<i>f</i> -Re(bpy)(PMe ₂ Ph)Cl ₃	-0.50	-0.71	0.14	39	Re(<i>o</i> -phen(PPh ₂) ₂) ₂ Cl ₂ ⁺	-0.08	0.67	1.32
47	<i>f</i> -Re(bpy)(PPh ₃)Cl ₃	-0.46	-0.66	0.19	39	Re(<i>o</i> -phen(PPh ₂) ₂) ₂ Br ₂ [†]	0	0.71	1.36
54	ReCl ₃ (PMe ₂ Ph) ₃	-0.69	-0.53	0.30	40	Re(dppee) ₂ Cl ₂ [†]	-0.03	0.85	1.48
47	<i>m</i> -Re(PPh ₃) ₂ (NCMe)Cl ₃	-0.60	-0.41	0.40	40	Re(dppee) ₂ Br ₂ [†]	0.06	0.90	1.52
36	Re(dmpe) ₂ Cl ₂ ⁺	-0.19	-0.13	0.64	15	Re(CNCMe) ₃ (dppe) ₂ Cl	1.22	1.09	1.68 ^c
23	Re(NCS) ₃ (PEt ₂ Ph)(phen)	-0.14	-0.08	0.68	15	Re(CNMe)(dppe) ₂ Cl	1.23	1.10	1.69 ^c
34	Re(dmpe) ₂ Br ₂ ⁺	-0.10	-0.08	0.68	15	Re(CNPh-4-OMe)(dppe) ₂ Cl	1.28	1.20	1.78 ^c
23	Re(NCS) ₃ (PEt ₂ Ph)(bpy)	-0.14	-0.08	0.68	15	Re(CNPh-4-Me)(dppe) ₂ Cl	1.34	1.21	1.79 ^c
47	<i>t</i> , <i>c</i> -Re(bpy)(PMe ₂ Ph) ₂ Cl ₂ [†]	-0.15	-0.04	0.72	15	Re(CNPh-2-Me)(dppe) ₂ Cl	1.33	1.21	1.79 ^c
34	Re(diars) ₂ Cl ₂ [†]	-0.12	0.15	0.88	15	Re(CNPh-2,6-Cl ₂)(dppe) ₂ Cl	1.46	1.32	1.88 ^c
Rhenium(IV)/Rhenium(III)									
55	ReCl ₆ ⁴⁻	-0.88	-0.73	-1.44	54	ReCl ₃ (PMe ₂ Ph) ₃	0.88	0.76	0.30
56	ReBr ₆ ⁴⁻	-0.66 ^d	-0.62	-1.32	47	<i>m</i> -Re(PPh ₃) ₂ (NCMe)Cl ₃	0.90	0.85	0.40
47	Re(bpy)Cl ₄	0.20	0.13	-0.44	23	Re(NCS) ₃ (PEt ₂ Ph)(bpy)	0.92	1.09	0.68
23, 24	Re(NCS) ₆ ⁴⁻	0.13	0.20	-0.36	47	<i>t</i> , <i>c</i> -Re(bpy)(PMe ₂ Ph) ₂ Cl ₂	1.12	1.12	0.72
51	<i>c</i> -Re(NCMe) ₂ Cl ₄	0.24	0.27	-0.28	23	Re(NCS) ₃ (PEt ₂ Ph)(dppe)	1.08	1.26	0.88
54	ReCl ₄ (PMe ₂ Ph) ₂	0.10	0.27	-0.28	39	Re(<i>o</i> -phen(PPh ₂) ₂) ₂ Cl ₂ [†]	1.71	1.64	1.32
47	<i>f</i> -Re(bpy)(PMe ₂ Ph)Cl ₃	0.71	0.62	0.14	39	Re(<i>o</i> -phen(PPh ₂) ₂) ₂ Br ₂ [†]	1.68	1.67	1.36
53	ReCl ₄ (CNPh) ₂ ⁻	0.77	0.63	0.14	40	Re(dppee) ₂ Cl ₂ [†]	1.75	1.77	1.48
57	ReCl ₃ (tetrahydrothiophene) ₃	0.86	0.66	0.18	40	Re(dppee) ₂ Br ₂ [†]	1.71	1.81	1.52
47	<i>f</i> -Re(bpy)(PPh ₃)Cl ₃	0.80	0.67	0.19					
57	ReBr ₃ (tetrahydrothiophene) ₃	0.87	0.71	0.24					

^a For abbreviations, see ref 1; dppe = *cis*-1,2-bis(diphenylphosphino)ethene. The charges indicated after some species refer to the charge on the bulk species being studied; if no charge is indicated, the bulk species is electrically neutral. The calculated data reported here were obtained from a Lotus program prior to rounding off the slope and intercept to two decimal places. The numbers shown here may therefore not always agree exactly with those obtained by using the equations in Table II. A superscript † identifies poor agreement between observed and calculated; error > 0.04 V. These entries were not included in the linear regression analysis. ^b Not included in linear regression analysis. ^c These isocyanide ΣE_L values contain the same correction factor as determined to best fit the Re^{II/I} data. ^d Both the [ReCl₆]²⁻ and [ReBr₆]²⁻ ions were initially reported to have irreversible Re^{IV/III} couples.³⁶ More recent studies on [ReCl₆]²⁻ reported a reversible couple at essentially the same potential.⁵⁵ Thus, the value reported here for [ReBr₆]²⁻ is likely correct; it was not, however, included in the linear regression analysis.

all the complexes under consideration (even if one could assume that the solid- and solution-phase structures were the same) and since indeed the stereochemistries are not always reported, the

data have been fitted in a general fashion except where a specific stereochemistry is known, when the appropriate correction is used.¹ A correction in volts is applied for each aliphatic or aromatic

Table II. Correlation Data for Rhenium and Technetium Couples^a

couple	S_M	I_M	R	MSD, ^{b,c} V	N^d	N^e	N^f
					>0.25 V	>0.15, <0.25 V	
Re ^{II/I} (upper)	0.76 (0.03)	-0.95 (0.13)	0.96	0.134	2	17	59 ^g
Re ^{II/I} (lower)	0.27 (0.07)	-1.43 (0.11)	0.76	0.104	0	2	12
Re ^{III/II}	1.17 (0.06)	-0.88 (0.17)	0.97	0.188	3	7	22 ^h
Re ^{IV/III}	0.86 (0.04)	0.51 (0.13)	0.98	0.124	0	6	20
Tc ^{II/I}	1.42 (0.12)	-2.09 (0.10)	0.94				14
Tc ^{III/II}	1.28 (0.08)	-0.89 (0.11)	0.86				22
Tc ^{IV/III}	1.00 (0.04)	0.65 (0.09)	0.92				12

^a S_M and I_M are the slope and intercept of eq 1; R is the correlation coefficient; standard deviations of slope and intercept are given in parentheses in volts. ^b MSD is the standard deviation in volts of calculated minus observed potential. ^c For comparison, previous MSD values include Cr^{III/II}(LS) 0.120, Cr^{II/I} 0.115, Fe^{III/II}(LS) 0.109, Mn^{II/I} 0.079, Mo^{I/O} 0.095, Os^{III/II} 0.099, and Ru^{III/II} 0.035 V.¹ ^d Number of data points deviating by more than 0.25 V from calculated value. ^e Number of data points deviating by more than 0.15 V but less than 0.25 V. ^f Total number of data points used in the correlation. The technetium data are taken from ref 2. ^g Excludes two very poorly behaved points.³⁷ ^h Excludes four very poorly behaved points; see text.

isocyanide ligand multiplied by the number of bound isocyanide ligands to a maximum of 4, being the maximum number of isocyanide ligands interacting with the HOMO orbital even in a hexakis(isocyanide) species. The actual numerical voltage correction per ligand was obtained by a statistical best fit, within the best 59 complexes (RPhNC 0.22 V, MeNC 0.12 V).

The most dramatic observation is that there are clearly two independent Re^{II/I} lines, a large data set with $\sum E_L$ above about 1.5 V and a second data set extending up to $\sum E_L = 1.5$ V with one additional entry at $\sum E_L = 2.2$ V (Figure 2). The two data sets are also distinguished by the fact that for those in the upper set, in all cases, the bulk species being studied contained six-coordinate rhenium(I); thus the first oxidation couple is being plotted. However, for the lower data set, the bulk species being studied was almost exclusively six-coordinate rhenium(III) and hence the second reduction couple is being plotted. The uppermost member of this lower data set, with $\sum E_L = 2.2$ V, is a rhenium(II) species in bulk solution.²²

If the couples are identical in both series, it should not matter what the bulk solution oxidation state is: they should all lie on the same line.¹ That they do not do so implies some critical difference between these lines.

The statistics for these two lines are shown in Table II. In particular, the mean standard deviations (MSD) (calculated minus observed potentials) are only 0.13 and 0.10 V for the upper and lower lines, respectively (excluding two very poorly behaved species), comparable to previous data (see footnote c of Table II).

Rhenium(III)/Rhenium(II). Data for 22 complexes are shown in Figure 2 and listed in Table I. The MSD is 0.16 V in this case, a little more scattered than the upper Re^{II/I} line. The top end of the line is secured by a set of isocyanide complexes with $\sum E_L = \text{ca. } 1.8$ V by using the same isocyanide correction as found for the Re^{II/I} line (above). These appear to be well-defined Re^{III/II} couples.¹⁵ The bottom end of the line is secured by the second reduction potential of the [Re(NCS)₆]²⁻ ion, whose assignment also seems secure.²³⁻²⁵ The slope (Table II) is near unity, but its precise value does depend upon the choice of the isocyanide correction, which is not well-defined. From a statistical viewpoint, a slightly better correlation is obtained by allowing the isocyanide correction to increase to 0.85 V/isocyanide ligand, at which point the slope of the line is about 0.85, being parallel to the Re^{IV/III} line. However, such a line passes close to the upper Re^{II/I} line, implying that a Re^{III/II} couple should be observed close in potential to the Re^{II/I} couple for species with $\sum E_L$ greater than 1.5 V. These have not been reported. Moreover, such an isocyanide correction seems inordinately large and unlikely.

There is a set of four species with $\sum E_L = \text{ca. } 1.3-1.5$ V which lies well off the line for no obvious reason. These complexes are

bis(diphosphine) species and are identified in the Re(III)/Re(II) section of Table I with †. They are otherwise well-behaved species whose Re^{IV/III} and Re^{II/I} couples do lie on their relevant lines. If one chose to tilt the line so as to include these species, then the points near $\sum E_L = \text{ca. } -0.4$ V and those near 1.8 V would lie well off the line. Moreover, the new less steep line would be much poorer, statistically, than the current line and would cut through negative of the Re^{II/I} line. This would lead to the expectation of observing Re^{III/II} two-electron couples, which are generally not observed. Thus, a more consistent interpretation of the data places the line as shown in Figure 2 but leaves the behavior of the four points unexplained. Conceivably, in these four cases, the Re^{III/II} species in solution is seven-coordinate by reaction with a counteranion or electrolyte anion. This would certainly cause a shift to more negative potential. However, this might also be expected to shift the Re^{IV/III} couple off its line, and yet these points are well-behaved.

Certainly, if one were to suppose that the rhenium(IV)/rhenium(III) [seven coordinate] correlation was in fact very similar to the six-coordinate correlation reported here, then the scatter in the Re^{III/II} line might arise because it is in fact two lines (one for six-coordinate Re^{III} and one for seven-coordinate Re^{III}), which are not resolved here. The seven-coordinate Re^{III} line would lie lower than the six-coordinate Re^{III} line and might run through [Re(bpy)Cl₄] and the four poorly behaved species, cutting negative of the Re^{II/I} (upper) line. This is a speculative hypothesis for the moment awaiting more data and detailed consideration of the reasonable possibility that some six-coordinate rhenium(III) species may bind an electrolyte anion (or perhaps solvent) in the electrochemical cell. Certainly, such an equilibrium has been observed when additional more strongly binding ligands are present;⁶ see further comment below.

Rhenium(IV)/Rhenium(III). This couple was discussed in the previous report (Figure 9)¹ and is extended in this contribution (Figure 2). It is a well-behaved couple, with all available data lying on one line with little scatter. The slope of this line is similar to that of the Tc^{IV/III} line, with an intercept slightly less positive.²

Discussion

As shown in Figure 2, the Re^{II/I} upper line if extended to more negative $\sum E_L$ would likely cut through the Re^{III/II} line. If it did, then all rhenium(III) couples with $\sum E_L$ more negative than the crossing would thermodynamically be required to be two-electron Re^{III/II} events. These are not observed in this region.

The appearance of the lower Re^{II/I} correlation avoids this situation by interposing a discontinuity such that the upper Re^{II/I} correlation evidently ceases to exist before it crosses the Re^{III/II} line.

This must have structural or bonding significance, but there are no additional data available to define just how these rhenium(I) species formed at such negative potentials differ from those on the upper Re^{II/I} line, which are much more stable toward oxidation.

The only reasons identified that would lead to two different lines for the same couple would be differing spin states and/or stereochemistries or coordination numbers. Considering the upper

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Re^{II/I} line, certainly the bulk starting materials in this data set are all six-coordinate low-spin rhenium(I). Few rhenium(II) oxidation products (with $\sum E_L \geq 2.0$ V) have been isolated, but one has been identified as low-spin six-coordinate rhenium(II)²⁶ and another has been similarly characterized by X-ray structural analysis;²¹ thus, the upper line most likely represents the low-spin six-coordinate Re^{II/I} couple.

Heavy transition elements such as rhenium are expected to be low spin, but if any high-spin species were to be observed, then they would occur with smaller $\sum E_L$ values, since such values are derived from ligands that are good σ - and π -electron donors, a situation favoring high-spin behavior. It is inconceivable that d⁶ Re^I would become high spin but more likely that d⁵ Re^{II} could become high spin, given the much larger exchange stabilization of this spin state.

This possibility is however excluded because of the following:

(i) One member of the lower group contains two CO ligands; it is unreasonable to expect such a species to be high spin.

(ii) A big shift to negative potentials, from the upper line to the lower line, requires a significant destabilization of rhenium(I) or stabilization of rhenium(II) (relative to the upper-line complexes). A switch to high-spin Re^{II} would provide the opposite effect.

(iii) A reduced slope also implies relatively weaker binding to rhenium(I).

Rejecting a change in spin state for the lower line leaves only a change in stereochemistry or coordination number. The bulk species being studied in this region are all six-coordinate rhenium(III) or rhenium(II). It is possible that the rhenium(I) species being formed is five-coordinate, since such rhenium(I) species are known.⁵ However, any reasonable argument would predict that oxidation of a five-coordinate rhenium(I) species to a six-coordinate rhenium(II) species would occur at more positive potentials than oxidation of the corresponding six-coordinate rhenium(I) species,¹ which is not the case under consideration. Moreover, it is hard to believe that the successive reduction of a six-coordinate rhenium(III) species to a five-coordinate rhenium(I) species, thereby losing a ligand, would be electrochemically reversible.

Possibly, the rhenium(I) species has changed from octahedral to trigonal prismatic. Such a stereochemistry is well established for rhenium(V) and rhenium(VI) species²⁷⁻²⁹ but not previously observed for low-oxidation-state rhenium. Such a change might well be facile enough to retain electrochemical reversibility. A final answer must await some spectroscopic or structural studies of these difficult to obtain rhenium(I) species.

So far, all correlations with $\sum E_L$ have been linear, but one cannot exclude the possibility that the binding characteristics of a metal ion, however they may be defined, might change over a large range of E_L values such that a curved relationship is found. Possibly that is the case with the Re^{II/Re^I} relationship. It is possible to fit a nonlinear relationship such as that shown, as an example, in Figure 2 (dotted line).³⁰ Quite a few points lie well off this line so that statistically it is not very successful.

Crossing of Re^{III/II} and Lower Re^{II/I} Lines. Previous pairs of redox couples, for the same metal ion in different oxidation states either are essentially parallel or, if not, would cross one another in chemically nonsensical $\sum E_L$ regions. For example, the Tc^{III/II} and Tc^{II/I} lines are close to parallel; they would cross near $\sum E_L = \text{ca. } 1.9$ V. The rhenium data are then especially interesting in that the upper and lower Re^{II/I} lines might cross the Re^{III/II} line in an accessible $\sum E_L$ region. Evidently, the existence of the lower Re^{II/I} line precludes the upper crossing; i.e., the crossing is avoided. Yet it is still possible that the lower Re^{II/I} line will cross the Re^{III/II}

line, apparently near $\sum E_L = \text{ca. } -0.5$ V, with some uncertainty because of the poor statistics of both the lower Re^{II/I} line and the Re^{III/II} line.

Clearly, there is some interesting chemistry to explore with rhenium species whose $\sum E_L$ is near -0.5 V or more negative. For example, the reduction chemistry of the [ReX₆]²⁻ ions (X = halides, pseudohalides, etc.) would bear further exploration.

Seven-Coordinate Rhenium(III) Couples. The species *mer*-ReCl(CO)₃(PMe₂Ph)₂ ($\sum E_L = 3.41$ V) exhibits a two-electron oxidation process,^{14,31} at $E_{1/2} = 1.40$ V, apparently terminating with the seven-coordinate ReCl₃(CO)₂(PMe₂Ph)₂ species. In this particular case, the two-electron process is probably driven by the formation of this seven-coordinate rhenium(III) species, which evidently undergoes a Re^{III/II} oxidation process at potentials less positive than that calculated for the Re^{II/I} couple of the starting material (1.63 V)^{14,32} (Figure 2). Such a two-electron process is not expected, nor yet reported, if the final product is a six-coordinate rhenium(III) species. This observation is consistent with the hypothesis above that the extension of a Re^{III}(seven-coordinate)/Re^{II} line might cut through the Re^{II/I} upper line.

The oxidation of seven-coordinate ReCl₃(CO)(PMe₂Ph)₃ has been reported to be fairly reversible.²² The observed potential is almost exactly that predicted by the Re^{IV/III} correlation if $\sum E_L$ for the seven ligands is used, but the calculation cannot be that simple and the agreement is probably fortuitous.

Slope Analysis. The electrode potential depends upon many factors, including metal-ligand binding free energies and differential solvation (the difference between the solvation free energies of the oxidized and reduced species).³³ The fact that, in organic solvents, the overall charge on the complex does not seem to be an important factor may suggest that in many organic solvents the differential solvation term largely vanishes. However, given the relatively large magnitude of the solvation terms, it is rather surprising that a +/0 species, for example, would fit the same line as a +4/+3 species. Nevertheless they appear to do so. Possibly, the binding free energies are modified by these charges such that there is a leveling effect as the charge changes. As $\sum E_L$ increases, the potential becomes more positive and the free energy of metal-ligand binding to the lower oxidation state becomes progressively larger than that of the higher oxidation state.

The slope of the upper Re^{II/I} line is 0.76, relative to unity for the Ru^{III/II} data. Thus, relative to the data for ruthenium, the rhenium data show that, with increasing $\sum E_L$, the lower oxidation state, while still progressively favored, does not increase in stability to the same degree as Ru^{II}. The slope of this line is also very significantly less than that for the corresponding Tc^{II/I} line (Table II). Given that the E_L scale is basically one in which E_L values increase with decreasing availability of σ -electron density, and/or increasing π -acceptor ability, these results show that such ligands favor binding to technetium(I) (relative to technetium(II)) to a greater degree than they favor binding to rhenium(I) (relative to rhenium(II)). Similarly, electron-rich and π -donor ligands favor binding to rhenium(I) to a greater degree than they favor binding to technetium(I).

The slope of the Re^{III/II} line, albeit less well-defined, is certainly less than that for the corresponding Tc^{III/II} line. Previously, it had been noted that technetium(III) complexes had reduction couples about 0.2 V more positive than the corresponding rhenium(III) species.³⁴ It is now seen that this is only true for complexes of relatively large $\sum E_L$. The Re^{III/II} line crosses the Tc^{III/II} line near $\sum E_L = 0.1$;³⁵ below this value, the rhenium

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complex will have the higher redox potential.

Final Comments

Data have been reported in this study for 119 redox couples displayed in Figure 2. Allowing that agreement between calculated and observed values of <0.25 V represents good behavior, only nine redox couples are poorly fitted, possibly three for reasons of experimental error and six for more subtle reasons.³⁷ Certainly, most of the data reported here fit predicted potentials to within 0.15 V (Table II).

The appearance of a pair of lines for the $\text{Re}^{\text{II/I}}$ redox couple is unexpected; the observation suggests some important structural or electronic differences between the rhenium(I) species in the upper and lower lines. However, the possibility that the $\text{Re}^{\text{II/Re}^{\text{I}}}$ line is really a curve cannot be excluded. It is therefore desirable to obtain data for $\sum E_L$ values in the intermediate range between the two lines. Such data should provide better statistics for the lower line or disprove the discontinuity. If two lines are present, then physical data are needed to define the differences between the complexes on each line.

Study of the electrochemistry of definitive seven-coordinate rhenium(III) species is clearly desirable. Some reversible electrochemistry has been observed with seven-coordinate hydride rhenium species.^{13,38} Controlled-potential reduction studies of

rhenium species of negative $\sum E_L$ values should prove especially interesting.

Acknowledgment. I am grateful for the continued financial support of the Natural Sciences and Engineering Research Council (Ottawa) and the Office of Naval Research (Washington). My appreciation is also extended to Drs. Armando Pombeiro and Mike Clarke for sharing unpublished information and for useful comments. I thank a reviewer for useful comments on the solvation energy problem.

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Valence Trapping of Mixed-Valence $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3]\text{S}$ (S = Solvent) Complexes at High Pressure

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Received August 22, 1989

The transformation from valence detrapped to valence trapped for two oxo-centered trinuclear iron acetate complexes is studied at pressures up to 95 kbar with the use of a diamond anvil cell. Variable-pressure ⁵⁷Fe Mössbauer spectra are presented for ⁵⁷Fe-enriched $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3]\text{py}$ (**1**) and $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3]\cdot\text{CHCl}_3$ (**2**), where py is pyridine. At 298 K and applied pressures less than ~20 kbar, each of the complexes gives a spectrum with a single quadrupole-split doublet, which indicates that complexes **1** and **2** are interconverting faster than the Mössbauer time scale under these conditions. Application of pressure in excess of ~80 kbar leads to both complexes becoming valence trapped, as indicated by two doublets in the Mössbauer spectrum with an area ratio of ~2:1 ($\text{Fe}^{\text{III}}:\text{Fe}^{\text{II}}$). At intermediate pressures, each of these complexes gives a Mössbauer spectrum that can be fit as a superposition of a valence detrapped doublet and a valence trapped four-line pattern. The nature of the pressure-induced transformations observed in complexes **1** and **2** is discussed with reference to the phase diagram derived from a spin-Hamiltonian theoretical approach that parametrizes intermolecular interactions in terms of the molecular field approximation.

Introduction

The study of intramolecular electron-transfer events in mixed-valence⁴ complexes in the solid state has yielded exquisite details

about the factors controlling electron-transfer processes.⁵ The influence of nearby solvate molecules on the rate of electron

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