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Electron Transfer. 134. Reduction of Bound Ruthenium(III) by Indium(I)[1]

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Aqueous solutions of the hypovalent state indium(I) react with oxidants of the type $[(NH_3)_5Ru^{III}(Lig)]^{3+}$, in which the sixth ligand, "Lig", is devoid of groups allowing inner-sphere bridging. Reaction stoichiometry conforms to the relationship $In^I + 2Ru^{III} \rightarrow In^{III} + 2Ru^{II}$. Kinetic profiles are consistent with a two-step sequence initiated by the formation of metastable In^{II}, which then reacts rapidly with Ru^{III}. Rate constants for the rate-determining steps in this series ($k_{Ru,In}$ values) are proportional to those for reductions of the corresponding $(NH_3)_5Co^{III}$ oxidants with $V^{2+}(aq)$, $Cr^{2+}(aq)$, $Eu^{2+}(aq)$, and $U^{3+}(aq)$, even though, for each comparison, no metal center is common to the two series chosen. This implies that changes in $\Delta G^{\ddagger}_{redox}$ arising from substitution of one N-donor ligand for another are nearly independent of the metal centers involved in the net transfer. The rate for the reduction of $(NH_3)_6Ru^{3+}$, considered in the framework of the Marcus model, leads to an estimated rate constant of 10^{-9} M^{-1} s^{-1} for electron self-exchange in the system $In^{2+/+}$. This value lies well below the range characteristic of the most usual aqua-substituted cationic couples, suggesting a more severe H_2O−metal bond contraction in going from the uni- to the dipositive cation.

Historically, the experimental background for mechanistic electron transfer chemistry is based largely on the examination of reactions between metal ion centers in solution. Although an immense body of literature pertaining to this area has been generated since the 1950s,[2] such studies have been subject to a notable constraint. With rare exceptions,[3] reducing centers in quantitative work have been d- or f-electron donors.

The symmetry characteristics of s subshells are obviously different from those of d or f orbitals, and the coordination properties of the main group cations are dissimilar in several respects from those of transition metal ions. Since both of these factors have been shown to exert major influences on redox behavior,[4] an extension of quantitative studies to one or more s-electron donors may be expected to add instructive detail to the electron transfer picture.

The most accessible soluble s donor is Sn^{2+}. However, its oxidation potential ($E°$ for Sn(IV,II) = +0.15 V in 1 M HCl) is modest, and it appears to undergo single-electron changes only under extreme conditions.[5] The much more strongly reducing state, In(I) ($E°_{III,I} = -0.43$ V),[6] is therefore a more attractive alternative.

The recent preparation[7] of aqueous In(I) solutions having much greater concentrations (10^{-2}−10^{-3} M) of this reductant than those previously recorded[8] (and exhibiting substantially improved stability) has made it possible to examine the behavior of this hypovalent center in inorganic redox transformations. Reactions with complexes of the type $(NH_3)_5Co^{III}(Lig)$ entail a slow formation of the metastable state In^{II}, which is then rapidly oxidized to In^{III}. Evidence has been presented[7] that reductions of halo-substituted oxidants (Lig = Cl^-, Br^-, I^-) proceed through halide-bridged paths. Reductions of carboxylato-substituted oxidants are slow unless aided by an O-donor function in a position favorable for chelation with In(I). Outer-sphere Co(III)−In(I) reactions in this series proceed inconveniently slowly, reflecting, in large part, the very low self-exchange rates associated with such Co(III, II) systems.[9]

The present contribution extends this study to Ru(III)−In(I) systems, for which outer-sphere redox rates are readily accessible.

Experimental Section

Materials. Indium powder (150 mesh), anhydrous acetonitrile, and anhydrous silver trifluoromethanesulfonate were Aldrich products. Indium(I) solutions were prepared under argon by a modification[7] of the procedure of Headridge,[8b] and their In(I) content was estimated iodometrically as described.[7] Aqueous In(I) solutions in O_2-free water for kinetic experiments were stable for over 5 h at 25 °C in the absence of added electrolyte and in 0.13 M $LiClO_4$ but decomposed perceptibly (17% loss in 5 min) in 0.06 M $HClO_4$.

Ruthenium(III) complexes, $[(NH_3)_5Ru^{III}(Lig)]^{3+}(ClO_4^-)_3$, were prepared from $Cl(NH_3)_5Ru^{III}Cl_2$, using slight modifications of the procedure of Gaunder,[10] in which the chloro complex was first converted, using CF_3COOAg, to its trifluoroacetate salt. The latter was then treated with Zn(Hg) and a 30-fold excess of the organic ligand (Lig), forming $[(NH_3)_5Ru(Lig)]^{2+}$, which was precipitated as its perchlorate. The Ru(II) complex, after recrystallization, was oxidized to the desired Ru(III) derivative by addition, in small portions, to cold aqueous CF_3COOAg,[11,12] and stirring of the mixture for 2−3 min. The resulting elemental Ag was removed, and the pale yellow Ru(III) complex was

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[2] For a recent review, see: Lappin, G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Horwood: New York, 1994; Chapters 1−4.

[3] Taylor, R. S.; Sykes, A. G. *J. Chem. Soc. A* **1971**, 1628.

[4] See, for example: (a) Creutz, C.; Sutin, N. In *Inorganic Reactions and Mechanisms*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 5, p 50. (b) Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 441. (c) Bose, R. N.; Wagner, P. A.; Earley, J. E. *Inorg. Chem.* **1984**, *23*, 1132.

[5] (a) Higginson, W. C. E.; Leigh, R. T.; Nightingale, R. J. *J. Chem. Soc.* **1962**, 435. (b) Ghosh, M. C.; Gelerinter, E.; Gould, E. S. *Inorg. Chem.* **1991**, *30*, 1039.

[6] Biedermann, G.; Wallin, T. *Acta Chem. Scand.* **1960**, *14*, 594.

[7] Chandra, S. K.; Gould, E. S. *J. Chem. Soc., Chem. Commun.* **1996**, 809; *Inorg. Chem.* **1996**, *35*, 3881.

[8] (a) Taylor, R. S.; Sykes, A. G. *J. Chem. Soc. A* **1969**, 2419. (b) Headridge, J. B.; Pletcher, D. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 475.

[9] Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 385.

[10] Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627.

[11] Reversal of the order of addition in this oxidation, i.e. adding the CF_3COOAg solution to a solution of the Ru(II) complex, resulted in much lower product yields. Yields and purities of the desired Ru(III) products were significantly improved by carrying out the final recrystallization from aqueous $HClO_4$ rather than from aqueous sodium perchlorate. Dried products, while stored, were protected from light.

[12] Since the explosive character of organic ruthenium perchlorates has been noted,[10] all work with these complexes was carried out with quantities of 200 mg or less.

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precipitated by addition of $NaClO_4$ and cooling, after which it was recrystallized from 0.4 M $HClO_4$ (yields 50−65%). Ultraviolet spectra of the Ru(III) products corresponded closely to those described.[10,13] Elemental analyses (C, H, N) of the complex of *N*,*N*-diethylnicotinamide (ϵ_{275}(sh) 5.0×10^3, ϵ_{240}(sh) 6.5×10^3 M^{-1}), which appears to be reported here for the first time, were in accord with the indicated structure.

Stoichiometric Studies. Stoichiometric determinations were carried out under argon[7] in solutions which were 0.03 M in triflic acid and 0.2 M in sodium triflate. Reactions were monitored at the low-energy maximum of the Ru(II) product (400−440 nm). Measured deficient quantities of In^I were added to a known excess of the oxidant. After 10 min reaction times, increases in absorbance were compared with values calculated from the molar absorbances of the $[(NH_3)_5Ru^{II}(Lig)]^{2+}$ complexes as determined from measurements on pure samples of the latter. Solutions of the Ru^{II} species appeared to be stable for over 60 min in the medium used. Such measurements yielded stoichiometries $\Delta[Ru^{II}]/\Delta[In^I] = 2.00 \pm 0.05$.

Kinetic Experiments. Reactions, under argon, were examined at the high-wavelength maximum of the Ru(II) product, using either a Cary 14 recording spectrophotometer, a Beckman Model 5260 instrument, or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. Ionic strength, which was regulated by addition of $NaClO_4/HClO_4$, was generally maintained at 0.2 M. Concentrations of reagents were customarily adjusted so that no more than 10% of the reactant in excess was consumed in the reaction.[14] In no case was kinetic variation with acidity perceived within the range $[H^+] = 0.030-0.10$ M. All reactions in the present series yielded simple exponential curves, and rate constants were obtained by nonlinear least-squares fitting to the relationship describing first-order decay. Values from replicate runs agreed to better than 6%. These reactions were first order in both redox partners. Profiles for reactions in this group showed no indication of transients formed or destroyed on a time scale comparable to that of the principal redox reaction.[15]

Results and Discussion

The stoichiometry observed for these reactions, 2.00 ± 0.05 mol of Ru^{III}/mol of In^I, allows representation of these conversions as eq 1. Each exhibits only one kinetic component and is

$$2Ru^{III} + In^{I} \rightarrow 2Ru^{II} + In^{III} \qquad (1)$$

first order in each of the two redox partners, thus being consistent with the two-step sequence (2),which is initiated by

$$In^{I} \xrightarrow{Ru^{III}} In^{II} \xrightarrow[\text{rapid}]{Ru^{III}} In^{III} \qquad (2)$$

formation of the metastable state, In^{II}, after which the latter reacts more rapidly than does In^I. The structures of the oxidants taken dictate outer-sphere redox paths,[16,17] and the lack of kinetic $[H^+]$ dependence is in accord with the absence of basic centers which undergo partial protonation in the interval examined.

Table 1. Reductions of Pentaammineruthenium(III) Complexes, $[(NH_3)_5Ru^{III}(Lig)]^{3+}$, Having Nonbridging Ligands, with Indium(I)

Lig[a]	$[Ru^{III}]$, mM	$[In^I]$, mM	$k\,(Ru^{III},In^I)^b$	$k\,(Co^{III},V^{II})^c$
ammonia	20−40	1.0	0.98^d	0.010
imidazole	5.0−9.8	0.8−1.3	1.51	0.020
pyrazole	1.5−2.0	0.27	11.1 11.0^e 13.9^d	0.120
pyridine	0.06−0.09	1.2−3.6	6.0	0.24
N,*N*-diethylnicotinamide	0.30−1.8	0.06	1.9×10^2	1.21^f

[a] Structures of ligands are indicated in Figure 1. [b] Rate constants in $M^{-1}\,s^{-1}$ at 25 °C; $\mu = 0.2$ M ($NaClO_4$); $[H^+] = 0.03-0.10$ M. [c] Rate constants, in $M^{-1}\,s^{-1}$, pertaining to reduction of the analogous cobalt(III) complexes, $[(NH_3)_5Co(Lig)]^{3+}$, with V^{2+} (aq), at 25 °C and $\mu = 1.0$ M.[19] [d] Reaction in 0.1 M Cl^-. [e] Reaction in 0.2 M $CF_3SO_3^-$. [f] Value taken as 0.88 times the rate for the *N*,*N*-dimethyl analog.[18b]

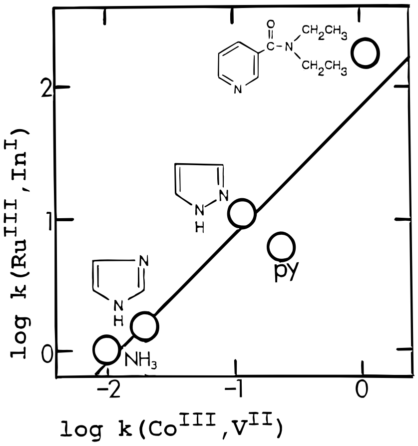

Figure 1. log−log plot comparing the rate constants for outer-sphere reductions of pentaammineruthenium(III) complexes, $[(NH_3)_5Ru^{III}(Lig)]^{3+}$, using In^I(aq), with those for reductions of the corresponding cobalt(III) complexes, $[(NH_3)_5Co(Lig)]^{3+}$, using V^{2+}(aq). Reaction conditions are listed in Table 1. The regression line shown corresponds to the equation

$$\log k_{Ru,In} = (1.04 \pm 0.20) \log k_{Co,V} + (1.90 \pm 0.25) \qquad (3)$$

Rate constants pertaining to this redox series are summarized in Table 1. Both the range in values and the relative rates within the series call to mind similar patterns observed when Co^{III} complexes featuring the same array of “sixth ligands” are reduced with several metal-center reductants, among them Cr^{2+}(aq),[18] Eu^{2+}(aq),[18] V^{2+}(aq),[19] U^{3+}(aq),[20] and $Ru(NH_3)_6^{2+}$.[17] Figure 1, a log−log plot, compares rate constants obtained in this study ($k_{Ru,In}$ values, adjusted, where necessary, to 0.2 M ClO_4^-) with those for reductions, using V^{2+}(aq), of the corresponding $(NH_3)_5Co^{III}$ oxidants ($k_{Co,V}$ values).[19] The approach to linearity, with a near-unit slope of the regression line, is reminiscent of analogous plots which compare the rates of a series of oxidants with two different reductants.[17] Comparisons of this type (reflecting linear free energy relationships) are in agreement with Marcus’s early stipulation that the ratio of outer-sphere rates in such a series should remain nearly invariant throughout.[21]

In the present case, our $k_{Ru,In}$ values are seen to be nearly proportional to the corresponding $k_{Co,V}$ values *even though no metal center is common to the two series.* Moreover, since the

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(13) (a) Sundberg, R. J.; Bryan, R. F.; Taylor, I. F., Jr.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381. (b) Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 2745.

(14) Reactions carried out with In(I) in excess were sometimes complicated by precipitation of elemental ruthenium. In such cases, measurements were carried out with excess oxidant.

(15) More complex patterns were, however, encountered with pyridine-bound Ru(III) oxidants having carbonyl-bearing substituents (e.g., $-CONH_2$, $-CO_2CH_3$, and $-COC_6H_5$) on the heterocyclic ring. Strong autocatalysis was observed when such groups were at the 4-position, whereas profiles obtained with 3-substituted ligands of this type featured major segments in which reduction rates were very nearly independent of [In(I)]. Further examination of these systems is in progress.

(16) Except for *N*,*N*-diethylnicotinamide, the Ru(III)-bound ligands taken are devoid of unsaturated donor centers considered to be necessary for redox bridging by organic groups. Much earlier experiments with Co(III) complexes of the above highly hindered amide[17] indicate that it is ineffective as an inner-sphere redox bridge.

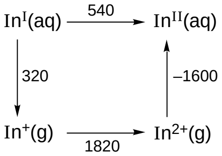
(17) Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

(18) (a) Dockal, E. R.; Gould, E. S. *J. Am. Chem. Soc.* **1972**, *94*, 6673. (b) Fanchiang, Y.-T.; Carlson, R. R.; Thamburaj, P. K.; Gould, E. S. *J. Am. Chem. Soc.* **1977**, *99*, 1073.

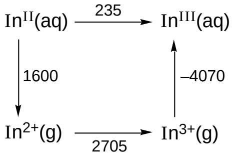
(19) Chen, J. C.; Gould, E. S. *J. Am. Chem. Soc.* **1973**, *95*, 5539.

(20) Loar, M. K.; Sens, M. A.; Loar, G. W.; Gould, E. S. *Inorg. Chem.* **1978**, *17*, 326.

Scheme 1. Conversion of In^{I} to In^{II} (ΔG Values in kJ)



Scheme 2. Conversion of In^{II} and In^{III} (ΔG Values in kJ)



rates for the Co^{III} + V^{II} reactions have been shown in turn to be proportional to those for the analogous reductions of Co(III) complexes with Cr^{2+}, Eu^{2+}, and U^{3+},[17,20] the proportionalities governing our Ru^{III} + In^{I} rates will extend to these Co(III) systems as well. The implication is then that alterations in $\Delta G^{\ddagger}_{redox}$ arising from substitution of one N-donor ligand for another are independent of the metal centers in both the oxidant and the reductant. This conclusion is in accord with Linck's suggestion that the influence of nonbridging ligands on external electron transfer to an acceptor center reflects, in the main, the σ-bonding strengths of the donor atoms.[22]

The rate of reduction of Ru(NH$_3$)$_6$$^{3+}$, the "parent" member of this series, for which both the formal potential (+0.067 V vs NHE) and the electron-self-exchange rate (4×10^3 M^{-1} s^{-1}) have been recorded,[23] would, in conjunction with the Marcus model, allow an estimate of the self-exchange rate, k(In$^{II/I}$), for the initial step in the reduction if the potential $E°$(In$^{II/I}$) for that step were known.[24] The early value for this couple, which was recorded by Hepler (−0.40 V),[25] is open to objection, for it was based upon the assumption that halides of the type In$_2$X$_4$ are salts of the In^{2+} ion, whereas they are now recognized to be mixed halides of In(I) and In(III).[26]

A more defensible estimate of $E°$(In$^{II/I}$) may be made by comparing ΔG associated with the conversion of In^{I} to In^{II} (Scheme 1) to that for conversion of In^{II} to In^{III} (Scheme 2). For this comparison, the ionic radius for In^{3+} is taken as 0.76 Å,[27] that for In^{+} is taken as 1.50 Å,[7,28] and that for In^{2+} is calculated as 1.20($r_{In(III)}$), or 0.90 Å.[27,29] Since $\Delta G_{hydration}$ values for ions of the representative metals are closely related to their ionic charges and radii,[29] free energy terms for hydration of In^{+} and In^{2+} are assumed to lie near those for Rb^{+} and Ca^{2+}.[29] Note that the greater energy input[27] needed to ionize In^{2+} is more than balanced by the much higher ΔG for hydration of In^{3+}. The difference in net ΔG for the two oxidations, 305 kJ/mol, corresponds to a potential difference of 0.31 V, from which $E°$'s for In(I,II) and -(II,III) are calculated as −0.27 and −0.59 V.

On the basis of the simplified Marcus relationship[30,31] (eq 4), the self-exchange rate, $k_{In(II,I)}$ is calculated to be near 10^{-9}

$$\log k_{In(II,I)} = 2 \log k_{Ru,In} - \log k_{Ru(III,II)} - \log K_{Ru,In} \quad (4)$$

M^{-1} s^{-1} (25 °C). This lies well below the range characteristic of aqua-substituted cationic d-block couples (Fe$^{3+/2+}$, $10^{0.1}$ M^{-1} s^{-1}; Mn$^{3+/2+}$, $10^{-3.5}$ M^{-1} s^{-1}; V$^{3+/2+}$, $10^{-2.0}$; [TiOH]$^{3+/2+}$, $\geq 10^{-3.5}$; Cr$^{3+/2+}$, $\leq 10^{-4.7}$ M^{-1} s^{-1}).[32] The implication here is that the Franck−Condon barrier to self-exchange in the In$^{2+/+}$ system is somewhat greater than that for the more rapid 3d-block reductants, probably reflecting a more severe contraction of H$_2$O−metal bond(s) in going from the reduced (unipositive) to the oxidized (dipositive) form.[32]

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(21) (a) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853. (b) *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(22) Bifano, C.; Linck, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3945.

(23) See, for example: Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374.

(24) Note that the formal potential measured for the conversion of In(III) to In(I) (−0.43 V)[6] is necessarily the arithmetic mean of the potentials of the two single-electron processes, $E°$(In^{II,I}) and $E°$(In^{III,II}).

(25) Hepler, L. G.; Hugus, Z. Z., Jr.; Latimer, W. M. *J. Am. Chem. Soc.* **1953**, *75*, 5652.

(26) Khan, M. A.; Tuck, D. G. *Inorg. Chim. Acta* **1985**, *97*, 73.

(27) (a) Both ionic radii and ionization enthalpies of the atoms have been tabulated by: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 1381, 1387. (b) See also: Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(28) Dronskowski, R. *Inorg. Chem.* **1994**, *33*, 5927.

(29) See, for example: Rosseinsky, D. R. *Chem. Rev.* **1965**, *54*, 465.

(30) The approximate nature of this calculation does not justify a more elaborate treatment.

(31) See, for example: Creutz, C.; Sutin, N. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, pp 13−51.

(32) Brunschwig, B. S.; Creutz, C.; Macartney, D. H.; Sham, T.-K.; Sutin, N. *Faraday Discuss. Chem. Soc.* **1982**, *74*, 113.