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Electron-Transfer Reactions of Oxovanadium(IV) and Dioxovanadium(V) Ions with Metal Tris(polypyridine) Complexes in Aqueous Media

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The kinetics of the oxidation of oxovanadium(IV), $VO(H_2O)_5^{2+}$, by RuL_3^{3+} and NiL_3^{3+} and the reduction of dioxovanadium(V), $VO_2(H_2O)_4^+$, by OsL_3^{3+} (L is 2,2′-bipyridine, 1,10-phenanthroline, or a substituted derivative) were studied in acidic aqueous media at 25 °C. The oxidations of VO^{2+} displayed an inverse rate dependence on acid concentration with a rate law of the form $k_{obsd} = k_a + k_b[H^+]^{-1}$, while the rate constants for the reduction of VO_2^+ increased with $[H^+]$; $k_{obsd} = k_c + k_d[H^+]$. The more reactive vanadium(IV) and -(V) species are the $VO(OH)^+$ and $VO(OH)^{2+}$ ions, respectively, and an application of the Marcus relationship to the cross-reaction data yields a self-exchange rate constant of $\sim 10^{-3}$ M^{-1} s^{-1} for the $VO(OH)^{+/2+}$ couple. The exchange rate constant is similar to the corresponding values derived from Marcus calculations for $Fe^{2+/3+}(aq)$ and the isoelectronic $TiOH^{2+/3+}(aq)$ couple.

Introduction

The electron-exchange reactions of 2+ and 3+ aquo ions of transition metals have been investigated both experimentally[1-5] and theoretically[5-8] in considerable detail. The self-exchange rate constants for $M(H_2O)_6^{2+/3+}$ couples span several orders of magnitude, and the differences are attributed primarily to the size of the barrier for the reorganization of the inner-sphere configurations. Kinetic and structural studies[5] on these systems have revealed relationships between (i) the magnitudes of the electron-exchange rate constants and the change in the M–O bond distances and (ii) the nature of the orbital in which the transferring electron residues (nonbonding $d\pi^*$ vs. antibonding $d\sigma^*$).

For the higher oxidation states of the first transition series simple hexaaquo complexes are not common as the higher charge to size ratio of the metal center results in the formation of hydroxo and oxo ions in solution. For vanadium the +4 and +5 oxidation states are considered to be represented by oxovanadium(IV), $VO(H_2O)_5^{2+}$, and dioxovanadium(V), $VO_2(H_2O)_4^+$, in acidic aqueous solution.[9] Numerous kinetic investigations of the oxidation of $VO^{2+}(aq)$ and the reductions of $VO_2^+(aq)$ have been reported,[10-14] although frequently these reactions involve inner-sphere redox processes due to the lability of the $VO^{2+}(aq)$ and $VO_2^+(aq)$ ions or processes via an oxo bridge. Direct electron exchange between $VO^{2+}(aq)$ and $VO_2^+(aq)$ in solution was found to be very rapid;[14] however, the recent observation[15] of a mixed-valence $V_2O_3^{3+}(aq)$ species in equimolar solutions of $VO^{2+}(aq)$ and $VO_2^+(aq)$ suggests that this exchange also proceeds by an inner-sphere mechanism.

The rate constant for outer-sphere electron exchange between the oxo ions of vanadium(IV) and (V) may be estimated from the kinetic and equilibrium data for cross-reactions with suitable outer-sphere redox reagents. In this paper the results of a kinetic study of the oxidation of $VO^{2+}(aq)$ by RuL_3^{3+} and NiL_3^{3+} and the reduction of $VO_2^+(aq)$ by OsL_3^{3+} (L = 2,2′-bipyridine, 1,10-phenanthroline, or a substituted derivative) in acidic aqueous media are reported. The metal tris(polypyridine) complexes are well characterized outer-sphere reactants and have been employed in cross-reaction kinetic studies with a number of metal aquo ions. The cross-reaction rate constants are correlated by means of the Marcus relationships,[16] with the derived V(IV/V) self-exchange rate constant compared with the corresponding values for other metal aquo ion couples, including the isoelectronic Ti(III/IV) couple.[17]

Table I. Acid Dependence of Rate Constants for the Oxidation of $VO^{2+}(aq)$ by RuL_3^{3+} and NiL_3^{3+} at 25 °C, I = 1.0 M ($LiClO_4$)

$[H^+]$, M	k_{obsd}, M^{-1} s^{-1}			
	$Ru(dmbpy)_3^{3+}$	$Ru(bpy)_3^{3+}$	$Ni(dmbpy)_3^{3+}$	$Ni(bpy)_3^{3+}$
0.10	4.61	6.37	7.38	92.3
0.20	2.38	3.73	4.68	77.7
0.40	1.26	2.43	3.38	69.8
0.50	1.05	2.12	3.17	66.6
0.70	0.84	1.75	2.65	64.3
1.00	0.75	1.48	2.53	63.6
k_a, M^{-1} s^{-1}	0.22 ± 0.04	1.0 ± 0.1	2.0 ± 0.1	61 ± 1
k_b, s^{-1}	0.44 ± 0.01	0.54 ± 0.01	0.54 ± 0.01	3.1 ± 0.2
$10^{-5}k_2$, M^{-1} s^{-1}	5.2 ± 0.2	6.4 ± 0.2	6.4 ± 0.2	36 ± 2

Experimental Section

Materials. Stock solutions of the $VO(H_2O)_5^{2+}$ ion in perchlorate media were prepared by the stoichiometric addition of barium perchlorate to vanadyl sulfate (Fisher) or by electrochemical reductions of V_2O_5 (Fisher) in perchloric acid. Solutions of $VO(H_2O)_4^+$ were prepared by dissolving V_2O_5 in either perchloric acid or *p*-toluenesulfonic acid (Baker). Vanadium concentrations were determined spectrophotometrically;[18] for $VO^{2+}(aq)$ at 764 nm (ϵ = 17.0 M^{-1} cm^{-1}) and for $VO_2^+(aq)$ at 350 nm (ϵ = 141 M^{-1} cm^{-1}) and 432 nm (ϵ = 5.8 M^{-1} cm^{-1}). Lithium perchlorate was prepared by the neutralization of perchloric acid with lithium carbonate, followed by several recrystallizations from distilled water.

Tris(2,2′-bipyridine)nickel(III) perchlorate and tris(4,4′-dimethyl-2,2′-bipyridine)nickel(III) perchlorate were prepared by electrochemical oxidation of the corresponding nickel(II) salts in anhydrous acetonitrile at 0 °C.[19] The solid nickel(III) complexes were isolated by slow crystallization from a dry dichloromethane/acetonitrile solution at 0 °C. The tris(polypyridine) complexes of ruthenium and osmium were prepared as described previously.[20]

Kinetic Measurements. Kinetic studies were performed on a Durrum D-110 stopped-flow spectrophotometer or a Cary 210 spectrophotometer. All experiments were performed under pseudo-first-order conditions of excess $VO^{2+}(aq)$ or $VO_2^+(aq)$ concentrations, and plots of ln $(A_t - A_\infty)$ or ln $(A_\infty - A_t)$ against time were linear for at least 3 half-lives. Reac-

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Table II. Acid Dependence of Rate Constants for the Reduction of $VO_2^+(aq)$ by OsL_3^{3+} at 25 °C, I = 1.00 M (p-$CH_3(C_6H_4)SO_3Li$)

	[H⁺], M						
L in OsL_3^{2+}	0.2	0.4	0.6	0.8	1.0	k_c, $M^{-1}\ s^{-1}$	k_d, $M^{-2}\ s^{-1}$
4,4′-$(CH_3)_2$bpy	58	92	133	169	204	21 ± 2	185 ± 3
4,4′-$(C_6H_5)_2$bpy	29.3	46.2	57.5	75.3	90.0	15 ± 2	75 ± 3
5,6-$(CH_3)_2$phen	17.3	24.7	30.1	33.8	53.4	7.5 ± 3.2	41 ± 5
4,7-$(C_6H_5)_2$phen	14.8	26.0	33.8	42.1	45.5	9.2 ± 2.6	39 ± 4
5-CH_3phen	4.82	6.60	8.66	10.2	11.6	3.2 ± 0.3	8.6 ± 0.4
phen	2.77	4.47	5.58	6.93	7.92	1.7 ± 0.2	6.4 ± 0.3
bpy	3.85	5.91	7.50	8.72	9.90	2.7 ± 0.4	7.5 ± 0.5
bpy[a]	4.88	7.07	9.95	12.2	14.4	2.5 ± 0.2	12 ± 1
5-Clphen	0.31	0.51	0.69	0.85	1.05	0.14 ± 0.01	0.91 ± 0.02

[a] In perchlorate media, I = 1.00 M ($LiClO_4$).

tions involving NiL_3^{3+}, RuL_3^{3+}, and OsL_3^{2+} were monitored at 400, 460, and 480 nm, respectively. The kinetic studies were carried out in solutions at an ionic strength of 1.00 M using lithium p-toluenesulfonate or lithium perchlorate. The temperature was maintained at 25.0 ± 0.1 °C by means of an external water bath.

Results

Oxidation of VO^{2+}. The oxidations of the $VO^{2+}(aq)$ ion by ruthenium(III) and nickel(III) tris(bipyridine) complexes (ML_3^{3+}) were investigated at 25.0 °C in perchlorate media (I = 1.00 M, $LiClO_4$) with acid concentrations in the range 0.10–1.00 M.

$$ML_3^{3+} + VO^{2+}(aq) \rightarrow ML_3^{2+} + VO_2^+(aq) + 2H^+ \qquad (1)$$

The pseudo-first-order rate constants displayed a first-order dependence on $[VO^{2+}]$

$$\frac{-d[ML_3^{3+}]}{dt} = k_{obsd}[ML_3^{3+}][VO^{2+}] \qquad (2)$$

with an inverse dependence of k_{obsd} (Table I) on $[H^+]$; $k_{obsd} = k_a = k_b/[H^+]$. Plots of k_{obsd} against $[H^+]^{-1}$ were linear with a positive intercept. The values of the intercepts k_a and slopes k_b are presented in Table I.

Reduction of VO_2^+. The kinetics of the reduction of the VO_2^+ ion by a series of osmium(II) tris(polypyridine) complexes (OsL_3^{2+}) were studied in 1.00 M p-toluenesulfonate media.

$$OsL_3^{2+} + VO_2^+(aq) + 2H^+ \rightarrow OsL_3^{3+} + VO^{2+}(aq) \qquad (3)$$

A first-order dependence of the pseudo-first-order rate constant on $[VO_2^+]$ was observed:

$$\frac{-d[OsL_3^{2+}]}{dt} = k_{obsd}[OsL_3^{2+}][VO_2^+] \qquad (4)$$

Rate constants were measured over the $[H^+]$ range 0.20–1.00 M (Table II) and displayed a first-order dependence on $[H^+]$; $k_{obsd} = k_c + k_d[H^+]$. The rate constants k_c and k_d derived from plots of k_{obsd} against $[H^+]$ are summarized in Table II. The $Os(bpy)_3^{2+}/VO_2^+$ reaction was also studied in 1.00 M perchlorate media. The values of k_c (Table II) in perchlorate and p-toluenesulfonate media are similar, with a slightly larger value of k_d observed in perchlorate solutions.

Discussion

The inverse acid dependence observed in the oxidation of $VO^{2+}(aq)$ by the tris(bipyridine)nickel(III) and ruthenium(III) complexes is consistent with the following mechanism:

$$VO(H_2O)_5^{2+} \overset{K_1}{\rightleftharpoons} VO(OH)(H_2O)_4^+ + H^+ \qquad (5)$$

$$VO(H_2O)_5^{2+} + ML_3^{3+} \xrightarrow{k_1} VO(H_2O)_5^{3+} + ML_3^{2+} \qquad (6)$$

$$VO(OH)(H_2O)_4^+ + ML_3^{3+} \xrightarrow{k_2} VO(OH)(H_2O)_4^{2+} + ML_3^{2+} \qquad (7)$$

The hydrolysis constant K_1 for $VO^{2+}(aq)$ is 8.5×10^{-7} M at 25 °C (I = 1.00 M).[20] With $K_1 << [H^+]$ in this study an expression for k_{obsd} (eq 2) may be written as $k_{obsd} = k_1 + k_2K_1/[H^+]$, where $k_a = k_1$ and $k_b = k_2K_1$. The rate constants k_1 and k_2 for the nickel and ruthenium oxidants are presented in Table I. Similar acid dependences have been reported previously for the oxidation of $VO^{2+}(aq)$ by $Fe(bpy)_3^{3+}$,[11] $IrCl_6^{2-}$,[12] and a series of nickel(III) macrocycle complexes.[13]

In the reductions of $VO_2^+(aq)$ by the osmium(II) tris(polypyridine) complexes the acid dependence of the observed rate constants is consistent with the mechanism in eq 8–10. Similar

$$VO(OH)(H_2O)_4^{2+} \overset{K_2}{\rightleftharpoons} VO_2(H_2O)_4^+ + H^+ \qquad (8)$$

$$VO_2(H_2O)_4^+ + OsL_3^{2+} \xrightarrow{k_3} VO_2(H_2O)_4 + OsL_3^{3+} \qquad (9)$$

$$VO(OH)(H_2O)_4^{2+} + OsL_3^{2+} \xrightarrow{k_4} VO(OH)(H_2O)_4^+ + OsL_3^{3+} \qquad (10)$$

acid dependences, with a lack of rate saturation at high $[H^+]$, have been reported for other reductions of $VO_2^+(aq)$.[10] The kinetic studies implicate the protonation of the VO_2^+ species (as opposed to protonation of OsL_3^{2+}) in very acidic media, and an estimate for K_2 of 4.5 M (ionic strength not held constant) has been reported from the ion-exchange behavior of vanadium(V) species in perchloric acid.[22] With $K_2 >> [H^+]$ for the range of acidities in this study, $k_{obsd} = k_3 + k_4[H^+]/K_2$, where $k_c = k_3$ and $k_d = k_4/K_2$ in eq 6.

The observed rate constants for the oxidations of VO^{2+} and $VO(OH)^+$ and the reductions of VO_2^+ and $VO(OH)^{2+}$ increase, in general, with an increase in the thermodynamic driving force of the cross-reaction. This dependence is in accord with the Marcus relationship for outer-sphere electron transfer.[16] In terms of a recent modification of the theory,[23] the rate constant for a cross-reaction k_{12} is related to the rate constants for the component exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross-reaction K_{12} by

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (11)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \frac{w_{11} + w_{22}}{RT}\right]} \qquad (12)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (13)$$

$$w_{ij} = \frac{z_iz_je^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}I^{1/2})} \qquad (14)$$

In these expressions w_{ij} is the work required to bring the ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken as equal to the sum of a_i and a_j, the radii of the ions i and j), $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, D_s is the static dielectric constant, $A_{ii} = (4\pi N\sigma^2\nu_n(\delta r)/1000)_{ii}$, and δr is the thickness of the reaction shell.[23] The values of σ_{ii} in these calculations are 13.6 Å for $ML_3^{2+/3+}$ and 6.5 Å for VO^{2+}/VO_2^+, and $A_{11}A_{22}$ was taken equal to 4×10^{24} M^{-2} s^{-2} for the cross-reactions in this study.

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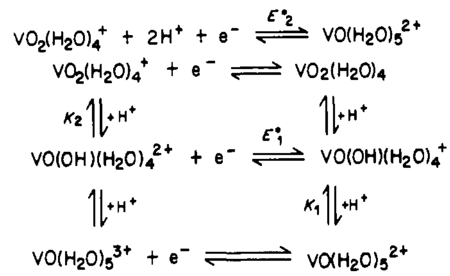
Scheme I



The Marcus relationship may be used with outer-sphere electron-transfer reactions to estimate the electron-exchange rate constant k_{11} for a metal complex couple, providing that the partners in the couple differ only in their oxidation level and not in their proton content. In this respect the exchange rate constant for the VO^{2+}/VO_2^+ couple, which involves species differing by two protons, cannot be evaluated by this treatment. The vanadium(IV/V) couples in which the number of protons are equivalent include $VO(H_2O)_5^{2+/3+}$, $VO(OH)(H_2O)_4^{+/2+}$, and $VO_2(H_2O)_4^{0/+}$. These couples are related to each other and to the VO^{2+}/VO_2^+ couple by the proton equilibria in Scheme I.

Of the three exchange couples it is for $VO(OH)(H_2O)_4^{+/2+}$ that the most information is known. Rate constants for the reduction of $VO(OH)^{2+}$ and the oxidation of the $VO(OH)^+$ ion are available from the cross-reaction kinetic measurements in this study and others. The correlation of these rate parameters in the framework of the Marcus theory requires a value for K_2, the acid dissociation constant of the very acidic $VO(OH)(H_2O)_4^{2+}$ ion. With an estimate for K_2 the composite rate constant k_4/K_2 for the reductions of $VO(OH)^{2+}$ may be resolved and the reduction potential of $VO(OH)^{2+/+}$ may be calculated from the expression

$$E°_1 = E°_2 - 0.059(pK_1 + pK_2) \qquad (15)$$

where $E°_2 = 1.03$ V and $K_1 = 8.5 \times 10^{-7}$ M.[21] An estimate of K_2 may be obtained from a self-consistent fit of the data for cross-reactions involving the $VO(OH)^{+/2+}$ couple to eq 11. For a range of values of k_{11} and K_2 (from which $E°_1$ was derived), the best fit was achieved when $K_2 = 30$ M and $E°_1 = 0.76$ V, yielding a value of $k_{11} \sim 10^{-3}$ M^{-1} s^{-1} for $VO(OH)^{+/2+}$. The value of K_2 derived from the present kinetic fit is in reasonable agreement with the aforementioned estimate of 4.5 M.[22] The cross-reaction rate constants calculated for reactions of $VO(OH)^+$ and $VO(OH)^{2+}$ by using this value of k_{11} are presented in Table III. There is very good agreement between the observed and calculated k_{12} values, and this is also demonstrated in the Marcus correlation plot shown in Figure 1. The data fit very well the theoretical curve of slope unity, with the exception of the points corresponding to the $IrCl_6^{2-}/VO(OH)^+$ and $IrCl_6^{3-}/VO(OH)^{2+}$ reactions. The value of k_{11} derived from these reactions is $\sim 10^{-1}$ M^{-1} s^{-1}. The agreement observed for the $V(H_2O)_6^{2+}/VO(OH)^{2+}$ cross-reaction may be somewhat fortuitous because of the large thermodynamic driving force, K_{12}. The k_{11} values calculated from eq 11 have been observed to decrease with increasing K_{12} in some systems.[20b] Larger calculated self-exchange rate constants for the $VO(OH)^{+/2+}$ couple ($10-10^3$ M^{-1} s^{-1}) have been derived from cross-reactions involving nickel polyaza macrocycle complexes.[13]

The inconsistencies in the calculated self-exchange rate constants for the $VO(OH)^{+/2+}$ couple likely arise from deviations from the assumptions in the Marcus model. One of these assumptions is that the self-exchange and cross-reaction processes are adiabatic. The Marcus relationship (eq 11 and 12) may be modified to account for nonadiabaticity by replacing k_{12} by $k_{12}/(\kappa_{el})_{12}$ and $k_{11}k_{22}$ by $k_{11}k_{22}/(\kappa_{el})_{11}(\kappa_{el})_{22}$, where κ_{el} is the electron-transfer probability.[23] If it is assumed that effective metal d–d or ligand π^*–π^* (for $ML_3^{2+/3+}$ with strong d–π^* mixing) overlap results in relatively adiabatic self-exchange reactions, then the nonadiabaticity arises from the cross-reactions. Primarily as a result of the poor d–d orbital overlap between small, hydrophilic metal aquo ions and large, hydrophobic metal tris(polypyridine) complexes, the $M(bpy)_3/M(H_2O)_6$ cross-reaction reactions are invariably slower than predicted by the Marcus relationship.[19,20b] This nonadiabaticity would likely extend to the $VO(OH)/M(bpy)_3$ reactions and account for the much smaller values of k_{11} from these cross-reactions than those with the other oxidants such as $IrCl_6^{2-}$ and the nickel(III) macrocycle complexes, where d–d overlap is more favorable.

It has previously been suggested[9,13] that oxidants approach a pyramidal face in VO^{2+}(aq), allowing access to the unpaired d electron residing in a nonbonding t_{2g} orbital. The interaction of a cationic oxidant with this region of the asymmetrical $VO(OH)^+$(aq) ion, in an oriented configuration, would result in a

Table III. Rate Parameters for Cross-Reactions Involving the $VO(OH)^+$ and $VO(OH)^{2+}$ Ions

reacn no.[g]	cross-reactant	log K_{12}[a]	k_{12}(obsd),[b] M^{-1} s^{-1}	k_{12}(calcd),[c] M^{-1} s^{-1}
	oxidant			
1	$Ni(bpy)_3^{3+}$	16.2	3.6×10^6	7.0×10^6
2	$Ni(4,4'-(CH_3)_2bpy)_3^{3+}$	13.9	6.4×10^6	1.1×10^6
3	$Ru(bpy)_3^{3+}$	7.9	6.4×10^5	3.5×10^6
4	$Ru(4,4'-(CH_3)_2bpy)_3^{3+}$	5.8	5.2×10^5	4.6×10^5
5	$Fe(bpy)_3^{3+}$	5.0	6.3×10^4 [d]	9.2×10^4
6	$IrCl_6^{2-}$	3.3	1.1×10^5 [e]	1.7×10^4
	reductant			
7	$Os(4,4'-(CH_3)_2bpy)_3^{2+}$	1.0	5.9×10^3	3.1×10^3
8	$Os(4,4'-(C_6H_5)_2bpy)_3^{2+}$	0.3	2.4×10^3	1.4×10^3
9	$Os(5,6-(C_6H_5)_2phen)_3^{2+}$	0.2	1.3×10^3	1.3×10^3
10	$Os(4,7-(C_6H_5)_2phen)_3^{2+}$	0.0	1.2×10^3	1.0×10^3
11	$Os(5-CH_3phen)_3^{2+}$	−0.5	2.7×10^2	5.4×10^2
12	$Os(bpy)_3^{2+}$	−1.0	2.4×10^2	3.0×10^2
13	$Os(phen)_3^{2+}$	−1.0	2.0×10^2	3.0×10^2
14	$Os(5-Clphen)_3^{2+}$	−2.9	2.9×10	3.3×10
15	$IrCl_6^{3-}$	−3.3	9.9×10^e	7.9
16	$V(H_2O)_6^{2+}$	17.2	6.8×10^4 [f]	6.5×10^4

[a] The value log K_{12} is calculated by using $E° = 0.76$ V for the $VO(OH)^{2+/+}$ couple and the cross-reaction reduction potentials found in ref 17, 19, and 20. [b] The value of k_{12} for the reduction of $VO(OH)^{2+}$ is calculated by using $K_2 = 30$ M. [c] Calculated from eq 13 by using $k_1 = 1 \times 10^{-3}$ M^{-1} s^{-1} for the $VO(OH)^{+/2+}$ couple ($E° = 0.76$ V) and $k_{22} = 4 \times 10^8$ M^{-1} s^{-1} for $OsL_3^{2+/3+}$ and $RuL_3^{2+/3+}$ (Young, R. C.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2468), $k_{22} = 3 \times 10^8$ M^{-1} s^{-1} for $Fe(bpy)_3^{2+/3+}$ (Ruff, I.; Zimonyi, M. *Electrochim. Acta* **1973**, *18*, 515), $k_{22} = 1.5 \times 10^3$ M^{-1} s^{-1} for $NiL_3^{2+/3+}$,[19] $k_{22} = 2.3 \times 10^5$ M^{-1} s^{-1} for $IrCl_6^{3-/2-}$ (Hurwitz, P.; Kustin, K. *Trans. Faraday Soc.* **1966**, *62*, 427), and $k_{22} = 1 \times 10^{-2}$ M^{-1} s^{-1} for $V(H_2O)_6^{2+/3+}$.[2] [d] Reference 11. [e] Reference 12. [f] Reference 10a. [g] These numbers correspond to those used in Figure 1.

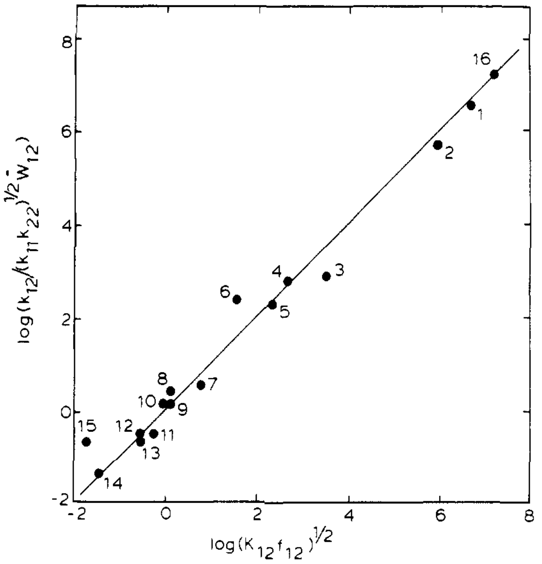


Figure 1. Marcus correlation of log $(k_{12}/(k_{11}k_{22})^{1/2}W_{12})$ against log $(K_{12}f_{12})^{1/2}$ for the oxidation of $VO(OH)^+$ and the reduction of $VO(OH)^{2+}$. The reactions are numbered as in Table III. The points are calculated by using $k_{11} = 1 \times 10^{-3}$ M^{-1} s^{-1} for $VO(OH)^{+/2+}$, and the solid line represents the theoretical slope of unity.

more stable precursor complex (by reducing electrostatic repulsions) than might be found with a symmetric $M(H_2O)_6^{2+}$ ion. This factor may also contribute to the dependence of the derived $VO(OH)^{+/2+}$ self-exchange rate constant on the nature of the oxidant. Less of a variance in the derived k_{11} value for the symmetrical $Fe(H_2O)_6^{2+/3+}$ couple (10^{-4}–10^{-2} M^{-1} s^{-1}) is observed with the same set of oxidants.[13]

A measurement of direct electron exchange between $VO^{2+}(aq)$ and $VO_2^+(aq)$ has been made by using ^{51}V NMR techniques.[14] The rate constant in 6.5 M hydrochloric acid is reported to be 1.5×10^6 M^{-2} s^{-1} with the rate expression having a first-order dependence on $[VO_2^+]$ and second-order dependences on $[VO_2^+]$ and $[H^+]^{-1}$. While no mechanism was established, an inner-sphere process is suggested by two recently reported observations: (a) a mixed-valence dimer $V_2O_3^{3+}(aq)$ exists in equimolar solutions of $VO^{2+}(aq)$ and $VO_2^+(aq)$, with $K = 0.8$ M^{-1} in 5 M $HClO_4$,[15] and (b) the ^{18}O exchange between $VO^{2+}(aq)$ and water is catalyzed by $VO_2^+(aq)$, with $k(VO_2^+) = 3.9$ M^{-1} s^{-1}.[24] The proposed mechanism for catalysis involves electron transfer in an inner-sphere $V_2O_3^{3+}(aq)$ complex followed by rapid ^{18}O exchange in $VO_2^+(aq)$ ($t_{1/2} = 0.15$ s).[25] The rate and equilibrium data suggest that electron transfer between $VO^{2+}(aq)$ and $VO_2^+(aq)$ is principally a rapid inner-sphere process.

The outer-sphere-exchange rate constants for metal aquo ion couples have been estimated by using a semiclassical model in which the rate constant k_{11} is expressed as a product of a preequilibrium constant K_A, an effective nuclear frequency ν_n, and electronic and nuclear factors κ_{el} and κ_n.[5,23] The nuclear factor contains contributions from inner-sphere and solvent reorganization energies along with a tunneling factor Γ_n.

$$\kappa_n = \Gamma_n \exp[-(\Delta G_{out}^* + \Delta G_{in}^*)/RT] \qquad (16)$$

For metal aquo couples the solvent term ΔG_{out}^* is about 7 kcal mol^{-1} for an activated complex radius of 6.5 Å. The relative magnitudes of k_{11} for metal aquo couples have been shown to depend largely on the size of the inner-sphere reorganization energy ΔG_{in}^*, which is a function of the difference in the equilibrium M–O bond distances in the two oxidation states. The instability of the $VO(OH)^+$ and $VO(OH)^{2+}$ ions would likely prevent a determination of the V–O bond distances in this couple. The V–O bond distances have been measured for $VO(H_2O)_5^{2+}$ by using X-ray crystallography[26] and for $VO(H_2O)_5^{2+}$ and $VO_2(H_2O)_4^+$ in solution by EXAFS techniques.[27] In the $VO^{2+}(aq)$ ion a short V=O bond distance of 1.59 (1) Å is found while the V—O bond distance in the trans position is 2.3 (1) Å. The four equatorial bonds have an average length of 2.06 (1) Å. For the $VO_2^+(aq)$ ion two short V=O bonds of length 1.65 (5) Å were observed. The distance of the two V—O bonds trans to the short V=O bonds is 2.3 (1) Å, while the two remaining V—O bonds have an average length of 2.15 (5) Å. In the $VO(OH)^{+/2+}$ couple, the deprotonation of V^{IV}—OH_2 and the protonation of V^V=O would likely reduce the respective bond distance differences for the V^{IV}—OH/V^V=OH bond and the V—O bond in the trans position. While a definitive value of ΔG_{in}^* appropriate for the $VO(OH)^{+/2+}$ couple cannot be determined, it is not expected to be significantly different from other metal aquo ion couples with similar electronic configurations. The $VO(OH)^{+/2+}$ couple is isoelectronic (d^1/d^0) with the $Ti^{3+/4+}(aq)$ and $Ti(OH)^{2+/3+}(aq)$ couples, for which self-exchange rate constants of $>3 \times 10^{-4}$ M^{-1} s^{-1} and $\sim 1 \times 10^{-2}$ M^{-1} s^{-1},[17] respectively, have been estimated from Marcus correlations in cross-reaction kinetic studies. These couples, along with $Fe(H_2O)_6^{2+/3+}$ ($k_{11} = 1.1$ M^{-1} s^{-1})[5] and $V(H_2O)_6^{2+/3+}$ ($k_{11} = 1 \times 10^{-2}$ M^{-1} s^{-1}),[2] involve the exchange of an electron from a nonbonding πd orbital. This range of rate constants is consistent with the moderate bond length changes (0.10–0.15 Å) observed for these couples. The average V–O bond length change accompanying electron exchange in $VO(OH)^{+/2+}$ is likely to fall within this range.

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Registry No. $Ru(dmbpy)_3^{3+}$, 65605-26-7; $Ru(bpy)_3^{3+}$, 18955-01-6; $Ni(dmbpy)_3^{3+}$, 65336-48-3; $Ni(bpy)_3^{3+}$, 64592-13-8; 4,4′-$(CH_3)_2$bpy, 1134-35-6; 4,4-$(C_6H_5)_2$bpy, 6153-92-0; 5,6-$(CH_3)_2$phen, 3002-81-1; 4,7-$(C_6H_5)_2$phen, 1662-01-7; 5-CH_3phen, 3002-78-6; phen, 66-71-7; bpy, 366-18-7; 5-Clphen, 4199-89-7; $VO(H_2O)_5^{2+}$, 15391-95-4; $VO_2(H_2O)_4^+$, 81738-79-6; $VO(OH)^+$, 73949-60-7; $VO(OH)^{2+}$, 41015-85-4.

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Photoaquation of *trans*-$[Cr(tn)_2F_2]^+$ in Acidic Aqueous Solution

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The photochemistry of the title molecule has been studied in acidic aqueous solution at room temperature. The main reaction mode is loss of fluoride ($\phi = 0.34$) with a smaller yield for amine aquation ($\phi = 0.18$). Firm evidence was obtained for the production of "one-ended" tn products in the latter reaction. The photostereochemistry of the reactions is consistent with the usual stereochemical change seen for Cr(III) complexes. The unusual reaction mode ratio can be ascribed to steric interactions with the six-membered tn ring.

Introduction

A central and continuing theme in Cr(III) photochemistry has been the importance and interplay of electronic and steric factors in determining the identity of the ligand(s) photosolvated and also the stereochemistry of the subsequent photosubstitution process. Approaches to the first aspect have ranged from the initial proposal of a set of rules[1] through molecular orbital theoretical calculations of metal/ligand bond labilization[2-5] to a fairly successful ligand field model for bond strengths in the excited state.[6-8] The stereochemical aspect has also progressed from the stage of a simple

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