

Figure 3. Illustration of scrambling of apical bond positions for the **5** (C_2) and **4** (C_s) structures. The **5** to **5'** conversion involves the indicated hydrogen motions. Two bridging hydrogens (5-4 and 3-2) adopt terminal positions (4 and 2) while two terminal hydrogens (5 and 2) migrate to bridging positions (5-4 and 2-1, respectively). The diamond-square-diamond (DSD)³⁴ transformation involves the formation of a 5-1-3-4 square and the formation of two bridge hydrogens (2-1 and 5-4) from terminal hydrogens (2 and 5, respectively).

(35–40 kcal/mol), provided that the entropy change is small. Structure **6** does not interchange apical and equatorial boron atoms and is therefore not suitable. The remaining structures are **4** (C_s) and **5** (C_2).

Structure **5** is a reasonable candidate for the low-temperature rearrangement in the presence of a Lewis base, because of the vacant orbital on the middle boron. The transient nature of this complex is consistent with absence of evidence for B_5H_9L adducts

under conditions that a stable complex might be expected.¹³ Structure **4** does not have a vacant orbital as written, although it could easily develop one if the three-center BBB bond becomes a two-center bond, leaving a vacant orbital on the boron atom at the right. If so, a ligand could bind in a transient intermediate. Finally, two ligands could act simultaneously, yielding intermediates that could be modeled by the X-ray diffraction studies of $B_5H_9L_2$ compounds.¹⁹

For the high-temperature rearrangement uncatalyzed by a Lewis base, structure **4** is one reasonable candidate. This structure combines a dsd mechanism³⁴ with a filled orbital structure, retains B–H bonds, and does rearrange the apex and equatorial BH units.

In Figures 2 and 3 we summarize motions of atoms that might plausibly occur in these proposed rearrangements, in the expectation that further experimental and theoretical studies will be stimulated.³⁵

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Registry No. B_5H_9 , 19624-22-7.

- (35) Added Feb 1, 1985: At the 1984 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec 16–21, 1984, D. F. Gaines reported experimental evidence for retention of BH units in the rearrangement of B_5H_9 (paper 07L19), and he suggested a geometrical rearrangement mechanism similar to ours. Also at this meeting, R. Hoffmann suggested that the outer pathway of Scheme I for the rearrangement of $C_5H_5^+$ may give further clues about the rearrangement of B_5H_9 (Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* 1972, 94, 1661, especially p 1664). Our preliminary examination of this pathway modified for B_5H_9 in place of $C_5H_5^+$ indicates an intermediate consisting of a BH apex having two hydrogen bridges to a B_4H_8 unit. This C_{2v} structure is 97 kcal/mol less stable than the C_{4v} structure at the [MP2/6-31G*] level after optimization at the 3-21G level. Our mechanism for rearrangement of B_5H_9 may be worth extending to the $C_5H_5^+$ system.

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Kinetics and Mechanisms of the Outer-Sphere Oxidation of *cis*-Aquaovanadium(IV) Complexes Containing Quadridentate Amino Polycarboxylates. Interpretation of the Difference in Activation Parameters with the Charge Type of Reactants

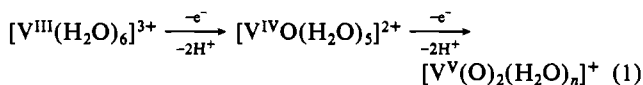
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Kinetics of the outer-sphere oxidation of *cis*-aquaovanadium(IV) complexes, $[V^{IV}O(\text{pmida})(\text{H}_2\text{O})]$ ($\text{H}_2\text{pmida} = [(2\text{-pyridylmethyl})\text{imino}]$ diacetic acid) and $[V^{IV}O(\text{nta})(\text{H}_2\text{O})]^-$ ($\text{H}_3\text{nta} = \text{nitrilotriacetic acid}$), with one-electron oxidants, $[\text{Ir}^{IV}\text{Cl}_6]^{2-}$ and $[(\text{en})_2\text{Co}^{III}(\mu\text{-NH}_2\text{O}_2)\text{Co}^{III}(\text{en})_2]^{4+}$ ($\text{en} = \text{ethylenediamine}$), have been studied by the stopped-flow method in aqueous solution at $I = 0.1\text{--}1.0\text{ M}$ (NaClO_4) ($1\text{ M} = 1\text{ mol dm}^{-3}$), pH 3.5–5.0 (acetate buffer, total acetate concentration 0.01 M), and 15–45 °C, under pseudo-first-order conditions with the vanadium complex in large excess. The observed rate law is rate = $(k_{\text{H}_2\text{O}} + k_{\text{OH}}K_a[\text{H}^+]^{-1})[\text{V}^{IV}][\text{oxidant}]$, where K_a is the acid-dissociation constant for the aqua ligand and $k_{\text{H}_2\text{O}}$ and k_{OH} are the second-order rate constants for the oxidation of the aqua and the hydroxo complexes, respectively. ΔS^\ddagger rather than ΔH^\ddagger seems to be responsible for the fact that k_{OH} is ca. 10^3 times bigger than $k_{\text{H}_2\text{O}}$ for each of the four redox couples. This is explained by the difference in electronic interaction between the redox couples at the transition state (nonadiabaticity) rather than the difference in the Franck–Condon barrier between the aqua and hydroxo complexes. Importance of the solvation for these reactions is discussed on the basis of the dependence of ΔH^\ddagger and ΔS^\ddagger on the charge product of redox couple.

Transition-metal ions of quadrivalent or higher oxidation states in aqueous media usually possess coordinated oxide ion(s), of which the number tends to increase as the oxidation number increases.^{1–3} Oxidation of the metal ions to such higher oxidation states in

aqueous solution is mostly accompanied by the formation of an “oxo–metal” bond. “Oxo–metal” bond formation on oxidation of aquated metal ions is coupled with release of the hydrogen ion as exemplified by vanadium(III):^{4,5}



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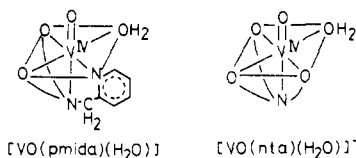
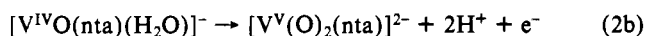
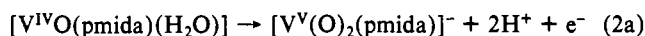


Figure 1. Schematic structures of $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})]$ (pmida = [(2-pyridylmethyl)imino]diacetate) and $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$ (nta = nitrilotriacetate).

The existence of coordinated oxide ion has been confirmed for some molybdenum enzymes,⁶ and redox reactions involving oxo-metal ions would be relevant to some enzyme reactions. Also, oxo-metal ions can be used as redox catalysts for various organic reactions.⁷ Despite the importance of redox reactions involving oxo-metal bonds, only a limited variety of systems, mostly involving aquated metal ions, has been studied kinetically.^{4,5,8}

We have recently reported substitution and inner-sphere oxidation reactions of newly characterized oxovanadium(IV) complexes, $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})]$ ($\text{H}_2\text{pmida} = [(2\text{-pyridylmethyl})\text{imino}]$ diacetic acid) and $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$ ($\text{H}_3\text{nta} = \text{nitrilotriacetic acid}$),⁹⁻¹² which have one water ligand cis to the oxo ligand (Figure 1).¹³ We thought that outer-sphere oxidation of these complexes to give dioxovanadium(V) complexes (reactions 2a and 2b) is suitable for studying the oxidation reaction involving



oxo-metal bond formation. Reaction products most certainly have a hexacoordinated *cis*-dioxo structure as indicated by the crystal structure of the closely related complex $[\text{V}^{\text{V}}(\text{O})_2(\text{S-peida})]^-$ ($\text{S-peida} = (\text{S})\text{-}[[1\text{-}(2\text{-pyridyl})\text{ethyl}]\text{imino}]$ diacetic acid).^{14,15} Thus the aqua ligand in the vanadium(IV) complexes changes into a new oxo ligand without changing its coordination site, and the quadridentate ligand is retained in the coordination sphere without any rearrangement or partial dissociation.

Our recent studies on the outer-sphere redox reactions of some binuclear molybdenum(V) and uninnuclear cobalt(III) complexes¹⁶⁻¹⁸ showed that activation parameters, ΔH^\ddagger , ΔS^\ddagger , and ΔV^\ddagger , are very sensitive to the charge type of the redox couple. Two one-electron oxidants, $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ and $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^-)]^{4+}$

Table I. Acid Dissociation Constants, $\text{p}K_a$, for the Deprotonation of Coordinated Water at 25 °C

complex ^a	<i>I</i> / <i>M</i> (NaClO ₄)	
	0.1	1.0
$[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})]$	6.5	6.4
$[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$	7.0	6.9

^a pmida = [(2-pyridylmethyl)imino] diacetate; nta = nitrilotriacetate.

Table II. Second-Order Rate Constants, k_1 , for the Oxidation of the pmida and nta Complexes of Oxovanadium(IV) with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ and $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^-)]^{4+}$ in Aqueous Solution at 25 °C^a

<i>I</i> / <i>M</i>	pH	$k_1/10^3 \text{ M}^{-1} \text{ s}^{-1}$	<i>I</i> / <i>M</i>	pH	$k_1/10^3 \text{ M}^{-1} \text{ s}^{-1}$
(a) $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})] + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$					
0.1	3.5	40.7 ± 0.6	0.1	4.1	116 ± 2
0.1	3.8	60.5 ± 0.8	0.1	4.4	213 ± 2
(b) $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^- + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$					
0.1	3.5	87.3 ± 0.8	1.0	3.5	530 ± 20
0.1	3.8	114 ± 2	1.0	3.8	770 ± 10
0.1	4.1	193 ± 3	1.0	4.1	1220 ± 70
0.1	4.4	345 ± 9			
(c) $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})] + [\mu\text{-O}_2^-]^{4+ b}$					
0.1	3.6	0.54 ± 0.02	0.1	5.1	12.4 ± 0.9
0.1	3.8	0.99 ± 0.04	0.5	5.1	6.3 ± 0.1
0.1	4.5	3.6 ± 0.3	1.0	5.1	4.8 ± 0.5
(d) $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^- + [\mu\text{-O}_2^-]^{4+ b}$					
1.0	3.6	0.23 ± 0.02	2.0	3.9	0.32 ± 0.01
1.0	3.9	0.42 ± 0.02	2.0	4.5	1.18 ± 0.03
1.0	4.5	1.39 ± 0.10	2.0	5.1	4.15 ± 0.20
1.0	5.1	6.0 ± 0.1			

^a pmida = [(2-pyridylmethyl)imino] diacetate; nta = nitrilotriacetate. ^b $[\mu\text{-O}_2^-]^{4+} = [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^-)]^{4+}$ (en = ethylenediamine).

$[\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ (en = ethylenediamine), have similar redox potentials (0.87¹⁹ and 0.863 V²⁰ vs. NHE, respectively) and are convenient for studying the effect of charge of oxidant on the activation parameters ΔH^\ddagger and ΔS^\ddagger . The observed activation parameters span a fairly wide range and increase as the charge product of the redox couple becomes more negative. An interpretation for this observation will be given on the basis of the role of solvation of the encounter complex between the redox couples. A preliminary account of this work has been published.²¹

Experimental Section

Materials. The vanadium complexes $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}^9$ and $\text{Na}[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}^{11}$ and the μ -superoxo (μ -hyperoxo) complex $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2^-)]^{4+}[\text{Co}^{\text{III}}(\text{en})_2\text{Cl}_4 \cdot 3\text{H}_2\text{O}]^{2-}$ were prepared as reported previously. Sodium hexachloroiridate(IV) hexahydrate (Johnson Matthey) was used without further purification.

Kinetic Runs. All the kinetic runs were carried out by the stopped-flow method, under pseudo-first-order conditions with the vanadium(IV) complex in at least 10-fold excess to the oxidant. The decrease in concentration of the oxidants was followed mostly at their absorption peaks (487 nm ($\epsilon = 4075$)²³ and 690 nm ($\epsilon = 485$)²² for $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ and the μ -superoxo ion, respectively). The first-order plots ($A_t - A_\infty$) against time (*t*), where *A_t* stands for the absorbance at time *t*, were linear up to at least 3 half-lives. First-order rate constants, k_{obsd} , were obtained from slopes of the plots. k_{obsd} did not depend on the wavelength at which the reaction was followed (360 and 487 nm for the $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ oxidation and 400, 450, and 690 nm for the μ -superoxo oxidation). Ionic strength (*I*)

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- (7) For a recent example, see: Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106–4115, 5070–5076 and references cited therein.
- (8) For recent examples, see: (a) Berrie, B. H.; Earley, J. E. *Inorg. Chem.* **1984**, *23*, 774–778 ($[\text{Ti}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$). (b) Durant, R.; Garner, C. D.; Hyde, M. R.; Mabbs, F. E.; Parsons, J. R.; Richens, D. *J. Less-Common Met.* **1977**, *54*, 459–464 (Mo(V) monomer). (c) Sasaki, Y.; Kawamura, R. *Bull. Chem. Soc. Jpn.* **1982**, *54*, 3379–3386 (Mo(V) dimer). (d) Binstead, R. A.; Moyer, B. A.; Samuels, Q. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2897–2899 and references cited therein (Ru(IV)).
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Table III. Rate Constants for the Oxidation of the pmida and nta Complexes of Oxovanadium(IV) with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ and $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ in Aqueous Solution

reductant ^a	oxidant ^b	I/M	temp/°C	$k_{\text{H}_2\text{O}}/10^3 \text{ M}^{-1} \text{ s}^{-1}$	$k_{\text{OH}}/10^6 \text{ M}^{-1} \text{ s}^{-1}$
$[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})]$	$[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$	0.1	25.0	0.91 ± 0.02	2.9 ± 0.4
		0.1	35.0	1.7 ± 0.2	5 ± 1
		0.1	42.0	2.4 ± 0.1	8 ± 1
		1.0	25.0	2.62 ± 0.09	6.6 ± 0.9
$[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$	$[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$	0.1	25.0	0.137 ± 0.003	1.4 ± 0.2
		0.1	35.0	0.238 ± 0.009	2.4 ± 0.3
		0.1	45.0	0.38 ± 0.01	3.8 ± 0.5
		1.0	25.0	1.1 ± 0.1	9 ± 2
$[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})]$	$[\mu\text{-O}_2]^{4+}$	0.1	15.0		0.17 ± 0.03
		0.1	25.0		0.42 ± 0.05
		0.1	35.0		1.0 ± 0.2
		1.0	25.0		0.10 ± 0.02
$[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$	$[\mu\text{-O}_2]^{4+}$	0.1	13.5		0.8 ± 0.1^c
		0.1	25.0		2.4 ± 0.4^c
		0.1	36.0		7 ± 1^c
		1.0	25.0		0.52 ± 0.07
		2.0	25.0	130 ± 110	0.35 ± 0.07

^a pmida = [(2-pyridylmethyl)imino] diacetate; nta = nitrilotriacetate. ^b $[\mu\text{-O}_2]^{4+} = [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ (en = ethylenediamine). ^c Correspond to $k_e K_{\text{OS}}$ (see text).

was adjusted with sodium perchlorate. The pH was adjusted with acetate buffer, of which the total concentration did not affect the k_{obsd} in the region $[\text{CH}_3\text{COO}^-]_{\text{T}} = 0.01\text{--}0.02 \text{ M}$ ($1 \text{ M} = 1 \text{ mol dm}^{-3}$).

Measurements. A Union Giken RA-401 stopped-flow spectrophotometer was used for the kinetic measurements. The pH of solution was measured by a Metrohm Herisau E300B pH meter. The acid dissociation constants of the two vanadium(IV) complexes were determined by the pH titration with the same pH meter.

Results

Determination of $\text{p}K_a$ for the Vanadium(IV) Complexes. The $\text{p}K_a$ values of the coordinated water are shown in Table I. The value at $I = 0.1 \text{ M}$ is slightly greater than that at $I = 1.0 \text{ M}$ for a given complex. The values for the pmida complex at 35°C (6.4) and 42°C (6.5) indicate very small temperature dependence of the $\text{p}K_a$ value. The $\text{p}K_a$ value, 6.19, was reported for the nta complex at $I = 0.12 \text{ M}$ (sodium acetate).²⁴ The divergence from our value may be due to the difference in the medium.

Preliminary Studies of the Redox Reactions. The vanadium(IV) complexes undergo acid hydrolysis in aqueous solutions of $\text{pH} < 3.0$.¹⁰ They are oxidized with the two oxidants at $\text{pH} > 5.5$ too rapidly to be followed by our stopped-flow apparatus ($t_{1/2} < 10 \text{ ms}$). Therefore, the kinetic studies were limited in the pH range 3–5.5. The stoichiometry of the four reactions was determined by use of an excess of oxidant to the vanadium complexes. After the redox reaction was completed, the amount of remaining oxidant was estimated from the absorbance at its absorption peak. One mole of the oxidant was consumed per mole of the vanadium(IV) complex in all four reactions. Both $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ ^{4,8c} and $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ ^{8c} are known to behave as one-electron oxidants to give $[\text{Ir}^{\text{III}}\text{Cl}_6]^{3-}$ and $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{3+}$, respectively. Thus, one-electron oxidation of the vanadium(IV) complexes was verified, and the oxidation of coordinated ligands is not significant.

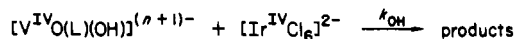
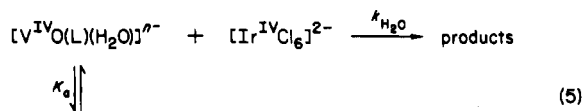
Kinetics of the Oxidation with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$. The kinetics was studied at $I = 0.1$ and 1.0 M and at $25\text{--}45^\circ\text{C}$. The first-order rate constants, k_{obsd} , at a given pH are proportional to the concentration of reductant ($(1\text{--}7) \times 10^{-3} \text{ M}$) (Figure 2)²⁵ and are expressed by (3). The k_1 values at 25°C were listed in Table

$$-d[\text{Ir}^{\text{IV}}]/dt = k_{\text{obsd}}[\text{Ir}^{\text{IV}}] = k_1[\text{V}^{\text{IV}}][\text{Ir}^{\text{IV}}] \quad (3)$$

II. Plots of k_1 against $[\text{H}^+]^{-1}$ give straight lines with small intercepts (Figure 3),²⁵ suggesting the rate formula

$$k_1 = k_2 + k_3[\text{H}^+]^{-1} \quad (4)$$

These results are most reasonably interpreted by the reaction 5, involving conjugate bases of the complexes. Here, L denotes



nta ($n = 1$) or pmida ($n = 0$). Since K_a is much less than $[\text{H}^+]$ under the experimental conditions, the rate law (6) is derived.

$$-d[\text{Ir}^{\text{IV}}]/dt = (k_{\text{H}_2\text{O}} + k_{\text{OH}}K_a[\text{H}^+]^{-1})[\text{V}^{\text{IV}}][\text{Ir}^{\text{IV}}] \quad (6)$$

Thus, the experimentally obtained rate constants, k_2 and k_3 , correspond to $k_{\text{H}_2\text{O}}$ and $k_{\text{OH}}K_a$, respectively. The k_{OH} values were calculated by using $\text{p}K_a$ values at 25°C in Table I. The $k_{\text{H}_2\text{O}}$ and k_{OH} values at various temperatures and different ionic strengths are summarized in Table III.

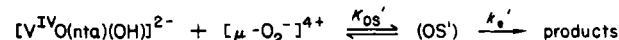
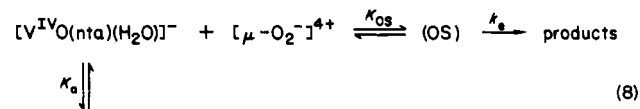
Kinetics of the Oxidation with the μ -Superoxo Complex. The kinetics was studied at $I = 0.1$ and 1.0 M (also 2.0 M for the oxidation of the nta complex) and at $13.5\text{--}36^\circ\text{C}$. Except for the oxidation of $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$ at $I = 0.1 \text{ M}$, the first-order rate constants, k_{obsd} , can be treated similarly to those for the oxidation with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$. The rate constants, $k_{\text{H}_2\text{O}}$ and k_{OH} , are listed in Table III.

k_{obsd} for the oxidation of the nta complex at $I = 0.1 \text{ M}$ depends nonlinearly on the reductant concentration as shown in Figure 4a.²⁵ Plots of k_{obsd}^{-1} against $[\text{V}^{\text{IV}}]^{-1}$ give straight lines with small intercepts (Figure 4b).²⁵ Such a behavior of k_{obsd} conforms to the rate formula (7). The values of a and b evaluated from the

$$\frac{d[\mu\text{-O}_2^-]}{dt} = k_{\text{obsd}}[\mu\text{-O}_2^-] = \frac{b[\text{V}^{\text{IV}}]}{1 + a[\text{V}^{\text{IV}}]}[\mu\text{-O}_2^-] \quad (7)$$

slope and intercept of the plots, k_{obsd}^{-1} vs. $[\text{V}^{\text{IV}}]^{-1}$, increase as pH becomes higher.

The reaction 8 ($[\mu\text{-O}_2^-]^{4+} = [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2\text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$) and rate equation 9 are consistent with eq 7.^{8c} Here,



K_{OS} and $K_{\text{OS}'}$ are the formation constants of the encounter complex (also called ion-pair or outer-sphere complex), and k_e and k_e' are

(24) Nelson, J.; Shepherd, R. E. *Inorg. Chem.* 1978, 17, 1030–1034.

(25) Supplementary material.

Table IV. Activation Parameters for the Outer-Sphere Oxidation of the pmida and nta Complexes of Oxovanadium(IV) at $I = 0.1$ M (25 °C)

reactn ^b	$\Delta G^\ddagger / \text{kJ mol}^{-1}$	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{J K}^{-1} \text{mol}^{-1}$
$[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})] + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$	54 ± 19	52 ± 8	-8 ± 38
$[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^- + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$	60 ± 14	46 ± 8	-46 ± 17
$[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{OH})]^- + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-a}$	36 ± 1	42 ± 0.4	$+21 \pm 2$
$[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{OH})]^{2-} + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-a}$	38 ± 3	37 ± 3	-2 ± 8
$[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{OH})]^- + [\mu\text{-O}_2]^{4+a}$	41 ± 8	65 ± 4	$+80 \pm 13$
$[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{OH})]^{2-} + [\mu\text{-O}_2]^{4+a}$	39 ± 15	69 ± 7	$+107 \pm 21$

^a Calculated by assuming that ΔH for K_a is zero. ^b $[\mu\text{-O}_2]^{4+} = [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ (en = ethylenediamine); pmida = [(2-pyridylmethyl)imino] diacetate; nta = nitrilotriacetate.

the first-order rate constants of electron-transfer within the encounter complexes, (OS) and (OS'), respectively. Equation 9 is

$$-\frac{d[\mu\text{-O}_2]}{dt} = \frac{(k_e K_{\text{OS}} + k_e' K_{\text{OS}} K_a [\text{H}^+]^{-1}) [\text{V}^{\text{IV}}] [\mu\text{-O}_2]}{1 + (K_{\text{OS}} + K_{\text{OS}} K_a [\text{H}^+]^{-1}) [\text{V}^{\text{IV}}]} \quad (9)$$

of the same form as the experimentally obtained rate law (7). The dependence of a and b on $[\text{H}^+]^{-1}$ gives all the parameters in eq 9. The values at 25 °C are as follows: $K_{\text{OS}} = 26 \pm 3$ M, $K_{\text{OS}}' = 2000 \pm 1200$ M, $k_e < 3$ s⁻¹, and $k_e' = 1300 \pm 600$ s⁻¹ (the $\text{p}K_a$ value in Table I was used for the calculation). A composite term, $k_e' K_{\text{OS}}'$, corresponds to k_{OH} for the oxidation with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$, and therefore the values of $k_e' K_{\text{OS}}'$ are listed in the corresponding column of Table III.

When the second term of the denominator of eq 9 is much less than unity, the equation can be simplified to eq 6. This is the case for the oxidation of the nta complex at $I = 1.0$ and 2.0 M and that of the pmida complex at all ionic strengths.

Activation Parameters. The activation parameters (Table IV) were obtained in the temperature range from 15 to 45 °C. The k_{OH} values were evaluated by using the $\text{p}K_a$ values at 25 °C; i.e., the activation parameters for k_{OH} were evaluated under the assumption that K_a was independent of temperature. Such an assumption would be reasonable, since the $\text{p}K_a$ for $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$ at $I = 0.1$ M did not show appreciable temperature dependence.

Discussion

Assignment to the Outer-Sphere Mechanism. The present electron-transfer reactions must proceed through the outer-sphere mechanism, since the rate constants are ca. 10^4 times bigger than those of anation (for example, the second-order rate constant for the reaction of $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^-$ with NCS^- is 0.3 s⁻¹ at 25 °C in the pH range from 3.0 to 4.5) and acid-catalyzed hydrolysis of the present vanadium(IV) complexes,⁹⁻¹³ and the oxidants are substitution inert.

The oxidation products are *cis*-dioxo species, $[\text{V}^{\text{V}}(\text{O})_2(\text{L})]^{(n+1)-}$.^{3,14,26} Neither change in coordination number nor significant rearrangement of the donor atoms is required in the electron transfer. The aqua or hydroxo ligand *cis* to oxo in the vanadium(IV) complexes must be converted into another oxo ligand by liberating proton(s) on electron transfer.

Activation Parameters. (1) General Trend. Although all the reactions are believed to proceed through the outer-sphere mechanism, both ΔH^\ddagger and ΔS^\ddagger in Table IV span a fairly wide range. It is seen, however, that ΔG^\ddagger values at 25 °C for the oxidation of the hydroxo complexes are very similar to one another. The contribution of ΔH^\ddagger and ΔS^\ddagger to ΔG^\ddagger (namely to the rate constants) seems to compensate mutually at 25 °C. A good

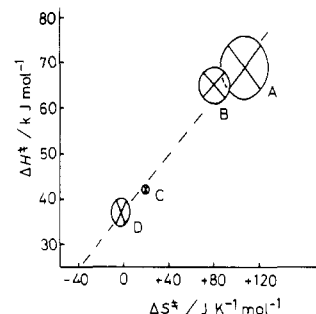


Figure 5. Isokinetic relationship for the oxidations of $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{OH})]^-$ and $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{OH})]^{2-}$ with $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ and $[(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$ at $I = 0.1$ M: (A) $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{OH})]^{2-} + [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$; (B) $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{OH})]^- + [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$; (C) $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{OH})]^- + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$; (D) $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{OH})]^{2-} + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$.

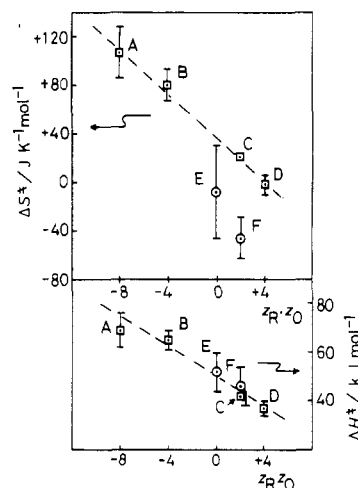


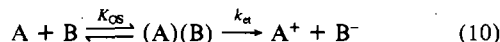
Figure 6. Relationship between the activation parameters (ΔH^\ddagger and ΔS^\ddagger) at $I = 0.1$ M and the charge product ($Z_R Z_O$) of the redox couple: (A) $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{OH})]^{2-} + [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$; (B) $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{OH})]^- + [(\text{en})_2\text{Co}^{\text{III}}(\mu\text{-NH}_2, \text{O}_2)\text{Co}^{\text{III}}(\text{en})_2]^{4+}$; (C) $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{OH})]^- + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$; (D) $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{OH})]^{2-} + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$; (E) $[\text{V}^{\text{IV}}\text{O}(\text{pmida})(\text{H}_2\text{O})]^- + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$; (F) $[\text{V}^{\text{IV}}\text{O}(\text{nta})(\text{H}_2\text{O})]^{2-} + [\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ (line for ΔS^\ddagger is drawn for points A-D).

isokinetic relationship (Figure 5) clearly indicates that the predominant factor controlling ΔS^\ddagger must be highly relevant to that determining ΔH^\ddagger . This is further discussed below with reference to the solvation state of the encounter complex.

ΔG^\ddagger at 25 °C is much larger for the oxidation of the aqua complexes than for those of the hydroxo complexes.

(2) Relationship of Activation Parameters to the Charges of Reactants. Figure 6 shows the relation between ΔH^\ddagger and ΔS^\ddagger with the charge product of redox couples. It is remarkable that the ΔH^\ddagger values lie on a straight line for all the six reactions, in spite of the rather arbitrary nature of the abscissa. The ΔS^\ddagger 's for the hydroxo complexes also lie on a straight line, while two ΔS^\ddagger values for the reactions of the aqua complexes are ca. 60 J K⁻¹ mol⁻¹ more negative than the values expected on the above line. Such facts seem to indicate that the large difference between $k_{\text{H}_2\text{O}}$ and k_{OH} (namely the difference in ΔG^\ddagger values at 25 °C) comes from the difference in ΔS^\ddagger rather than ΔH^\ddagger values.

(3) General Expression for the Activation Parameters. Outer-sphere electron-transfer reactions may generally be expressed by reaction 10 (corresponds to reaction 8), where K_{OS} is the rapid



equilibrium for the encounter complex formation between the redox couple A and B and k_{et} the first-order electron-transfer rate constant within the encounter complex.¹⁶⁻¹⁸ The pseudo-first-order rate constant, k_{obsd} , is expressed by eq 11, whenever a large excess

$$k_{\text{obsd}} = K_{\text{OS}} k_{\text{et}} [\text{A}] / (1 + K_{\text{OS}} [\text{A}]) \quad (11)$$

(26) Zare, K.; Lagrange, P.; Lagrange, J. *J. Chem. Soc., Dalton Trans.* 1979, 1372-1376.

Table V. Values of ΔH_{OS}^\ddagger , ΔS_{OS}^\ddagger , ΔH_{et}^\ddagger , and ΔS_{et}^\ddagger for Some Outer-Sphere Redox Reactions Whose Ion-Pair Formation Constants and Electron-Transfer Rate Constants Were Separately Obtained

oxidant ^a	reductant ^a	ΔH_{OS}^\ddagger kJ mol ⁻¹	ΔS_{OS}^\ddagger J K ⁻¹ mol ⁻¹	ΔH_{et}^\ddagger kJ mol ⁻¹	ΔS_{et}^\ddagger J K ⁻¹ mol ⁻¹	ref
[Co ^{III} (NH ₃) ₅ (Me ₂ SO)] ³⁺	[Fe ^{II} (CN) ₅ (im)] ³⁻	~0	+52 ± 8	92 ± 2	+71 ± 8	27
	[Fe ^{II} (CN) ₅ (NH ₃)] ³⁻	~0	+52 ± 8	94 ± 2	+71 ± 8	27
	[Fe ^{II} (CN) ₅ (py)] ³⁻	~0	+51 ± 10	100 ± 2	+75 ± 8	27
	[Fe ^{II} (CN) ₅ (<i>i</i> -nic)] ³⁻	~0	+52 ± 10	102 ± 7	+71 ± 24	27
	[Fe ^{II} (CN) ₅ (pyra)] ³⁻	~0	+50 ± 8	108 ± 6	+75 ± 20	27
	[Fe ^{II} (CN) ₅ (pyca)] ³⁻	~0	+53 ± 4	109 ± 2	+75 ± 8	27
[Co ^{III} (NH ₃) ₅ (py)] ³⁺	[Fe ^{II} (CN) ₅] ⁴⁻	~0	+63	91 ± 9	+24 ± 29	28
[Co ^{III} ₂ (O ₂ ⁻)(NH ₃) ₁₀] ⁵⁺	[Mo ^V ₂ O ₄ (edta)] ²⁻	~0	+48 ^b	118 ± 17	+76 ± 46	16
[Co ^{III} ₂ (NH ₂ ⁻ ,O ₂ ⁻)(en) ₄] ⁴⁺	[Mo ^V ₂ O ₄ (OH)(hedta)] ²⁻	~0.9 ± 4.0	+50 ± 14	79 ± 3	+44 ± 10	29

^a py = pyridine; en = ethylenediamine; im = imidazole; *i*-nic = isonicotinamide; pyra = pyrazine; pyca = pyridine-2-carboxamide; edta = ethylenediaminetetraacetate ion; hedta = *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetate ion. ^b Calculated from the average ion-pair formation constant, 313 M,¹⁶ by assuming $\Delta H_{OS} = 0$.

of A is used to maintain the pseudo-first-order condition. For most reactions, $K_{OS}[A]$ is negligible as compared to unity. Thus, eq 11 can be simplified to eq 12. Therefore, the activation parameters for the second-order rate constant are given by eq 13 and 14.

$$k_{\text{obsd}} = K_{OS}k_{et}[A] \quad (12)$$

$$\Delta H^\ddagger = \Delta H_{OS}^\ddagger + \Delta H_{et}^\ddagger \quad (13)$$

$$\Delta S^\ddagger = \Delta S_{OS}^\ddagger + \Delta S_{et}^\ddagger \quad (14)$$

The separation of ΔH^\ddagger and ΔS^\ddagger into their components is not kinetically possible, when the rate law is expressed by eq 12. When the two reactants have high and opposite charges, however, the full rate formula (eq 11) is sometimes used to obtain individual value of K_{OS} and k_{et} .²⁷⁻²⁹ Table V summarizes the entropy and enthalpy changes for each of these terms so far reported.

(4) ΔH_{OS}^\ddagger and ΔS_{OS}^\ddagger Values. Table V shows that ΔH_{OS}^\ddagger 's are almost zero and ΔS_{OS}^\ddagger 's are highly positive for the reactions between oppositely charged reactants. The positive entropy change (ΔS_{OS}^\ddagger) is explained by the disordering of solvent molecules at the solvation sphere as a consequence of partial compensation of the charges on forming the encounter complex (ion pair).²⁸ A small ΔH_{OS}^\ddagger value is reasonable for a predominantly electrostatic process such as an encounter complex formation. The temperature dependence of K_{OS} between [V^{IV}O(ota)(OH)]²⁻ and [(en)₂Co^{III}(μ-NH₂,O₂⁻)Co^{III}(en)₂]⁴⁺ is in accord with the general trend.

No data of ΔH_{OS}^\ddagger and ΔS_{OS}^\ddagger are available for the reactions between the reactants with charges of the same sign. Such reactions usually have highly negative ΔS^\ddagger values (corresponding to $\Delta S_{OS}^\ddagger + \Delta S_{et}^\ddagger$). It has been suggested recently that the major contribution to the negative ΔS^\ddagger comes from the encounter complex formation.^{30,31} Substantial ordering of the solvation sphere on encounter complex formation must be responsible for the negative ΔS_{OS}^\ddagger . The change in overall ΔS^\ddagger ($=\Delta S_{OS}^\ddagger + \Delta S_{et}^\ddagger$) with the charges of reactants (Figure 6) should be predominantly the reflection of the change in ΔS_{OS}^\ddagger .

(5) ΔH_{et}^\ddagger and ΔS_{et}^\ddagger Values. Figure 6 indicates that ΔS^\ddagger rather than ΔH^\ddagger is responsible for the difference between k_{H_2O} and k_{OH} . Since ΔS_{OS}^\ddagger is unlikely to contribute significantly to the difference between k_{H_2O} and k_{OH} (vide supra), ΔS_{et}^\ddagger should reflect the difference between the reactivities of the aqua and the hydroxo complexes toward a given oxidant.

It would be worthwhile to mention here that the large difference in k_{H_2O} and k_{OH} may be attributed to the difference in nonadiabaticity, the reactions of the aqua complexes being considerably more nonadiabatic. Such a conclusion is based on the expectation that if the electronic interaction of the redox couple at the tran-

sition state is small, namely if the electronic transmission coefficient (κ) is small ($\kappa = 1$ for an adiabatic reaction and $\kappa < 1$ for a nonadiabatic reaction), more negative entropy of activation would be observed and the enthalpy of activation would remain virtually unchanged.³² The conclusion is also supported by the view of Earley and his co-workers.³³ They noted in the studies of the outer-sphere oxidations involving [Ti^{III}(H₂O)₆]³⁺ that a small k_{OH}/k_{H_2O} value (on the order of 10, two rate constants represent [Ti^{III}(OH)(H₂O)₅]²⁺ and [Ti^{III}(H₂O)₆]³⁺) is found for the reactions involving oxidants with delocalized π -electron systems. They pointed out that a large k_{OH}/k_{H_2O} value ($> \sim 10^3$) is indicative of nonadiabaticity for the reactions of the aqua complex. According to this suggestion, present reactions of the two aqua complexes would have considerable nonadiabatic character since the ratio k_{OH}/k_{H_2O} exceeds 10^3 .

One may consider that the V^{IV}-OH bond is structurally more close to the V^V=O bond than the V^{IV}-OH₂ bond is, and thus the hydroxo complex would be more accessible to oxidative attack.³⁴ Such a structural factor, which is considered to constitute the so-called "Franck-Condon barrier", would be reflected in ΔH_{et}^\ddagger as well as ΔS_{et}^\ddagger . Since ΔH_{et}^\ddagger , which is almost equal to overall ΔH^\ddagger as ΔH_{OS}^\ddagger is very small, is virtually indiscriminate between k_{H_2O} and k_{OH} , the structural factor seems to be less important as compared with the electronic coupling factor.

Strong dependence of ΔH_{et}^\ddagger on the charge product of the redox couple may be explained in terms of the solvation state at the encounter complex. Since the isokinetic relationship in Figure 5 has now turned out to be the relationship between ΔS_{OS}^\ddagger and ΔH_{et}^\ddagger , it would be reasonable to consider that the solvation state of the encounter complex should play an important role in determining ΔH_{et}^\ddagger . ΔH_{et}^\ddagger is the enthalpy change for the rearrangement of the inner sphere (bond lengths and/or angles) and also the solvation sphere of the reactants to reach a transition state within the encounter complex. Since the encounter complex formed from the reactants with the same charge sign is highly solvated, small ΔH^\ddagger values indicate that the highly solvated state would require a small amount of energy for the rearrangements of the reactants. Less solvated encounter complexes from the oppositely charged reactants need more energy for the rearrangements as indicated by large ΔH_{et}^\ddagger values.

(6) Further Comments on the Activation Parameters.³⁵ It is

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 (35) It is interesting that the activation parameters, ΔH^\ddagger and ΔS^\ddagger , for the oxidation of the dimeric hydroxo complex (hydroxo ligand is not bridging) [Mo^V₂O₄(OH)(hedta)]²⁻ (H₃hedta = *N*-(2-hydroxyethyl)-ethylenediamine-*N,N',N'*-triacetic acid) with [Ir^{IV}Cl₆]²⁻ and [(en)₂Co^{III}(μ-NH₂,O₂⁻)Co^{III}(en)₂]⁴⁺ lie "perfectly" on the line in Figure 6.^{8c} Of particular interest is that the ΔS_{et}^\ddagger value experimentally observed for the oxidation with the latter oxidant ($Z_R Z_O = -8$) is +40 J K⁻¹ mol⁻¹, which is in accord with the ΔS^\ddagger value ($=\Delta S_{OS}^\ddagger + \Delta S_{et}^\ddagger$) expected for a reaction with $Z_R Z_O = 0$ (ΔS_{OS} may be zero in an ideal case).

noted that large ΔH^\ddagger values are frequently observed for the outer-sphere electron-transfer reactions with highly negative charge products.^{36,27-29} The interpretation of ΔH^\ddagger stated above may be applicable to such reactions. However, it should be mentioned that there are some examples that the reactions between oppositely charged reactants give small ΔH^\ddagger (and negative ΔS^\ddagger) values,³⁶⁻³⁸ none of which have yet been experimentally separated into ΔH_{OS} and ΔH_{et}^\ddagger . Obviously these facts deserve further studies for a general understanding of the factors controlling activation pa-

rameters of the outer-sphere redox reactions.

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Registry No. [V^{IV}O(pmida)(H₂O)], 67904-95-4; Na[V^{IV}O(нта)(H₂O)], 73711-58-7; [(en)₂Co^{III}(μ-NH₂O₂)Co^{III}(en)₂]Cl₄, 79304-91-9; [IrCl₆]²⁻, 16918-91-5.

Supplementary Material Available: Plots of k_{obsd} vs. [V^{IV}O] for the oxidation of [V^{IV}O(нта)(H₂O)]⁻ with [Ir^{IV}Cl₆]²⁻ at $I = 0.1$ M and 25 °C (Figure 2), plots of k_1 vs. [H⁺]⁻¹ for the oxidation of [V^{IV}O(pmida)(H₂O)] with [Ir^{IV}Cl₆]²⁻ at $I = 0.1$ M (Figure 3), and plots of (a) k_{obsd} vs. [V^{IV}O] and (b) k_{obsd}^{-1} vs. [V^{IV}O]⁻¹ for the oxidation of [V^{IV}O(нта)(H₂O)]⁻ with [(en)₂Co^{III}(μ-NH₂O₂)Co^{III}(en)₂]⁴⁺ at $I = 0.1$ M and 25 °C (Figure 4) (3 pages). Ordering information is given on any current masthead page.

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Kinetics of the Oxidation of an Ethylenediaminetetraacetate Complex of the Oxovanadium(IV) Ion with Hexachloroiridate(IV) in Aqueous Solution

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Na[V^{IV}O(edtaH)] (H₄edta = ethylenediaminetetraacetic acid) has been prepared and the acid-dissociation constant of the free carboxylate arm determined: $pK_a = 3.22$ (25 °C; $I = 1.0$ M (NaClO₄); 1 M = 1 mol dm⁻³). Kinetic studies of the outer-sphere oxidation of the new complex with [Ir^{IV}Cl₆]²⁻ to the *cis*-dioxovanadium(V)-EDTA complex have shown the presence of a steady-state intermediate, a "monooxovanadium(V)-EDTA complex", which is converted into the dioxo complex accompanied by the dissociation of one of the coordinated carboxylate arms. Second-order rate constants of the electron-transfer process to give the intermediate are 3.3×10^2 and 6.5×10^2 M⁻¹ s⁻¹ for the protonated and the deprotonated EDTA complexes, respectively, at 25 °C and $I = 1.0$ M (NaClO₄). These values are smaller by less than 1 order of magnitude than those for the one-step oxidation of *cis*-aquaquo(quadridentate)vanadium(IV) ions with [Ir^{IV}Cl₆]²⁻.

Metal ions of quadrivalent or higher oxidation state usually exist as "oxo-metal" ions in aqueous media, the number of coordinated oxo ions increasing with the increase in oxidation number.^{1,2} Thus the redox reactions involving oxo-metal ions are accompanied by simultaneous change in the number of coordinated oxide ions. We have reported the kinetics of outer-sphere oxidation of *cis*-aquaquo(quadridentate)vanadium(IV) ions, where the quadridentate ligands are [(2-pyridylmethyl)imino]diacetate(2-) (pmida) and nitrilotriacetate(3-) (nta) ions.³ The products are *cis*-dioxovanadium(V) complexes with the same amino carboxylate ligand. The aqua ligand of the vanadium(IV) complexes must be converted into an oxo ligand in the vanadium(V) complexes simply by the loss of two protons coupled with the oxidation of the metal center. The oxidation reaction proceeds in one step in accordance with the fact that the proton loss is generally rapid.

The structure of the vanadium(IV) ethylenediaminetetraacetate (edta) complex is expected to be as shown in Figure 1a,⁴ while that of the vanadium(V)-EDTA⁵ complex was determined by the

X-ray crystallography as shown in Figure 1b.⁶ It is interesting to find how the oxidation occurs whenever the formation of a new oxo ligand requires dissociation of a coordinated ligand. This paper deals with the oxidation of the oxovanadium(IV)-EDTA⁵ complex with [Ir^{IV}Cl₆]²⁻.

Experimental Section

Materials. (1) Sodium [*N*-(Carboxymethyl)ethylenediamine-*N,N'*-*N''*-triacetato]oxovanadate(IV) Tetrahydrate, Na[V^{IV}O(edtaH)]·4H₂O. [V^{IV}O(acac)₂] (acac = acetyl acetonate ion) (4.0 g, 15 mmol)⁷ and NaClO₄ (1.84 g, 15 mmol) in 500 cm³ of 0.05 M HClO₄ (1 M = 1 mol dm⁻³) were kept at 40-50 °C for 20 min and treated with H₄edta (4.4 g, 15 mmol) and slowly with ca. 50 cm³ of 0.5 M NaHCO₃. The solution was filtered, the pH adjusted to 2-3 with a small amount of perchloric acid solution, and the solution evaporated in a rotary evaporator at 40 °C to reduce the volume to 35 cm³. An ethanol solution (60 cm³) of 4.5 mmol of NaClO₄ was added to the solution, and the pale blue precipitate was filtered off, washed with ethanol until the washings became colorless, and dried in vacuo (yield 5.5 g).

Ethanol (ca. 12 cm³) was added dropwise to the solution of the crude salt in ca. 45 cm³ of 0.01 M HClO₄ at 70-80 °C. The solution was kept in a refrigerator overnight. Pale blue needles were filtered off, washed with ethanol, and dried in vacuo; yield 2.8 g (41% based on [V^{IV}O(acac)₂]). Anal. Calcd for C₁₀H₂₁N₂O₁₃NaV: C, 26.62; H, 4.69; N, 6.21. Found: C, 26.49; H, 4.63; N, 6.27.

(2) **Other Compounds.** Sodium *cis*-dioxo(ethylenediaminetetraacetato)vanadium(V) hexahydrate, Na₃[V^V(O)₂(edta)]·6H₂O, was prepared by the method of Amos and Sawyer.⁸ Sodium hexachloro-

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 (5) EDTA represents variously protonated forms of the ethylenediaminetetraacetate ion. The vanadium(IV) and vanadium(V) complexes of EDTA have one and two free carboxylate arms, respectively. They can exist in aqueous solution as a mixture of species with protonated and deprotonated free arms. We use the expressions "monooxovanadium(IV)-EDTA" and "dioxovanadium(V)-EDTA" to represent both of the deprotonated and the protonated forms.

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