Inorg. Chem. **1986**, *25*, 3745–3749 **3745**

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Kinetics of Ligand Substitution and Oxidation Reactions of the [((Phosphonomethyl)imino)diacetato]aquaoxovanadium(IV) Ion: Role of the Hydrogen Bond between the Coordinated Water and the Phosphonate Arm

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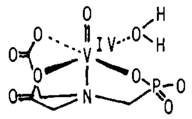
Received April 9, 1986

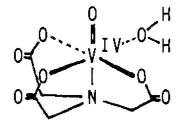
A new complex of *cis*-aquaoxovanadium(IV) with quadridentate ((phosphonomethyl)imino)diacetate (pida^{4-}), Na$_2$[V^{IV}O(pida)(H$_2$O)]·3.5H$_2$O (**1**), undergoes protonation at the phosphonate oxygen with pK_{a1} = 3.8 and deprotonation from the coordinated water with pK_{a2} = 8.4 at 25 °C and I = 1.0 M (NaClO$_4$) (1 M = 1 mol dm^{-3}). The larger pK_{a2} than those of the other aquaoxovanadium(IV) complexes (pK_a = 6.4–6.9) [V^{IV}O(nta)(H$_2$O)]$^-$ (nta^{3-} = nitrilotriacetate(3−)) (**2**) and [V^{IV}O(pmida)(H$_2$O)] (pmida^{2-} = ((2-pyridylmethyl)imino)diacetate(2−)) (**3**) suggests hydrogen bonding between the aqua ligand and the adjacent phosphonate oxygen. Second-order rate constants for the anation of NCS$^-$ and N$_3^-$ (4 × 10^{-3} and 5.6 × 10^{-2} M^{-1} s^{-1}, respectively, at I = 1.0 M (NaClO$_4$)) to **1** at 25 °C are more than 1 order of magnitude smaller than those of the corresponding reactions of **2** and **3**, ΔH^* being larger and ΔS^* more positive. The outer-sphere oxidation of **1** with [Ir^{IV}Cl$_6$]$^{2-}$ gives a second-order rate constant, 1.13 × 10^4 M^{-1} s^{-1} (pH 5.7, I = 0.1 M (NaClO$_4$), 25 °C), that falls between the corresponding values for **2** and **3** (ca. 10^3 M^{-1} s^{-1}) and their conjugate bases, *cis*-hydroxooxovanadium(IV) derivatives (ca. 10^6 M^{-1} s^{-1}). All these characteristic kinetic parameters can be accounted for by the existence of the hydrogen bond.

Introduction

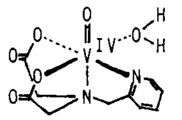
The following oxovanadium(IV) complexes are discussed in this paper:[2]



[VO(pida)(H$_2$O)]$^{2-}$
(1)



[VO(nta)(H$_2$O)]$^-$
(2)



[VO(pmida)(H$_2$O)]
(3)

Regioselectivity on ligand substitution reactions for the aqua ligand of *cis*-aquaoxovanadium(IV) complexes was demonstrated with complexes **2** and **3**, containing the quadridentate ligands nta^{3-} and pmida^{2-}, which block the apical site of oxovanadium(IV).[3-6] Direct basal substitution gives second-order rate constants of the order of 10^{-1} M^{-1} s^{-1} at 25 °C.[3]

Outer-sphere oxidation of **2** and **3** to give *cis*-dioxovanadium(V) complexes was inversely dependent on [H$^+$] of the solution.[7] Kinetic analysis of the observed second-order rate constant indicated that the oxidation rate is much larger for the conjugate base complexes (ca. 10^6 M^{-1} s^{-1}), *cis*-hydroxooxovanadium(IV), than their parent complexes (ca. 10^3 M^{-1} s^{-1}).[7] The difference in the contribution of "nonadiabaticity" to the electron-transfer process was reckoned to be responsible for the different oxidation rate.[7]

We have prepared a new *cis*-aquaoxovanadium(IV) complex, **1**, with pida^{4-} as a quadridentate ligand. This complex gave pK_a values of 3.8 and 8.4 at I = 1.0 M (NaClO$_4$) and 25 °C, corresponding to the deprotonation of coordinated phosphonate and water, respectively. The latter is significantly greater than the pK_a values of 6.4 and 6.9 of the pmida and nta complexes, respectively, reflecting the hydrogen bridge formation between the phosphonate and the water ligand. Kinetic studies of the substitution and redox reactions were carried out with reference to the effect of such mutual ligand interaction.

Experimental Section

Materials. (1) Sodium *cis*-Oxo[((phosphonomethyl)imino)diacetato]aquavanadium(IV)–3.5-Water, Na$_2$[VO(pida)(H$_2$O)]·3.5H$_2$O. [VO(acac)]$_2$[8] (2.65 g, 0.01 mol) and H$_4$pida[9] (2.27 g, 0.01 mol) were stirred in 50 cm^3 of water until a clear solution was obtained. The solution was made pH 4 with aqueous NaHCO$_3$ solution, evaporated to 10 cm^3, and made pH 5 with aqueous NaHCO$_3$ solution. Ethanol was added until the solution became turbid, which was made clear by dripping water. The solution was mixed with 15 cm^3 of methanol and kept in a refrigerator. The yield of sky blue needles was 3 g.

The complex was purified by treating with the cation-exchange column of Dowex 1-X8 resin in Cl$^-$ form. The complex anion was loaded on the column by passing 10^{-3} M solution at pH 3.5–4.0 (adjusted with HCl), eluted with 0.5 M NaCl (pH 3.5–4.0), and obtained as sodium salt by evaporating the eluate. The solid was recrystallized once from water. Anal. Calcd for C$_5$H$_{15}$NO$_{12.5}$PNa$_2$V: C, 14.40; H, 3.62; N, 3.36. Found: C, 14.32; H, 3.76; N, 3.12. The KBr pellet of the crystals shows the characteristic V=O stretching IR band at 958 cm^{-1}.

(2) Other Materials. The pmida complex, [VO(pmida)(H$_2$O)]·2H$_2$O, was prepared as stated previously[3] and recrystallized twice from water. Sodium thiocyanate (special grade reagent) was recrystallized from water. The concentration of an aqueous solution of NaNCS was determined by the Volhard method. Special grade reagents of sodium azide, sodium perchlorate, and lithium perchlorate were used as received. The purity of commercial sodium hexachloroiridate(IV) hexahydrate was checked by the intensity of its absorption peak at 488 nm (ϵ = 4075 M^{-1} cm^{-1})[10] in water.

Kinetic Runs. All the kinetic runs were carried out by the stopped-flow method. The reaction of the pida complex with NCS$^-$ or N$_3^-$ was studied under pseudo-first-order conditions with NCS$^-$ or N$_3^-$ in at least 20-fold excess to the vanadium complex by monitoring the change in absorbance at 310 nm. The oxidation of the pida complex with [IrCl$_6$]$^{2-}$ was studied under pseudo-first-order conditions with the pida complex in at least 40-fold excess to the oxidant. The decrease of the absorbance at 488 nm was followed. The pseudo-first-order rate constants (k_{obsd}) were obtained from the first-order plots of the absorbance change, which were linear for at least 5 half-lives. The pH of the reactant solutions were carefully adjusted with HClO$_4$ and NaOH solutions. The pH at the end of the reactions was recorded as reaction pH, which was not significantly changed from the initially adjusted pH. Buffer was not used unless otherwise stated (a part of the redox kinetics).

Measurements. Electronic absorption spectra were recorded on a Hitachi 323 spectrophotometer. Infrared absorption spectra were measured by a JASCO IRA-1 diffraction grating infrared spectrophotometer. Kinetic measurements were carried out by the use of a Union-Giken

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(2) Abbreviations used in this paper: pida^{4-} = ((phosphonomethyl)imino)diacetate(4−), nta^{3-} = nitrilotriacetate(3−), pmida^{2-} = ((2-pyridylmethyl)imino)diacetate(2−), acac$^-$ = acetylacetonate, 1 M = 1 mol dm^{-3}.

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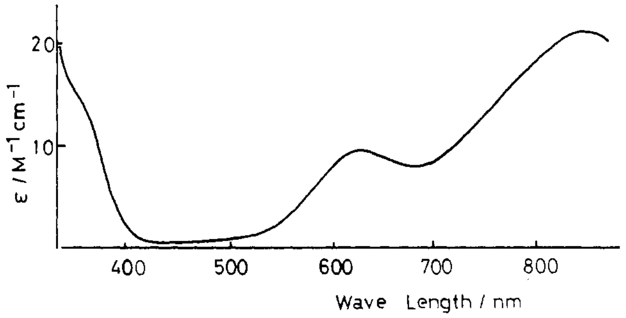


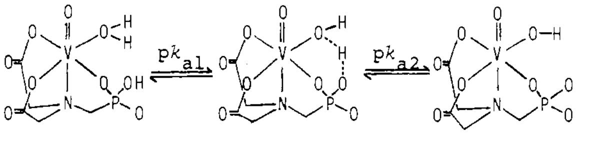
Figure 1. Absorption spectrum of $[VO(pida)(H_2O)]^{2-}$ in aqueous solution at pH 6.1.

RA-401 stopped-flow spectrophotometer. The pHs of the solutions were measured and acid dissociation constants were determined by the pH titration with a Metrohm Herisau E300B pH meter.

Results

Properties of the pida Complex of Oxovanadium(IV). (1) Structure. The structure given in the Introduction is the most reasonable among possible geometrical isomers for the following reasons. All the oxovanadium(IV) complexes of amino polycarboxylates whose structures were determined by the X-ray diffraction method have a nitrogen atom of the ligand at the site trans to the oxo ligand.[11] The phosphonate arm should be cis to the water ligand to form hydrogen bond (vide infra).

(2) pK_a Values. An aqueous solution of 0.017 M $Na_2[VO(pida)(H_2O)]$ shows the pH ca. 5 at I = 1.0 M ($NaClO_4$) and 25 °C. The solution was titrated with 0.10 M $HClO_4$ and 0.094 M NaOH solutions under nitrogen atmosphere. Two inflections were observed in the pH range $1.5 < pH < 11$ to give $pK_{a1} = 3.8 \pm 0.1$ and $pK_{a2} = 8.4 \pm 0.1$ (I = 1.0 M, 25 °C). These values should correspond to the protonation equilibria



$[VO(pidaH)(H_2O)]^-$ $[VO(pida)(H_2O)]^{2-}$ $[VO(pida)(OH)]^{3-}$

The protonation constants at the phosphonate group of the free $pida^{4-}$ ligand are known to be 2.00 and 5.57 at I = 0.1 M (KCl) and 20 °C.[12] Since the pK_a values of carboxylate or phosphonate groups become smaller by 2–3 pK_a units on coordination to a metal ion,[13] $pK_{a1} = 3.8$ can be reasonably assigned to the protonation at the phosphonate arm of **1**. The value $pK_{a2} = 8.4$ should then be assigned unequivocally to the deprotonation of the coordinated water molecule in **1**.

The pK_{a2} value of **1** is significantly larger than those for **2** and **3** (6.9 and 6.4, respectively, at I = 1.0 M ($NaClO_4$)).[7] Hydrogen bonding between aqua ligand and the adjacent phosphonate arm of the pida ligand should be responsible for the difference. Such hydrogen bonding is unlikely for the pmida and nta ligands.

The pK_{a2} values of **1** decrease linearly with an increase in square root of ionic strength, reflecting the electrostatic effect on deprotonation.

(3) Electronic Absorption Spectra. The spectrum of **1** in the region 340–1000 nm depends significantly on pH of the solution ($0 < pH < 11$), but the main peak at around 800 nm remains throughout the region. The spectrum is constant at pH 1.8–2.4 with a peak at 833 nm (ϵ = 18.5 M^{-1} cm^{-1}), and at pH 4.8–7.3 with peaks at 852 nm (20.0) and 629 nm (9). These spectra should correspond to $[VO(pidaH)(H_2O)]^-$ and $[VO(pida)(H_2O)]^{2-}$ (Figure 1), respectively. Outside and between these pH ranges, the spectrum changes with pH. The spectrum of $[VO(pida)(OH)]^{3-}$ was not observed since the spectrum changed rapidly with time at pH > 8, probably owing to air oxidation of the complex.

Table I. Dependence of the First-Order Rate Constant (k_{obsd}) on pH for the Reaction of the pida Complex[a] of *cis*-Aquaoxovanadium(IV) (0.002 M) with NaNCS (0.24 M) at I = 1.0 M ($NaClO_4$) and at 25 °C

pH	k_{obsd}/s^{-1}	pH	k_{obsd}/s^{-1}	pH	k_{obsd}/s^{-1}
0.8	4.74	3.1	0.33	5.5	0.04
1.1	2.13	3.4	0.23	5.7	0.03
1.3	1.30	3.7	0.18	5.9	0.03
1.6	0.93	4.0	0.12	6.1	0.03
1.9	0.64	4.6	0.07	6.4	0.03
2.5	0.46	4.9	0.05	7.6	0.03
2.8	0.38	5.2	0.04		

[a] $pida^{4-}$ = ((phosphonomethyl)imino)diacetate(4−).

Table II. Rate Constants for the Anation (k_1) and the Aquation (k_{-1}) Reactions of $[VO(pida)(H_2O)]^-$ with NCS^- and N_3^- in Aqueous Solution at I = 1.0 M ($NaClO_4$)[a]

X^-	temp/°C	$k_1/M^{-1}\ s^{-1}$	k_{-1}/s^{-1}
NCS^{-}[b]	25.0	0.0043 ± 0.0042	0.028 ± 0.001
	35.0	0.038 ± 0.006	0.074 ± 0.002
	40.0	0.110 ± 0.002	0.104 ± 0.002
	45.0	0.20 ± 0.02	0.183 ± 0.003
N_3^{-}[c]	25.0	0.056 ± 0.007	0.084 ± 0.002
	35.0	0.210 ± 0.007	0.202 ± 0.002
	45.0	0.60 ± 0.04	0.460 ± 0.012

[a] $pida^{4-}$ = ((phosphonomethyl)imino)diacetate(4−). [b] pH 5.7. [c] pH 7.4.

Kinetics of the Ligand Substitution. (1) Preliminary Studies. On mixing of an aqueous solution of **1** (8.8 × 10^{-3} M) with the same volume of an aqueous solution containing either NaNCS or NaN_3 (0.9 M), the absorbance increased in the region <350 nm without appreciable change in the region >400 nm. The change was significantly smaller than those of similar mixtures containing **2** or **3** under similar conditions. The change at <350 nm for **1** should be due to the substitution of NCS^- or N_3^- for the coordinated water. The extent of anation, however, is significantly smaller than that of **2** or **3** (Table V).

(2) Ligand Substitution Reaction with NCS^-. a. pH Dependence. The pH dependence of the rate was studied at constant reagent concentrations ([**1**] = 2.0 × 10^{-3} M; [NaNCS] = 0.24 M; I = 1.0 M ($NaClO_4$)) at 25 °C. The first-order rate constant (k_{obsd}) decreased with an increase in pH in the region 0.8–5.5 and is constant at $5.6 < pH < 7.6$ (Table I). The constant value is considered to represent the reaction of $[VO(pida)(H_2O)]^{2-}$. The protonated form, $[VO(pidaH)(H_2O)]^-$, seems to react more rapidly.

b. [NCS^-] Dependence. This was studied at pH 5.7 ± 0.2 and 25–45 °C. At each temperature a plot of k_{obsd} vs. [NCS^-] gave a straight line with distinct intercept (Figure 2).[14] The results were interpreted by the following equilibrium similar to those of **2** and **3**:[7]

$$[VO(pida)(H_2O)]^{2-} + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [VO(pida)(NCS)]^{3-} + H_2O \quad (1)$$

k_{obsd} should be expressed as eq 2 in the presence of a large excess of NCS^-. The k_1 and k_{-1} values are summarized in Table II.

$$k_{obsd} = k_1[NCS^-] + k_{-1} \quad (2)$$

c. Ionic Strength Dependence of k_1 and k_{-1}. The k_1 and k_{-1} values were obtained at different ionic strengths at 35 °C. The k_1 value increased with an increase in I, while k_{-1} decreased (Figure 3). These results were interpreted in terms of a simple salt effect at least in a qualitative sense. The k_1 path should involve

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(11) See discussions in: Sasaki, Y.; Kanesato, M.; Okazaki, K.; Nagasawa, A.; Saito, K. *Inorg. Chem.* **1985**, *24*, 772–775.

(12) Schwarzenbach, G.; Ackermann, H.; Ruckstuhl, P. *Helv. Chim. Acta* **1949**, *32*, 1175–1186.

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(14) Supplementary material.

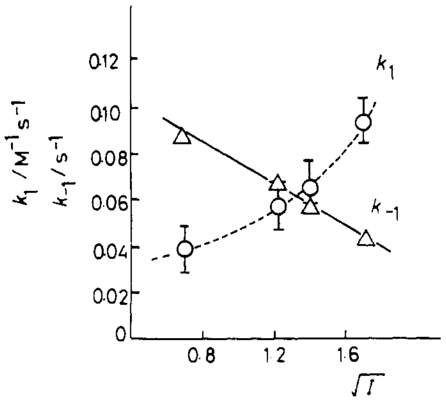

Figure 3. Dependence of k_1 and k_{-1} on ionic strength of the solution for the reaction of $[VO(pida)(H_2O)]^{2-}$ with NCS^- at 35 °C and at pH 5.7–5.8 (ionic strength adjusted with $NaClO_4$).

initial encounter complex formation between **1** and NCS^- and the ligand substitution within the encounter complex. The formation constant of the encounter complex between two negatively charged reactants should increase with an increase in ionic strength. The k_{-1} path involves a charge separation process. The highly charged species $[VO(pida)(NCS)]^{3-}$ can be more stabilized at higher ionic strength.

d. Effect of D_2O. A large effect was observed for both k_1 and k_{-1} processes. The k_1 value in 50% D_2O was (6.2 ± 0.1) × 10^{-2} M^{-1} s^{-1} at 40 °C and I = 1.0 M ($NaClO_4$), which is compared to k_1 = (1.10 ± 0.02) × 10^{-1} M^{-1} s^{-1} in water (100% H_2O). The k_{-1} value (0.145 ± 0.002 s^{-1}) in 50% D_2O is, on the contrary, larger than the value in water (0.104 ± 0.002 s^{-1}). Both forward- and backward-reaction rate constants for the corresponding reaction of **3** did not show a significant difference in 50% D_2O and in ordinary water. The results clearly indicate that the circumstance of the coordinated water of **1** is different from that of **3**, supporting the existence of the hydrogen bond in **1**.

(3) Ligand Substitution Reaction with N_3^-. The first-order rate constant, k_{obsd}, was practically constant in the pH range 6.0–7.8 under the conditions [**1**] = 2.0 × 10^{-3} M, [NaN_3] = 0.20 M, I = 1.0 M ($NaClO_4$), and 25 °C. Further measurements were carried out at pH 7.4 to avoid any possible influence of the protonation of N_3^- (pK_a = ca. 5).[15] The observed k_1 and k_{-1} values for reaction 3 are summarized in Table II.

$$[VO(pida)(H_2O)]^{2-} + N_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [VO(pida)(N_3)]^{3-} + H_2O \quad (3)$$

Kinetics of Oxidation with $[IrCl_6]^{2-}$. (1) Stoichiometry of the Reaction. The stoichiometry was determined at I = 0.1 M ($NaClO_4$), pH 4.39 (0.01 M acetate buffer), and 25 °C. A solution of **1** ((0.977–2.42) × 10^{-4} M) was mixed with an equal amount of (1.63–4.02) × 10^{-4} M $[IrCl_6]^{2-}$ solution. The characteristic strong band at 488 nm of $[IrCl_6]^{2-}$[10] decreased instantaneously. The consumed $[IrCl_6]^{2-}$ was estimated from the extent of the decrease. Three determinations in the above reagent concentration ranges clearly indicated the 1:1 stoichiometry.

$$[VO(pida)(H_2O)]^{2-} + [IrCl_6]^{2-} \xrightarrow{k_2} [VO_2(pida)]^{3-} + [IrCl_6]^{3-} + 2H^+ \quad (4)$$

(2) Kinetic Studies. a. pH Dependence. The pH dependence was studied at constant reagent concentrations ([**1**] = 9.4 × 10^{-3} M; [$IrCl_6^{2-}$] = 1.99 × 10^{-4} M; I = 0.1 M ($NaClO_4$)) at 25 °C in the pH range 4.5–7.0. The first-order rate constant (k_{obsd}) increased with an increase in pH (Table III). The change in k_{obsd} is very small in the pH range 5.5–5.8, where the hydrogen-bonded species $[VO(pida)(H_2O)]^{2-}$ is the major component in solution.

b. Kinetics at pH <5. This was studied in order to estimate the oxidation rate of $[VO(pidaH)(H_2O)]^-$, in which the hydrogen bond is absent. Since k_{obsd} depends strongly on pH, acetate buffer (0.01 M) was used to avoid any influence of pH change during the reaction. k_{obsd} depended linearly on the vanadium complex concentration in the range (0.75–2.40) × 10^{-3} M at [$IrCl_6^{2-}$] = (3.87–5.63) × 10^{-5} M at 25 °C and I = 0.1 M ($NaClO_4$). Second-order rate constants obtained from the linear relationship are approximately 6.1, 7.8, 8.3, and 9.3 M^{-1} s^{-1} at pH 3.8, 4.2, 4.4, and 4.7, respectively. From these values and pK_{a1} = 3.8, the second-order rate constants for the oxidation of $[VO(pidaH)(H_2O)]^-$ and $[VO(pida)(H_2O)]^{2-}$ were estimated to be (7 ± 6) × 10^2 and (1.04 ± 0.03) × 10^4 M^{-1} s^{-1}, respectively, under the assumption that the contribution of $[VO(pida)(OH)]^{3-}$ is negligible in the pH range.

Table III. Dependence of the First-Order Rate Constant (k_{obsd}) on pH for the Oxidation of the pida Complex[a] of *cis*-Aquaoxovanadium(IV) (0.0094 M) with $[IrCl_6]^{2-}$ (1.99 × 10^{-4} M) at I = 0.1 M ($NaClO_4$) and 25 °C

pH	4.5	5.2	5.5	5.8	6.0	6.5	7.0
k_{obsd}/s^{-1} [b]	70.6	84.9	86.6	87.7	94.5	98.0	107.9

[a] $pida^{4-}$ = ((phosphonomethyl)imino)diacetate(4–). [b] Each value is an average of at least three kinetic runs.

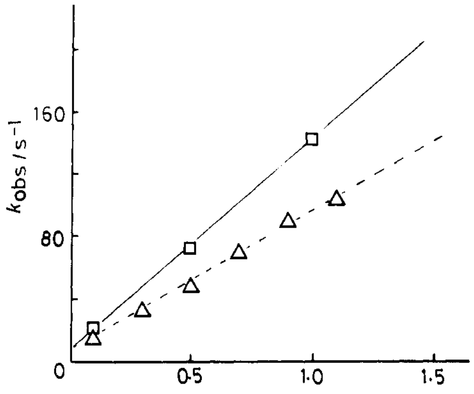

Figure 5. Dependence of k_{obsd} on ionic strength adjusted with $NaClO_4$ (—) or $LiClO_4$ (---) for the oxidation of $[VO(pida)(H_2O)]^{2-}$ (2.00 × 10^{-3} M) with $[IrCl_6]^{2-}$ (2.75 × 10^{-5} M) at pH 5.7 ± 0.2 at 25 °C.

c. Kinetic Studies at pH 5.7. Detailed kinetic parameters of the hydrogen-bonded species, $[VO(pida)(H_2O)]^{2-}$, were obtained at pH 5.7; the contribution of $[VO(pidaH)(H_2O)]^-$ is negligible (vide supra). If the hydroxo species $[VO(pida)(OH)]^{3-}$ reacted with $[IrCl_6]^{2-}$ at a similar rate as $[VO(pmida)(OH)]^-$ (2.9 × 10^6 M^{-1} s^{-1} at I = 0.1 M and 25 °C) and $[VO(nta)(OH)]^{2-}$ (1.4 × 10^6 M^{-1} s^{-1})[7] did, its contribution should be negligible at pH 5.7 (judged from the pK_{a2} value).

Under the reagent concentrations [V^{IV}] = (1–3) × 10^{-3} M and [Ir^{IV}] = 2.75 × 10^{-5} M, a k_{obsd} vs. [V^{IV}] plot gave excellent straight lines virtually without intercept (Figure 4).[14] Thus, rate law 5 holds. The k_2 values at I = 0.1 M ($NaClO_4$) are (1.13 ± 0.02) × 10^4, (1.79 ± 0.04) × 10^4, and (2.65 ± 0.05) × 10^4 at 25.0, 35.0, and 47.5 °C, respectively.

$$-d[Ir^{IV}]/dt = k_{obsd}[Ir^{IV}] = k_2[Ir^{IV}][V^{IV}] \quad (5)$$

Figure 5 shows that k_{obsd} at [V^{IV}] = 2.00 × 10^{-3} M, [Ir^{IV}] = 2.75 × 10^{-5} M, and 25 °C increases with an increase in ionic strength and is larger in $NaClO_4$ than in $LiClO_4$ media. The ionic strength dependence may be explained primarily by a salt effect for the reactions between negatively charged reactants. The influence of the cationic species is consistent with those observed for other reactions between negatively charged reactants including $[Fe(CN)_6]^{3-}$ vs. $[Fe(CN)_6]^{4-}$[16] and photoexcited $[Mo_6Cl_{14}]^{2-}$ vs. $[IrCl_6]^{2-}$.[17] The smaller cation Na^+ (Stokes radius 1.80 Å)

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Table IV. Summary of the Kinetic Data for the Ligand Substitution Reactions of *cis*-Aquaoxovanadium(IV) Complexes in Aqueous Solution[a]

		anation			aquation				
ligand	complex[b]	k_1/M^{-1} s^{-1} (25 °C)	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	k_{-1}/s^{-1} (25 °C)	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$K = k_1/k_{-1}$, M^{-1} (25 °C)	ref
NCS^-	$[VO(pida)(H_2O)]^{2-}$	0.004	123 ± 3	+128 ± 5	0.028	66 ± 1	−54 ± 22	0.14	*c*
NCS^-	$[VO(nta)(H_2O)]^-$	0.62	41 ± 1	−122 ± 3	0.170	69 ± 8	−25 ± 28	3.65	6
NCS^-	$[VO(pmida)(H_2O)]$	0.26	49 ± 1	−90 ± 3	0.061	61 ± 3	−61 ± 10	4.26	4
N_3^-	$[VO(pida)(H_2O)]^{2-}$	0.056	88 ± 11	+31 ± 37	0.084	62 ± 3	−53 ± 8	0.67	*c*
N_3^-	$[VO(nta)(H_2O)]^-$	4.10	54 ± 1	−52 ± 2	0.480	53 ± 3	−75 ± 8	8.50	6
N_3^-	$[VO(pmida)(H_2O)]$	3.70	47 ± 6	−75 ± 20	0.130	64 ± 1	−47 ± 42	28.5	4

[a] I = 1.0 M ($NaClO_4$). [b] $pida^{4-}$ = ((phosphonomethyl)imino)diacetate(4−), nta^{3-} = nitrilotriacetate(3−), $pmida^{2-}$ = ((2-pyridylmethyl)imino)diacetate(2−). [c] This work.

Table V. Kinetic Parameters of the Oxidation of Oxovanadium(IV) Complexes with Hexachloroiridate(IV) in Aqueous Solution at I = 0.1 M ($NaClO_4$)

complex[a]	k_2/M^{-1} s^{-1} (25 °C)	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	ref
$[VO(pidaH)(H_2O)]^-$	ca. 7 × 10^2			this work
$[VO(nta)(H_2O)]^-$	1.4 × 10^2	46 ± 8	−46 ± 17	7
$[VO(pmida)(H_2O)]$	9.1 × 10^2	52 ± 8	−8 ± 38	7
$[VO(pida)(H_2O)]^{2-}$	1.1 × 10^4	29 ± 3	−65 ± 11	this work
$[VO(nta)(OH)]^{2-}$	1.4 × 10^6	37 ± 3	−2 ± 8	7
$[VO(pmida)(OH)]^-$	2.9 × 10^6	42 ± 1	+21 ± 2	7

[a] $pida^{4-}$ = ((phosphonomethyl)imino)diacetate(4−), nta^{3-} = nitrilotriacetate(3−), $pmida^{2-}$ = ((2-pyridylmethyl)imino)diacetate(2−).

mediates more effectively the approach of negative ions than the larger cation Li^+ (2.40 Å).

The effect of D_2O was studied under the conditions $[V^{IV}]$ = (1–3) × 10^{-3} M, $[Ir^{IV}]$ = 3.75 × 10^{-5} M, I = 0.1 M ($NaClO_4$), and pH 5.7 and at 25 °C. The second-order rate constant in 99% D_2O was (6.9 ± 0.2) × 10^3 M^{-1} s^{-1}, which is 1.6 times smaller than the value in H_2O.[18]

Discussion

Characteristics of the Substitution Reactions. The present results are compared with the corresponding data for **2** and **3** in Table IV. It is clear that the kinetic parameters for the anation reactions of **1** are remarkably different from those of **2** and **3**. The k_1 value is almost 2 orders of magnitude smaller, $\Delta H^{\ddagger}$ is significantly larger, and $\Delta S^{\ddagger}$ is positive in contrast to the negative $\Delta S^{\ddagger}$ values for **2** and **3**. On the contrary, the parameters for the aquation reactions are similar to one another among all the three complexes.

The "hydrogen bond" should be responsible for the notably different kinetic parameters for the anation reaction of **1**. The V–O(aqua) bond in **1** should be stronger than those of other two complexes. The formation constant of precursor encounter complex, reflected in the ionic strength dependence (Figure 3), cannot be so different among them as the k_1 values.[19] Similar parameters for the aquation reactions among the three complexes suggest that the pida complex exhibits no exceptional ligand substitution properties unless the hydrogen bond is formed.

Mechanism of the Substitution Reactions. The associative interchange mechanism (I_a) has been suggested for the anation reactions of **2** and **3** on the basis of ligand discrimination (difference in k_1 for NCS^- and N_3^- anation) and negative activation entropies.[4,6] The aquation process is also reckoned to be associative from the rule of microscopic reversibility. Similar kinetic parameters for the aquation of the pida complex to those of the pmida and nta complexes seems to indicate that the mechanism of the substitution reactions of pida complex is also associative. The difference in k_1 values of NCS^- and N_3^- substitution also points to the associative mechanism for **1**. Activation parameters for the anation reactions of **1**, which seemingly indicate a dissociative mechanism, would be explained in terms of an associative mechanism by taking the hydrogen bonding into consideration.

The k_1 of **1** is smaller in D_2O. This fact indicates that the break of the hydrogen bond prior to ligand substitution controls the overall rate constant k_1, since ^2H is expected to form a stronger hydrogen bond than ^1H. If the bond break of V–O(aqua) were rate-determining, the k_1 in D_2O should be larger than that in H_2O, since the V–O bond is weaker for less basic D_2O. The observed activation parameters of k_1 must be the sum of those of the hydrogen bond break and the following ligand substitution. Break of the hydrogen bond would contribute positively to $\Delta S^{\ddagger}$. Such a stepwise consideration can explain at least qualitatively the trend of activation parameters. An actual reaction process would occur presumably in a concerted way with simultaneous hydrogen bond break and ligand substitution.[20]

We conclude that the reactions of the pida complex proceed essentially through an associative mechanism.

Characteristics of the Redox Reaction. The second-order rate constant, k_2, of the pida complex (Table V) is much larger than those of ligand substitution to indicate an outer-sphere mechanism. The k_2 for the protonated form $[VO(pidaH)(H_2O)]^{2-}$ is of similar magnitude to those of other *cis*-aquaoxovanadium(IV) complexes. The k_2 value for the hydrogen-bonded species, $[VO(pida)(H_2O)]^{2-}$, falls between those of *cis*-aquaoxo complexes without a hydrogen bond (10^2–10^3 M^{-1} s^{-1}) and those of *cis*-hydroxooxo complexes containing nta and pmida (10^6 M^{-1} s^{-1}). Such a difference can be understood since the hydrogen-bonded aqua ligand in $[VO(pida)(H_2O)]^{2-}$ has an intermediate character between aqua and hydroxo ligands.

We pointed out that $\Delta H^{\ddagger}$ of the outer-sphere oxidation reactions of the nta and pmida complexes correlate linearly with the charge product of the redox couple regardless of the unidentate ligand (water or hydroxo) and that $\Delta S^{\ddagger}$ for the reactions of the *cis*-hydroxooxo complexes also linearly correlate with the charge

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(18) The corresponding rate constant for the oxidation of **3** at pH 3.5 was (1.85 ± 0.03) × 10^4 M^{-1} s^{-1} (25 °C) in 99% D_2O, which should be compared with the value (4.00 ± 0.03) × 10^4 M^{-1} s^{-1} in H_2O. At pH 3.5 contribution of $[VO(pmida)(H_2O)]$ and $[VO(pmida)(OH)]^-$ to the observed second-order rate constant would be comparable. It is thus not clear whether either or both of the two species of pmida complex show a D_2O effect.

(19) Estimated precursor formation constants based on the Fuoss equation (Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059–5061) with the common closest distance 4.5 Å are 0.07, 0.12, and 0.30 M^{-1} for **1**, **2**, and **3**, respectively.

(20) The contribution of the encounter complex formation to $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ would be different among the three oxovanadium(IV) complexes. The temperature dependence of K_{OS} would be small, however, and $\Delta H^{\ddagger}$ should be virtually unaffected by K_{OS}. The K_{OS} value should be smaller for **1**, which has a higher negative charge than **2** and **3**. The effect to $\Delta S^{\ddagger}$ should be small and would cause small shift of $\Delta S^{\ddagger}$ to the negative direction for **1** as compared with the cases of **2** and **3**. Therefore, the encounter complex formation can not be responsible for the observed anomaly of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the anation reactions of **1**.

product (the $\Delta S^{\ddagger}$ values for the reactions of the aqua–oxo complexes are considerably more negative than those for the corresponding hydroxo–oxo complexes).[7] The present $\Delta H^{\ddagger}$ value also falls on the linear plot. The present $\Delta S^{\ddagger}$ value is clearly more negative than those for the *cis*-hydroxooxo complexes and closer to the values for the *cis*-aquaoxo complexes (the difference in charges of the complexes has been taken into account).

The effect of D_2O may be explained at least qualitatively in terms of the weaker V–O(aqua) bond in D_2O. Table V clearly indicates that the oxidation rate decreases with a decrease in the strength of V–O(aqua) bond.

Concluding Remarks. The existence of the hydrogen bond between the coordinated water and the adjacent phosphonate arm in $[VO(pida)(H_2O)]^{2-}$ has been predicted by the pK_{a2} value. Ligand substitution and outer-sphere oxidation reactions show characteristic features that are reasonably understood by the existence of hydrogen bonding. This work stresses the importance of mutual ligand interaction on the reactivity of metal complexes.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 58430010) to K.S. from the Ministry of Education, Science and Culture of Japan. We are indebted to Dr. Y. Hasegawa, School of General Education, Tohoku University, for the use of the stopped-flow spectrophotometer. Useful suggestions on the pK_a values by Professor K. Sawada, Department of Chemistry, Niigata University, are gratefully acknowledged.

Supplementary Material Available: Figure 2 (dependence of k_{obsd} on the concentration of NaNCS for the ligand substitution reaction of $[VO(pida)(H_2O)]^{2-}$ with NCS^- at $I = 0.1$ M ($NaClO_4$) and at pH 5.7 ± 0.2 ($[[VO(pida)(H_2O)]^{2-}] = 2.0 \times 10^{-3}$ M)) and Figure 4 (dependence of k_{obsd} on the concentration of $[VO(pida)(H_2O)]^{2-}$ for the oxidation of $[VO(pida)(H_2O)]^{2-}$ with $[IrCl_6]^{2-}$ (2.75×10^{-5} M) in aqueous solution at $I = 0.1$ M ($NaClO_4$) and pH 5.7 ± 0.2) (2 pages). Ordering information is given on any current masthead page.

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Direct Synthesis of Hexafluoroferrates(III) and Reaction of Thiocyanate and Fluoride with Iron(III) and Hydrogen Peroxide as an Access to Fluoro(sulfato)ferrates(III)

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Received March 11, 1986

The reaction of iron(III) hydroxide with alkali-metal or ammonium fluoride and 48% hydrofluoric acid in the presence of hydrogen peroxide, followed by the addition of ethanol, directly gives alkali-metal or ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K, or NH_4), in very high yields. An investigation of the reaction of ammonium or potassium thiocyanate and 48% HF with iron(III) hydroxide in the presence of hydrogen peroxide has been carried out. Sulfate has been obtained as the oxidation product of SCN^-, without involving reduction of iron(III) and providing an access to fluoro(sulfato)ferrates(III) of the types $(NH_4)_2[Fe(SO_4)F_3]$ and $K_3[Fe(SO_4)F_4]$. Similar reactions with sulfates in lieu of thiocyanates, either in the presence of or in the absence of H_2O_2, do not afford fluoro(sulfato)ferrates(III), however. IR spectroscopy and laser Raman spectroscopy provide evidence for a chelated sulfate in each of the fluoro(sulfato)ferrates(III).

Introduction

The chemistry of fluoro and mixed-fluoro complexes of transition metals continues to attract much attention and to produce new and exciting results.[1-4] Although much of the very recent activity in this area is devoted to studies related to kinetics[3] and magnetic properties,[1,4] a great deal of effort is required for the search for direct synthetic procedures and for synthesis of novel fluoro and mixed-fluoro complex species. These are the prerequisites for an heuristic approach in this field of chemistry. Importance of such compounds as insulators and semiconductors have been emphasized in the literature,[5] and pentafluoroferrates(III) have shown very interesting magnetic properties.[1]

In some of our recent publications we have dealt with the synthesis and structural assessment of fluoronickelates(II),[6] fluoromanganates(III),[7,8] and mixed-fluoromanganates(III).[2,9] We have decided to extend our work to iron analogues. To the best of our knowledge, within the context of fluoroferrates(III), there exists no direct and simple method for the synthesis of hexafluoroferrates(III), FeF_6^{3-}, thus limiting their accessibility. Moreover, mixed-fluoroferrates(III), for instance fluoro(sulfato)ferrates(III), have no reported existence.

The subject of this paper is the direct synthesis of alkali-metal and ammonium hexafluoroferrates(III), A_3FeF_6 (A = Na, K, or NH_4), and an account of the reaction of thiocyanate and hydrofluoric acid with iron(III) in the presence of hydrogen peroxide, with the latter leading to the first synthesis of fluoro(sulfato)ferrates(III).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrophotometer. The laser Raman (lR) spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 4880-Å laser line from a Spectra-Physics Model 165 argon laser was used as the excitation source. The light scattered at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by a photon-count processing system. The spectra were recorded at ambient temperatures by making pressed pellets of the compounds. Magnetic susceptibilities were measured by the Gouy method, using $Hg[Co(NCS)_4]$ as the calibrant.

Synthesis of Alkali-Metal and Ammonium Hexafluoroferrates(III), A_3FeF_6 (A = Na, K, or NH_4). Anhydrous iron(III) chloride (1.0 g, 6.2 mmol) was dissolved in water (5 cm^3) with gentle warming. Ammonium hydroxide solution (sp gr 0.9, 7 cm^3, excess) was added slowly with continuous stirring. The mixture was heated on a steam bath for 15 min,

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