Inorg. Chem. **1985**, *24*, 772–775

noted that large $\Delta H^{\ddagger}$ values are frequently observed for the outer-sphere electron-transfer reactions with highly negative charge products.[8c,27–29] The interpretation of $\Delta H^{\ddagger}$ 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 $\Delta H^{\ddagger}$ (and negative $\Delta S^{\ddagger}$) values,[36–38] none of which have yet been experimentally separated into ΔH_{OS} and $\Delta H_{ct}^{\ddagger}$. Obviously these facts deserve further studies for a general understanding of the factors controlling activation parameters of the outer-sphere redox reactions.

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.

Registry No. $[V^{IV}O(pmida)(H_2O)]$, 67904-95-4; $Na[V^{IV}O(nta)(H_2O)]$, 73711-58-7; $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^-)Co^{III}(en)_2]Cl_4$, 79304-91-9; $[IrCl_6]^{2-}$, 16918-91-5.

Supplementary Material Available: Plots of k_{obsd} vs. $[V^{IV}O]$ for the oxidation of $[V^{IV}O(nta)(H_2O)]^-$ with $[Ir^{IV}Cl_6]^{2-}$ at $I = 0.1$ M and 25 °C (Figure 2), plots of k_1 vs. $[H^+]^{-1}$ for the oxidation of $[V^{IV}O(pmida)(H_2O)]$ with $[Ir^{IV}Cl_6]^{2-}$ 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 $[V^{IV}O(nta)(H_2O)]^-$ with $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^-)Co^{III}(en)_2]^{4+}$ at $I = 0.1$ M and 25 °C (Figure 4) (3 pages). Ordering information is given on any current masthead page.

---

(36) de Araujo, M. A.; Hodges, H. L. *Inorg. Chem.* **1982**, *21*, 3167–3172.

(37) Yoneda, G. S.; Blackmer, G. L.; Holwerda, R. A. *Inorg. Chem.* **1977**, *16*, 3376–3378.

(38) McArdle, J. V.; Yucom, K.; Gray, H. B. *J. Am. Chem. Soc.* **1977**, *99*, 4141–4145.

Contribution from the Department of Chemistry,
Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980, Japan

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

YOICHI SASAKI,* MASATOSHI KANESATO, KENICHI OKAZAKI, AKIRA NAGASAWA, and KAZUO SAITO*

Received June 6, 1984

$Na[V^{IV}O(edtaH)]$ (H_4edta = 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 ($NaClO_4$); 1 M = 1 mol dm^{-3}). Kinetic studies of the outer-sphere oxidation of the new complex with $[Ir^{IV}Cl_6]^{2-}$ 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 ($NaClO_4$). These values are smaller by less than 1 order of magnitude than those for the one-step oxidation of *cis*-aquaoxo(quadridentate)vanadium(IV) ions with $[Ir^{IV}Cl_6]^{2-}$.

Metal ions of quadrivalent or higher oxidation state usually exist as "oxo–metal" ions in aqueous media, the number of coordinated oxide 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*-aquaoxo(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)–EDTA[5] 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)–EDTA[5] complex with $[Ir^{IV}Cl_6]^{2-}$.

Experimental Section

Materials. (1) Sodium [*N*-(Carboxymethyl)ethylenediamine-*N*,*N'*,*N'*-triacetato]oxovanadate(IV) Tetrahydrate, $Na[V^{IV}O(edtaH)]\cdot 4H_2O$. $[V^{IV}O(acac)_2]$ (acac = acetyl acetonate ion) (4.0 g, 15 mmol)[7] and $NaClO_4$ (1.84 g, 15 mmol) in 500 cm^3 of 0.05 M $HClO_4$ (1 M = 1 mol dm^{-3}) were kept at 40–50 °C for 20 min and treated with H_4edta (4.4 g, 15 mmol) and slowly with ca. 50 cm^3 of 0.5 M $NaHCO_3$. 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 cm^3. An ethanol solution (60 cm^3) of 4.5 mmol of $NaClO_4$ 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 cm^3) was added dropwise to the solution of the crude salt in ca. 45 cm^3 of 0.01 M $HClO_4$ 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 $C_{10}H_{21}N_2O_{13}NaV$: 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, $Na_3[V^V(O)_2(edta)]\cdot 6H_2O$, was prepared by the method of Amos and Sawyer.[8] Sodium hexachloro-

---

[1] Kepert, D. L. "The Early Transition Metals"; Academic Press: London, 1972; pp 164–174, 209–217, 274–321.

[2] Saito, K.; Sasaki, Y. *Adv. Inorg. Bioinorg. Chem.* **1982**, *1*, 179–216.

[3] Nishizawa, M.; Sasaki, Y.; Saito, K. *Inorg. Chem.*, preceding paper in this issue.

[4] Okazaki, K. Ph.D. Thesis, Tohoku University, 1982, pp 87–144.

[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.

[6] (a) Scheidt, W. R.; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3873–3877. (b) Scheidt, W. R.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3878–3882.

[7] Grdenic, D.; Korpar-Colig, B. *Inorg. Chem.* **1964**, *3*, 1328–1329.

Table I. Pseudo-First-Order Rate Constants, k_{obsd}, for the Oxidation of the Ethylenediaminetetraacetate Complex of Oxovanadium(IV) with Hexachloroiridate(IV) in Aqueous Solution

entry	temp/°C	pH	$[V^{IV}]$/ 10^{-3} M	$[Ir^{IV}]$/ 10^{-5} M	$[Ir^{III}]$/ 10^{-4} M	k_{obsd}/s^{-1}	$k_{calcd}{}^{a}/s^{-1}$
1	25.0	3.15	6.01	2.31	3.97	0.613	0.622
2	25.0	3.15	6.01	2.31	6.50	0.410	0.415
3	25.0	3.15	6.01	2.31	9.00	0.303	0.312
4	25.0	3.15	6.01	2.31	14.0	0.208	0.209
5	25.0	3.25	3.56	2.31	10.1	0.220	0.201
6	25.0	3.25	6.01	2.31	5.02	0.620	0.613
7	25.0	3.25	6.01	2.31	6.81	0.477	0.477
8	25.0	3.25	6.01	2.31	10.1	0.337	0.340
9	25.0	3.25	6.01	2.31	13.9	0.259	0.254
10	25.0	3.25	7.93	2.31	10.1	0.447	0.448
11	25.0	3.50	3.56	2.31	10.1	0.309	0.291
12	25.0	3.50	6.01	2.31	5.02	0.830	0.821
13	25.0	3.50	6.01	2.31	6.81	0.673	0.648
14	25.0	3.50	6.01	2.31	10.1	0.467	0.467
15	25.0	3.50	6.01	2.31	13.9	0.363	0.353
16	25.0	3.50	7.62	2.31	10.1	0.630	0.622
17	25.0	4.25	6.01	2.31	6.50	1.15	1.18
18	25.0	4.25	6.01	2.31	9.00	0.920	0.936
19	25.0	4.25	6.01	2.31	11.5	0.775	0.774
20	25.0	4.25	6.01	2.31	14.0	0.632	0.660
21[b]	25.0	4.35	4.06	5.13	10.1	0.558	
22[b]	25.0	4.35	5.80	5.13	10.1	0.780	
23[b]	25.0	4.35	9.04	2.56	10.1	1.20	
24[b]	25.0	4.35	9.04	5.13	10.1	1.16	
25[b]	25.0	4.35	9.04	5.13	10.1	1.17	
26[b]	25.0	4.35	9.04	7.69	10.1	1.18	
27[b]	25.0	4.35	12.0	5.13	10.1	1.62	
28	35.0	3.15	6.01	2.31	3.97	1.16	1.17
29	35.0	3.15	6.01	2.31	6.50	0.785	0.779
30	35.0	3.15	6.01	2.31	9.00	0.585	0.586
31	35.0	3.15	6.01	2.31	14.0	0.389	0.392
32	35.0	3.25	6.01	2.31	4.03	1.42	1.43
33	35.0	3.25	6.01	2.31	6.81	0.925	0.946
34	35.0	3.25	6.01	2.31	10.1	0.669	0.676
35	35.0	3.25	6.01	2.31	13.9	0.500	0.508
36	35.0	3.50	6.01	2.31	4.03	1.84	1.83
37	35.0	3.50	6.01	2.31	6.81	1.21	1.25
38	35.0	3.50	6.01	2.31	10.1	0.903	0.901
39	35.0	3.50	6.01	2.31	13.9	0.680	0.683
40	35.0	4.25	6.01	2.31	3.97	2.60	2.60
41	35.0	4.25	6.01	2.31	6.50	1.84	1.87
42	35.0	4.25	6.01	2.31	9.00	1.46	1.46
43	35.0	4.25	6.01	2.31	14.0	1.02	1.02
44	15.0	3.25	6.01	2.31	5.02	0.370	0.371
45	15.0	3.25	6.01	2.31	6.81	0.299	0.299
46	15.0	3.25	6.01	2.31	10.1	0.217	0.221
47	15.0	3.25	6.01	2.31	13.9	0.171	0.170
48	15.0	3.50	6.01	2.31	5.02	0.470	0.478
49	15.0	3.50	6.01	2.31	6.81	0.393	0.394
50	15.0	3.50	6.01	2.31	10.1	0.301	0.298
51	15.0	3.50	6.01	2.31	13.9	0.225	0.233
52	15.0	4.25	6.01	2.31	3.97	0.693	0.684
53	15.0	4.25	6.01	2.31	6.49	0.510	0.524
54	15.0	4.25	6.01	2.31	8.93	0.440	0.427
55	15.0	4.25	6.01	2.31	11.5	0.362	0.358

[a] Calculated from k_a, k_b, K_a, $[H^+]$ $(=10^{-(pH)})$, and k_2/k_{-1} (at given pH and temperature) by the use of eq 6 and 8 (see Table III for k_a and k_b values and Table II for k_2/k_{-1} values; $K_a = 6.03 \times 10^{-4}$ M, see text). [b] k_{calcd} is not given since the k_2/k_{-1} value is not available at pH 4.35.

iridate(III) hydrate, $Na_3[Ir^{III}Cl_6]\cdot H_2O$, was obtained by recrystallizing the commercially available reagent three times from water to remove contaminated $[Ir^{IV}Cl_6]^{2-}$. The salt gave the reported absorption peak at 358 nm with $\epsilon = 74$ M^{-1} cm^{-1}.[9] Commercial sodium hexachloroiridate(IV) hexahydrate, $Na_2[Ir^{IV}Cl_6]\cdot 6H_2O$, was recrystallized once from water.

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 80-fold excess to the oxidant, $[Ir^{IV}Cl_6]^{2-}$. The sodium salt of $[Ir^{III}Cl_6]^{3-}$ was added in excess to $[Ir^{IV}Cl_6]^{2-}$, since the first-order rate constant (k_{obsd}) showed dependence on the concentration of product, $[Ir^{III}Cl_6]^{3-}$. Decrease in the concentration of $[Ir^{IV}Cl_6]^{2-}$ was followed at 487 nm, where $[Ir^{IV}Cl_6]^{2-}$ has a strong absorption peak with $\epsilon = 4075$ M^{-1} cm^{-1}.[10] The k_{obsd} value was obtained from the slope of the first-order plot. Good linear first-order plots were not obtained without addition of $[Ir^{III}Cl_6]^{3-}$. Ionic strength (I) was adjusted with sodium perchlorate. The pH was adjusted with acetate buffer ($[CH_3COO^-]_T = 0.10$ M).

Effects of the following ingredients were examined as they can interfere with the reaction of interest. Neither the mixture of $Na[V^{IV}O(edtaH)]$ (1.03×10^{-2} M) and $Na_3[Ir^{III}Cl_6]$ (2.95×10^{-3} M) nor that of $Na_3[V^V(O)_2(edta)]$ (2.02×10^{-2} M) and $Na_3[Ir^{III}Cl_6]$ (7.42×10^{-3} M) in 0.1 M $NaClO_4$ solution caused any change in absorption spectrum after 1 h. Na_2H_2edta (4.57×10^{-4} M) was oxidized by $Na_2[Ir^{IV}Cl_6]$

---

(8) Amos, L. W.; Sawyer, D. T. *Inorg. Chem.* **1972**, *11*, 2692–2697.

(9) Sykes, A. G.; Thorneley, R. N. F. *J. Chem. Soc. A* **1970**, 232–238.

(10) Poulson, I. A.; Garner, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 2032–2037.

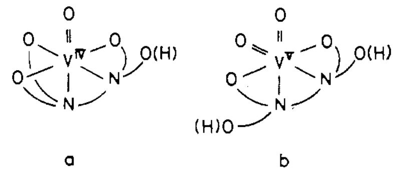


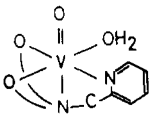
Figure 1. Schematic structures of (a) the oxovanadium(IV)–EDTA and (b) the dioxovanadium(V)–EDTA complexes.

(4.57×10^{-5} M) with the first-order rate constants 3.07×10^{-2} and 2.43×10^{-2} s^{-1} at pH 3.5 and 4.5, respectively. Also, $Na_3[V^V(O)_2(edta)]$ (9.14×10^{-4} M) was oxidized by $Na_2[Ir^{IV}Cl_6]$ (4.57×10^{-5} M) with $k_{obsd} = 1.80 \times 10^{-2}$ s^{-1} at pH 4.5. The k_{obsd} value of the aimed reaction of interest is larger than all of these rate constants by more than 1 order of magnitude. Thus, the kinetics of the principal redox reaction is not affected by these side reactions below pH 4.5.

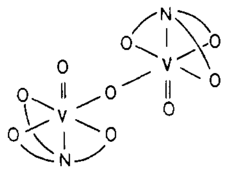
Measurements. Electronic absorption spectra were recorded on a Hitachi 330 spectrophotometer. Acid-dissociation constants were determined by the pH titration with a Metrohm Herisau E300B pH meter. Kinetic measurements were carried out by the use of a Union-Giken RA-401 stopped-flow spectrophotometer.

Results and Discussion

Structure of the Oxovanadium(IV)–EDTA Complex. This complex is presumed to have the structure shown in Figure 1a. This is based on the following facts. (1) All the oxovanadium(IV) complexes of aminopolycarboxylates whose structures were determined by the X-ray diffraction method amino polycarboxylates a nitrogen donor atom at the site trans to the oxo ligand; i.e. they include $[V^{IV}O(pmida)(H_2O)]$ (I),[11] $[V^{IV}O(S\text{-}peida)(H_2O)]$ (S-peida^{2-} = (S)-[(1-(2-pyridyl)ethyl)imino]diacetate(2–) ion),[12] and $[V^{IV}O(S,S\text{-}edpro)(H_2O)]$ (S,S-edpro^{2-} = (S,S)-N,N'-ethylenebis(2-pyrrolidinecarboxylate)(2–) ion).[4] Also, X-ray crystallography disclosed that mixed-valence divanadium(IV,V) complexes, $Na[V_2O_3(S\text{-}peida)_2]$,[12] $Na_3[V_2O_3(S\text{-}alada)_2]$ (S-alada^{3-} = (S)-alanine-N,N-diacetate(3–) ion),[4] and $(NH_4)_3[V_2O_3(nta)_2]\cdot 3H_2O$ (II),[13] have nitrogen donor atoms at the site trans to the oxo ligand. (2) The free carboxylate arm should be branched from the coordinated nitrogen at the site cis to the oxo ligand. It is sterically difficult for two carboxylate oxygen atoms and a nitrogen atom of an iminodiacetate group to coordinate meridionally to an octahedral metal center.



I



II

Electronic Absorption Spectra of the Oxovanadium(IV)–EDTA Complex. The electronic absorption spectra were recorded over the pH range 1.75–11.50. Acetate, tartrate, and phosphate buffers (all 0.1 M) were used for adjusting the pH. The spectrum in the visible region remained constant between pH 2.5 and 6.7, λ_{max} being at 777 nm (ϵ = 24.0 M^{-1} cm^{-1}) and at 585 nm (ϵ = 20.3). The two peaks are characteristic of the oxovanadium(IV) complexes with various aminocarboxylate ligands[3,4,11-14] and can be assigned to $d_{xy} \rightarrow d_{xz,yz}$ (777 nm) and $d_{xy} \rightarrow d_{x^2-y^2}$ (585 nm). The peak positions (nm) shift slightly outside the pH range 2.5–6.7 with smaller extinction coefficients (M^{-1} cm^{-1}): at pH 1.75, 777 (ϵ = 23.2) and 585 (19.2); pH 10.65, 780 (23.4) and 582 (19.5); pH 11.5, 785 (22.4) and 580 (18.3).

Table II. k_1 and k_2/k_{-1} Values for the Oxidation of the Oxovanadium(IV)–EDTA Complex with $[Ir^{IV}Cl_6]^{2-}$ in Aqueous Perchlorate Media[a]

	$k_1/10^2$ M^{-1} s^{-1}			$(k_2/k_{-1})/10^{-4}$ M		
pH	15.0 °C	25.0 °C	35.0 °C	15.0 °C	25.0 °C	35.0 °C
3.15		4.7 ± 0.6	8.9 ± 0.8		1.1 ± 0.3	1.1 ± 0.1
3.25	1.9 ± 0.2	5.0 ± 0.9	9.4 ± 0.7	2.5 ± 0.3	1.3 ± 0.2	1.4 ± 0.1
3.50	2.0 ± 0.2	5.4 ± 1.1	9.9 ± 1.3	3.4 ± 0.5	1.7 ± 0.4	1.8 ± 0.2
4.25	2.2 ± 0.3	6.1 ± 1.3	11.2 ± 0.6	4.3 ± 0.6	3.0 ± 0.7	2.5 ± 0.1

[a] Conditions: I = 1.0 M ($NaClO_4$); [V^{IV}O–EDTA] = (3.55–12.0) × 10^{-3} M; [$Ir^{III}Cl_6{}^{3-}$] = (3.97–14.0) × 10^{-4} M; [$Ir^{IV}Cl_6{}^{2-}$] = (2.31–7.69) × 10^{-5} M; pH adjusted with 0.10 M acetate buffer.

pH Titration of the Oxovanadium(IV)–EDTA Complex. An aqueous solution of $Na[V^{IV}O(edtaH)]$ (1.00×10^{-2} M) shows a pH of ca. 2.5 at 25 °C and I = 1.00 M ($NaClO_4$). The solution was titrated with 1.00×10^{-2} M NaOH solution at I = 1.00 M ($NaClO_4$). A sharp inflection was observed at an equimolar amount of sodium hydroxide, and no other inflection was observed up to pH 11. Absence of change in the visible absorption spectrum over the pH range 2.5–6.7 indicates that the protonation–deprotonation occurs at the site remote from the metal center, i.e. at the free carboxylate arm of coordinated edtaH:

$$[V^{IV}O(edtaH)]^- \overset{K_a}{\rightleftharpoons} [V^{IV}O(edta)]^{2-} + H^+ \qquad (1)$$

The pK_a value was 3.22 at 25 °C and was independent of the temperature at 25–35 °C.

Stoichiometry of the Reaction between the Oxovanadium(IV)–EDTA Complex and $[Ir^{IV}Cl_6]^{2-}$. Stoichiometry of the oxidation of the oxovanadium(IV)–EDTA complex with $[Ir^{IV}Cl_6]^{2-}$ was examined by the analysis of the absorption spectra in the region 400–800 nm, in the presence of a large excess of the oxovanadium(IV) complex to avoid possible consumption of $[Ir^{IV}Cl_6]^{2-}$ by the vanadium(V) complex (see Experimental Section). An aqueous solution of 2.00×10^{-3} M $[Ir^{IV}Cl_6]^{2-}$ was mixed with an equal amount of 3.42×10^{-2} M aqueous solution of the vanadium(IV) complex at pH 4.4 (0.20 M acetate buffer) and I = 1.00 M ($NaClO_4$) at room temperature. The characteristic absorption peaks of $[Ir^{IV}Cl_6]^{2-}$ in the region 400–500 nm disappeared immediately. The absorption spectrum of the mixture remained unchanged over 30 min and was in good agreement with that of the sum of $[Ir^{III}Cl_6]^{3-}$ (1.00×10^{-3} M), the dioxovanadium(V)–EDTA complex (1.00×10^{-3} M), and the oxovanadium(IV)–EDTA complex (1.61×10^{-2} M), particularly in the region 400–450 nm, where the oxovanadium(IV)–EDTA complex contributes less than one-fourth of the total absorption intensity. Thus the 1:1 stoichiometry was confirmed.

Kinetics. (1) Rate Law. The kinetics was studied at pH 3.15–4.35 (0.10 M acetate buffer) and I = 1.00 M ($NaClO_4$) at 15, 25, and 35 °C, with the reagent concentrations [V^{IV}O-EDTA] = (3.55–12.0) × 10^{-3} M, [$Ir^{III}Cl_6{}^{3-}$] = (3.97–14.0) × 10^{-4} M, and [$Ir^{IV}Cl_6{}^{2-}$] = (2.31–7.69) × 10^{-5} M. First-order rate constants are listed in Table I. The rate constant k_{obsd} = 1.18 ± 0.03 s^{-1} was independent of [$Ir^{IV}Cl_6{}^{2-}$] at given concentrations of [V^{IV}O–EDTA] (9.04×10^{-3} M) and [$Ir^{III}Cl_6{}^{3-}$] (1.01×10^{-3} M) at pH 4.35 (25 °C). Figure 2[15] shows that k_{obsd} depends linearly on [V^{IV}O–EDTA] at a given [$Ir^{III}Cl_6{}^{3-}$] at each pH. Figure 3[15] shows that the ratio [V^{IV}O–EDTA]/k_{obsd} has a good linear correlation with [$Ir^{III}Cl_6{}^{3-}$] at the given pH. Thus the rate formula (2) was derived.

$$k_{obsd} = p[V^{IV}]/(q[Ir^{III}] + r) \qquad (2)$$

(2) Mechanism of the Reaction. The dependence of k_{obsd} on [$Ir^{III}Cl_6{}^{3-}$] suggests the existence of a reactive intermediate, which is most reasonably assigned to "monooxovanadium(V)–EDTA". This intermediate should have a structure similar to that of the

---

(11) Ooi, S.; Nishizawa, M.; Matsumoto, K.; Kuroya, H.; Saito, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 452–457.

(12) Kojima, A.; Okazaki, K.; Ooi, S.; Saito, K. *Inorg. Chem.* **1983**, *22*, 1168–1174.

(13) Nishizawa, M.; Hirotsu, K.; Ooi, S.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1979**, 707–708.

(14) Okazaki, K.; Saito, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 785–791.

(15) Supplementary material.

Table III. Rate Constants and Activation Parameters for the Oxidation of $[V^{IV}O(edtaH)]^-$ (k_a) and $[V^{IV}O(edta)]^{2-}$ (k_b) in Aqueous Perchlorate Media[a]

rate constant	$k/10^2$ M^{-1} s^{-1} 15 °C	$k/10^2$ M^{-1} s^{-1} 25 °C	$k/10^2$ M^{-1} s^{-1} 35 °C	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
k_a	1.42 ± 0.08	3.3 ± 0.4	6.7 ± 0.3	55.0 ± 2.2	−13 ± 7
k_b	2.26 ± 0.05	6.5 ± 0.3	11.6 ± 0.2	58 ± 18	+1 ± 70

[a] $edta^{4-}$ = ethylenediaminetetraacetate(4−) ion.

parent vanadium(IV) complex. Thus the following mechanism is consistent with the rate law (2) at a given pH:

$$V^{IV}O\text{–EDTA} + [Ir^{IV}Cl_6]^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{“}V^{V}O\text{–EDTA”} + [Ir^{III}Cl_6]^{3-} \tag{3}$$

$$\text{“}V^{V}O\text{–EDTA”} \xrightarrow{k_2} V^{V}(O)_2\text{–EDTA} + 2H^+ \tag{4}$$

Equation 5 is derived by applying the steady-state approximation to the intermediate $V^{V}O$–EDTA. Equation 5 is of the same form

$$-\frac{d[Ir^{IV}]}{dt} = \frac{k_1k_2[V^{IV}][Ir^{IV}]}{k_{-1}[Ir^{III}] + k_2} \tag{5}$$

as eq 2. Thus, k_{obsd} is expressed by eq 6 and, hence, eq 7. Figure 4[15] shows the plot $[V^{IV}][Ir^{III}]^{-1}k_{obsd}^{-1}$ vs. $[Ir^{III}]^{-1}$, from the slope and the intercept of which k_1 and k_2/k_{-1} were obtained (Table II).

$$k_{obsd} = \frac{k_1k_2[V^{IV}]}{k_{-1}[Ir^{III}] + k_2} \tag{6}$$

$$\frac{[V^{IV}]}{k_{obsd}[Ir^{III}]} = \frac{k_{-1}}{k_1k_2} + \frac{1}{k_1[Ir^{III}]} \tag{7}$$

(3) Dependence of k_1 on pH. The dependence of k_1 on pH was analyzed by use of the pK_a of the vanadium(IV)–EDTA complex:

$$\begin{tikzcd}
{[V^{IV}O(edtaH)]^-} \arrow[r, "k_a"] \arrow[d, shift right, "K_a"'] & \text{“}[V^{V}O(edtaH)]\text{”} \\
{[V^{IV}O(edta)]^{2-}} \arrow[r, "k_b"] \arrow[u, shift right] & \text{“}[V^{V}O(edta)]^-\text{”}
\end{tikzcd}$$

The k_1 is now expressed as

$$k_1 = \frac{k_a[H^+] + k_bK_a}{[H^+] + K_a} \tag{8}$$

The plot $k_1([H^+] + K_a)$ vs. $[H^+]$ gives a straight line (Figure 5).[15] The k_a and k_b values were obtained as in Table III, as well as their activation parameters.

General Discussion on the Kinetic Results. The most interesting feature of the present results is the existence of a steady-state intermediate, the "monooxovanadium(V)–EDTA complex". This is in sharp contrast to the results of the outer-sphere oxidations of *cis*-aquaoxovanadium(IV) complexes of $pmida^{2-}$ and nta^{3-}, which proceed in one step. Here, the rate-determining oxidation is followed by rapid loss of proton(s) from the coordinated aqua (or hydroxo) ligand to give the stable *cis*-dioxovanadium(V) complex.[3] Conversion of the "monooxovanadium(V)–EDTA complex" into the stable *cis*-dioxo complex requires either the displacement of one of the coordinated carboxylate arms by water with simultaneous loss of protons or breakage of the bond between carbon and coordinated oxygen (with possible attack of water or hydroxo ion at the carbon center). Such a conversion cannot compete with the reduction to vanadium(IV) as the steady-state behavior indicates. Details of the mechanism of the conversion are still to be clarified.

k_a is smaller than k_b by only a factor of ca. 2. The oxidation rate is rather insensitive to the deprotonation at the remote free carboxylate arm. On the other hand, deprotonation of the aqua ligand in $[V^{IV}O(pmida)(H_2O)]$ and $[V^{IV}O(nta)(H_2O)]^-$ causes ca. 10^3 times enhancement of the rate of oxidation with $[Ir^{IV}Cl_6]^{2-}$ and $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^-)Co^{III}(en)_2]^{4+}$ (en = ethylenediamine).[3]

The k_a and k_b values are close to the second-order rate constants for the oxidation with $[Ir^{IV}Cl_6]^{2-}$ of $[V^{IV}O(pmida)(H_2O)]$ (2.62×10^3 M^{-1} s^{-1}) and $[V^{IV}O(nta)(H_2O)]^-$ (1.1×10^3 M^{-1} s^{-1}) and much smaller than those for their conjugate bases. Displacement of the aqua ligand by a carboxylate group does not make a significant influence on the oxidation rate of the oxovanadium(IV) center. The hydroxo ligand seems to provide a particularly favorable route for the oxidation.[3]

A good correlation of $\Delta H^{\ddagger}$ with the charge product of the redox couple is found for the oxidation of $[V^{IV}O(pmida)(H_2O)]$, $[V^{IV}O(nta)(H_2O)]^-$, and their conjugate bases.[3] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for $k_a([V^{IV}O(edtaH)]^-)$ are close to those of a neutral complex, $[V^{IV}O(pmida)(H_2O)]$.[3] Thus, the linear correlation does not seem to be extended to the reactions involving complexes without a coordinated aqua or hydroxo ligand.

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.

Registry No. edta, 60-00-4; $Na[V^{IV}O(edtaH)]$, 94323-80-5; $[Ir^{IV}Cl_6]^{2-}$, 16918-91-5.

Supplementary Material Available: Plots of k_{obsd} vs. $[V^{IV}O\text{–EDTA}]$ for the oxidation of the oxovanadium(IV)–EDTA complex with $[Ir^{IV}Cl_6]^{2-}$ ($(2.31\text{–}7.69) \times 10^{-5}$ M) in the presence of a given concentration of $[Ir^{III}Cl_6]^{3-}$ (1.01×10^{-3} M) at 25 °C and $I = 1.0$ M ($NaClO_4$) (Figure 2), plots of $[V^{IV}]k_{obsd}^{-1}$ vs. $[Ir^{III}Cl_6{}^{3-}]$ for the oxidation of the oxovanadium(IV)–EDTA complex with $[Ir^{IV}Cl_6]^{2-}$ (2.31×10^{-5} M) at 25 °C and $I = 1.0$ M ($NaClO_4$) (Figure 3), plots of $[V^{IV}][Ir^{III}]^{-1}k_{obsd}^{-1}$ vs. $[Ir^{III}]^{-1}$ for the oxidation of the oxovanadium(IV)–EDTA complex with $[Ir^{IV}Cl_6]^{2-}$ in the presence of $[Ir^{III}Cl_6]^{3-}$ at 15 °C and $I = 1.0$ M ($NaClO_4$) (Figure 4), and plots of $k_1([H^+] + K_a)$ vs. $[H^+]$ for the oxidation of the oxovanadium(IV)–EDTA complex with $[Ir^{IV}Cl_6]^{2-}$ in the presence of $[Ir^{III}Cl_6]^{3-}$ at $I = 1.0$ M ($NaClO_4$) (Figure 5) (4 pages). Ordering information is given on any current masthead page.