Table I. ^{57}Fe Mössbauer Parameters of $Fe_2F_5 \cdot 7H_2O$ at 298 K

sample		ΔE_Q, mm s^{-1}	δ,[a] mm s^{-1}	Γ, mm s^{-1}	rel integrated intens
initial[b] crystallization product ($\chi^2 = 539$, MISFIT = 0.06%)	Fe^{2+}	3.322 ± 0.001	1.228 ± 0.001	0.340 ± 0.002	5 ± 0.2
	$Fe^{3+}{}_I$	0.414 ± 0.004	0.462 ± 0.003	0.473 ± 0.003	3.05 ± 0.5
	$Fe^{3+}{}_{II}$	0.817 ± 0.003	0.459 ± 0.002	0.37 ± 0.01	2.24 ± 0.5
recrystallized[c] sample ($\chi^2 = 703$, MISFIT = 0.05%)	Fe^{2+}	3.319 ± 0.001	1.291 ± 0.001	0.340 ± 0.001	5 ± 0.1
	$Fe^{3+}{}_I$	0.431 ± 0.030	0.462 ± 0.002	0.50 ± 0.02	3.15 ± 0.2
	$Fe^{3+}{}_{II}$	0.83 ± 0.02	0.465 ± 0.003	0.37 ± 0.03	2.05 ± 0.2

[a] Relative to iron metal. [b] The off-resonant count = 2.4 × 10^6. For a two quadrupole doublet fit $\chi^2 = 1249$ and MISFIT = 0.1%. [c] The off-resonant count = 1.2 × 10^6. For a two quadrupole doublet fit $\chi^2 = 953$ and MISFIT = 0.1%.

That is to say, if there are 5 formula units per unit cell, then the two Fe^{3+} patterns are expected to occur with relative intensities of 3:2 or 1:4. It is clear from the data that the relative frequencies of the two sites are 3:2. The broad line widths of the more intense Fe^{3+} component could be indicative of local crystallographic disorder. This possibility makes an attempt to arrive at some tentative conclusion as to the nature of the coordination of the two Fe^{3+} sites less straightforward. The average Fe^{3+} coordination is $[FeF_5(H_2O)]^2$ which must therefore be divided into two crystal chemical species with a relative frequency of occurrence of 3:2. Of course, there could be just one combination of ligands for both species, i.e., five F^- and one H_2O. It is noteworthy that at 77 K the Mössbauer parameters of $K_2[FeF_5(H_2O)]$,[8] ($\Delta E_Q = 0.60$ mm s^{-1} and $\delta_{IS} = 0.43$ mm s^{-1}) in which there are isolated $[Fe(H_2O)F_5]^{2-}$ octahedra are intermediate to those of the two Fe^{3+} patterns in $Fe_2F_5 \cdot 7H_2O$; the difference in the temperatures at which the measurements have been made preclude a more critical comparison. The Mössbauer parameters of the Fe^{3+} patterns in $Fe_2F_5 \cdot 7H_2O$ and β-$FeF_3 \cdot 3H_2O$ are quite similar. It is significant, then, that the structure of β-$FeF_3 \cdot 3H_2O$ consists of infinite chains of vertex sharing (via a fluoride bridge) *trans*-$[Fe(H_2O)_2F_4]^-$ octahedra for which the equatorial positions are occupied in a disordered fashion by two water molecules and two fluoride ions.[9] Such a structure cannot be transferred simply to the Fe^{3+} environments in $Fe_2F_5 \cdot 7H_2O$ if the $[Fe(H_2O)F_5]^{2-}$ stoichiometry is correct. The line widths of the Fe^{3+} patterns in $Fe_2F_5 \cdot 7H_2O$ are also significantly larger than those in β-$FeF_3 \cdot 3H_2O$. Under any circumstance, it is not possible to arrive at two unique ligand groupings for isolated octahedra in the required 3:2 ratio which would give an average $[Fe(H_2O)F_5]^{2-}$ coordination. The Fe^{3+} octahedra are either disordered, share-polyhedral elements or are both disordered and share-polyhedral elements. Even though $K_2FeF_5(H_2O)$ contains isolated $[FeF_5(H_2O)]^{2-}$ octahedra, other pentafluoride hydrates, e.g., $K_2AlF_5(H_2O)$ and $K_2MnF_5(H_2O)$ contain infinite chains of vertex sharing MnF_6 octahedra. Therefore, the tentative conclusion arrived at in this investigation regarding the probable qualitative structural features of the Fe^{3+} coordination is not without precedence and the postulation of completely isolated and well-defined coordination polyhedra for all iron species in $Fe_2F_5 \cdot 7H_2O$ warrants further investigation by direct structural methods.

The complexity of the dehydration processes in $Fe_2F_5 \cdot 7H_2O$ and $Fe_2F_5 \cdot 2H_2O$ and the variable behavior of $Fe_2F_5 \cdot 2H_2O$ produced by different means[12] might be better understood not only in terms of differences in the changes of the ligation at structurally and chemically inequivalent Fe^{2+} and Fe^{3+} ions but also in terms of different processes at the structurally inequivalent Fe^{3+} sites, which must have available appropriate kinetic routes for the removal of the site inequivalence during the dehydration process.

Registry No. Fe_2F_5, 12061-94-8.

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(8) Syamal, A. *Curr. Sci.* **1974**, *43*.
(9) Teufer, G. *Acta Crystallogr.* **1964**, *17*, 1480.
(10) Edwards, A. J. *J. Chem. Soc. A* **1971**, 2653.
(11) Edwards, A. J. *J. Chem. Soc. A* **1972**, 816.
(12) Brown, D. B.; Dilts, J. A.; Walton, E. G. *J. Chem. Soc., Dalton Trans.*, in press.

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Kinetics and Mechanism of the Chromium(III)–Periodate Reaction

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The kinetics of oxidation of chromium(III) by periodate showed an unusual second-order dependence on chromium(III). Over the pH range 1.88–3.03 the kinetics obeyed the rate law $d[Cr(VI)]/2dt = a[Cr(III)]_T^2[I(VII)]_T/(b[H^+]^2 + [H^+])$. The values of a and b were determined as 12.8 ± 2.2 M^{-1} s^{-1} and 770 ± 26 M^{-1}, respectively, at $I = 0.25$ M and $T = 25$ °C. An inner-sphere mechanism in which two chromium(III) ions are bridged to I(VII) is proposed. The routes that may lead to the formation of dichromium(III)–iodine(VII) species are outlined. A single-step two one-electron transfer is suggested within the bridged species. An alternative mechanism may operate by inner- and outer-sphere mechanisms in which concurrent electron transfer occurs within $[Cr-(OH)-I(VII)]^+$ and from the Cr^{3+} ion.

Introduction

Chromium(III) is reported to catalyze oxidation by periodate.[1,2] Catalysis is believed to be caused by chromium(VI) produced by a relatively rapid oxidation process of chromium(III) by periodate.[2] This observation seems to contradict previous reports that an inner-sphere mechanism is the preferred, if not the only, path for periodate oxidation of metal complexes.[3-7] This conclusion is based on the observations

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(1) D. J. B. Galliford and J. M. Ottaway, *Analyst (London)* **91**, 415 (1972).
(2) D. P. Nikolelis and T. P. Hadjiiannou, *Mikrochim. Acta*, **2**, 105 (1978).
(3) Fouad R. El-Eziri and Yousif Sulfab, *Inorg. Chim. Acta*, **25**, 15 (1977).
(4) Yousif Sulfab and A. I. Abu-Shaby, *Inorg. Chim. Acta*, **21**, 115 (1977).
(5) Ahmed Y. Kassim and Yousif Sulfab, *Inorg. Chim. Acta*, **24**, 247 (1977).
(6) Yousif Sulfab, *J. Inorg. Nucl. Chem.*, **38**, 2271 (1976).

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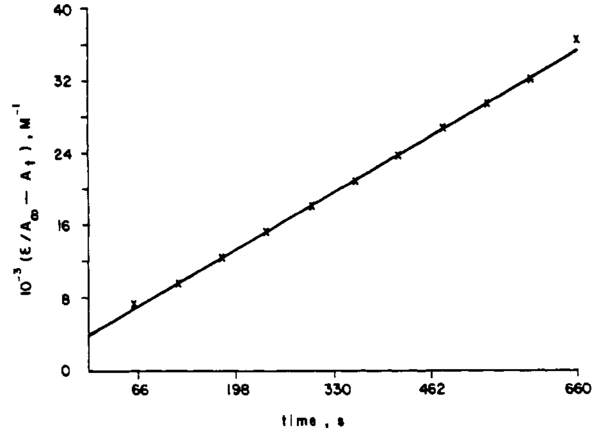

Figure 1. Plot of $\epsilon/(A_\infty - A_t)$ vs. time showing second-order dependence on chromium(III) concentration. [Cr(III)] = 2.44 × 10^{-4} M, $[IO_4^-]$ = 0.04 M, I = 0.25 M, and T = 25.0 °C.

that periodate oxidizes either labile complexes, $Fe(H_2O)_6^{2+}$,[3] $VO(H_2O)_5^{2+}$,[4] and $CoEDTA^{2-}$,[5] or inert complexes possessing a bridging ligand, $Fe(CN)_6^{4-}$[6] and $Mo(CN)_8^{4-}$.[7] Intermediates were detected spectrophotometrically in the oxidation of both $Fe(H_2O)_6^{2+}$ and $CoEDTA^{2-}$. The failure of periodate to oxidize $Fe(phen)_3^{2+}$ to $Fe(phen)_3^{3+}$ (phen = 1,10-phenanthroline), a process requiring outer-sphere electron transfer, lends support to this contention.[8]

Hexaaquochromium(III) is inert, and coordinated water, because of its extremely low basicity, is not expected to serve as a bridging ligand.[9] Thus $Cr(H_2O)_6^{3+}$ seems to lack the prerequisites for an inner-sphere electron-transfer process. Its oxidation by periodate sheds some doubt on the hypothesis that periodate is an inner-sphere oxidant. However, as shown later, an inner-sphere process may still be accommodated when the reactive chromium(III) species is $[Cr(H_2O)_5(OH)]^{2+}$.

Experimental Section

Reagents. Reagent grade sodium metaperiodate, chromium(III) nitrate hexahydrate, sodium acetate trihydrate, and nitric acid were used without further purification. A stock solution of periodate was made up by weight and wrapped with Al foil to avoid photochemical decomposition.[10] The chromium(III) stock solution was standardized spectrophotometrically after oxidation by H_2O_2 in an alkaline solution.[11] A stock solution of sodium acetate was made up by weight and that of nitric acid by dilution and standardization against sodium hydroxide. Buffer solutions were made up from sodium acetate–nitric acid mixtures.

Procedure. A Unicam SP 8000 spectrophotometer, equipped with a thermostated cell holder, was used to monitor the reaction. The reactants in buffer solutions, in the two compartments of an indented flask, were thermostated for about 20 min. These were thoroughly mixed and quickly transferred to an absorption cell. The formation of chromium(VI) was followed at 350 nm, the peak for chromium(VI), where the molar absorptivity ϵ = 1580 M^{-1} cm^{-1},[12] and the other species have negligible absorbances at the employed concentrations. At the low chromium(III) concentrations used, the product was the monomer $HCrO_4^-$.[13] The kinetics of this reaction was studied in presence of a large excess of periodate concentration, at least 15-fold, over that of chromium(III). The pH of the reaction solution was measured on a Radiometer digital pH meter, Model PHM 62. The ionic strength was maintained at 0.25 M by using the appropriate amounts of sodium acetate and nitric acid solutions.

Table I. Kinetic Data for the Chromium(III)–Periodate Reaction[a]

$10^2[IO_4^-]$, M	pH	k_2, M^{-1} s^{-1}	$10^{-2}k_3$, M^{-2} s^{-1}
0.75	2.23	2.79 ± 0.08	3.59 ± 0.10
1.25		4.42 ± 0.09	3.54 ± 0.07
2.00		7.11 ± 0.14	3.56 ± 0.07
3.50		12.26 ± 0.10	3.50 ± 0.03
4.00		13.50 ± 0.27	3.38 ± 0.07
4.50		15.45 ± 0.16	3.43 ± 0.04
5.50		18.63 ± 0.12	3.39 ± 0.02
6.00		21.10 ± 0.40	3.52 ± 0.07
6.50		22.612 ± 0.03	3.48 ± 0.05
7.50		26.12 ± 0.05	3.48 ± 0.07
3.50	1.88	2.97 ± 0.03	0.85 ± 0.01
	1.94	4.20 ± 0.08	1.20 ± 0.02
	2.00	5.22 ± 0.15	1.49 ± 0.04
	2.25	14.78 ± 0.03	4.22 ± 0.08
	2.37	24.63 ± 0.74	7.04 ± 0.21
2.00	2.43	18.67 ± 0.12	9.33 ± 0.06[b]
3.50	2.45	34.78 ± 0.30	9.94 ± 0.10
4.00	2.50	47.54 ± 0.70	11.89 ± 0.18[c]
		47.13 ± 0.52	11.78 ± 0.13[d]
		46.96 ± 0.50	11.74 ± 0.12[e]
	2.60	80.0 ± 0.80	20.0 ± 0.20[f]
	2.74	130.0 ± 3.9	32.50 ± 1.0[g]
1.00	3.03	85.3 ± 1.93	85.3 ± 1.93[h]

[a] Unless otherwise specified, [Cr(III)] = 5.72 × 10^{-4} M, I = 0.25 M, and T = 25.0 °C. [b] [Cr(III)] = 1.28 × 10^{-4} M. [c] [Cr(III)] = 4.58 × 10^{-4} M. [d] [Cr(III)] = 3.44 × 10^{-4} M. [e] [Cr(III)] = 2.44 × 10^{-4} M. [f] [Cr(III)] = 4.77 × 10^{-5} M. [g] [Cr(III)] = 1.35 × 10^{-4} M. [h] [Cr(III)] = 1.22 × 10^{-4} M.

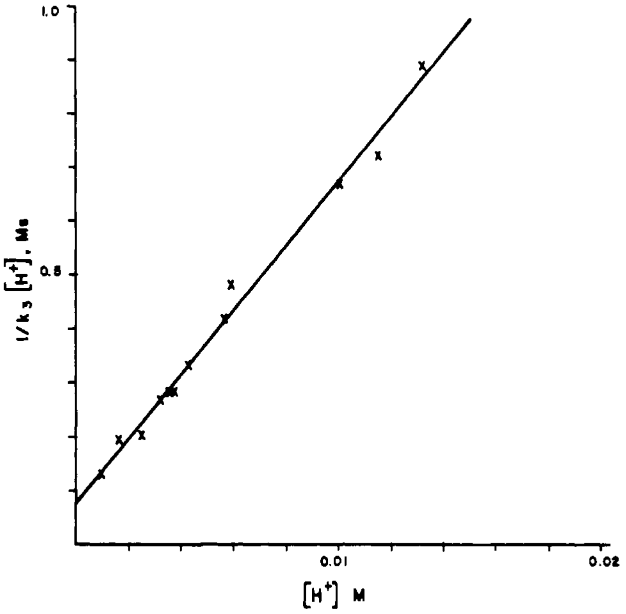

Figure 2. Plot of $1/k_3[H^+]$ vs. $[H^+]$ showing the mixed dependence on hydrogen ion concentration.

Results

The stoichiometry of the chromium(III)–periodate reaction can be represented by eq 1, where $Cr(H_2O)_6^{3+}$ and I(VII)

$$2Cr(H_2O)_6^{3+} + 3I(VII) + H_2O \rightarrow 2HCrO_4^- + 3IO_3^- + 8H_3O^+ \quad (1)$$

represent the total chromium(III) and periodate, respectively. The stoichiometry is consistent with the observations that (i) iodate does not oxidize chromium(III) and (ii) that, when chromium(III) is in excess, the concentration of chromium(VI) produced is two-thirds of the I(VII) present.

At all the chromium(III) concentrations used, in presence of vast excess of periodate, the kinetics showed marked deviation from first-order dependence on [Cr(III)]. Plots of log

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(7) Yousif Sulfab and Mohamed A. Hussein, unpublished results.
(8) Yousif Sulfab, unpublished results.
(9) Albert Haim, *Acc. Chem. Res.*, **8**, 264 (1975).
(10) M. C. R. Symon, *J. Chem. Soc.*, 2794 (1955).
(11) G. W. Haupt, *J. Res. Natl. Bur. Stand.* (*U.S.*), *48*, 414 (1952).
(12) G. P. Haight, Jr., Ellen Perchonock, Franzpeter Emmenegger, and Gilbert Gordon, *J. Am. Chem. Soc.*, **87**, 3835 (1965).
(13) J. N. Butler, "Ionic Equilibrium, A Mathematical Approach", Addison-Wesley, Reading, Mass., 1964, p 362.

$(A_\infty - A_t)$ vs. time, where A_∞ and A_t are the absorbances at infinity and time t, respectively, are all curved. However, plots of $\epsilon/(A_\infty - A_t)$ vs. time were linear up to ≥90% of reaction, over the concentration range $(0.477-5.72) \times 10^{-4}$ M, showing a second-order dependence on [Cr(III)]. Values of the pseudo-second-order rate constant, k_2, were obtained from the slope of plots similar to that shown in Figure 1 and are collected in Table I. The intercepts of the plots similar to that in Figure 1 are in good agreement with the corresponding reciprocals of the concentrations of chromium(III) initially present.

The dependence on periodate concentration was investigated over the range $(0.75-7.50) \times 10^{-2}$ M at fixed [Cr(III)], pH, ionic strength, and temperature. The last column in Table I clearly shows a linear dependence on periodate concentration as indicated by the constancy of k_3, where $k_3 = k_2/[\text{periodate}]$. From these results the rate law, at fixed pH, is given by eq 2.

$$d[\text{Cr(VI)}]/2dt = k_3[\text{Cr(III)}]_T^{\,2}[\text{I(VII)}]_T \qquad (2)$$

The effect of hydrogen ion on the reaction rate was investigated over the pH range 1.88–3.03. It was noted that the reaction is extremely slow at pH <1.0 and rapid at pH >3.0. Table I shows that k_3 is very sensitive to pH variation. A plot of log k_3 vs. log $[\text{H}^+]$ is linear with a slope of −1.8, which, although close to an inverse second-order dependence on $[\text{H}^+]$, pointed to a mixed-order dependence. This was confirmed by plotting $1/k_3[\text{H}^+]$ vs. $[\text{H}^+]$ which gave a linear plot with an intercept as shown in Figure 2. The dependence of k_3 on $[\text{H}^+]$ is, therefore, described by eq 3. From eq 3 and Figure 2 the

$$k_3 = \frac{a}{b[\text{H}^+]^2 + c[\text{H}^+]} \qquad (3)$$

slope is $b/a = 60.0 \pm 2.0$ s^{-1} and the intercept is $c/a = 0.078 \pm 0.013$ M s.

Discussion

The most striking feature of the kinetics of oxidation of chromium(III) by periodate is the second-order dependence on chromium(III) concentration. This was not expected as the oxidant, periodate, undergoes a two-electron gain and the reductant, Cr(III), a three-electron loss.

The inverse hydrogen ion concentration dependence observed points to the involvement of deprotonated forms of chromium(III) and periodate in the rate-determining step. In aqueous acidic solution periodate exists in three forms, IO_4^-, H_4IO_6^-, and H_5IO_6, which are in equilibrium[14] (L^- will be used to represent IO_4^- and H_4IO_6^-). Hexaaquochromium(III) is known to hydrolyze in aqueous solutions to form Cr(OH)^{2+} and has a p$K \approx 4.0$.[15]

The observed kinetics may be described by either Scheme I and/or Scheme II.

Scheme I

$$\text{L}^- + \text{H}^+ \rightleftharpoons \text{HL} \quad (K_1) \qquad (4)$$

$$\text{Cr}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{CrOH}^{2+} + \text{H}^+ \quad (K_h) \qquad (5)$$

$$\text{CrOH}^{2+} + \text{L}^- \rightleftharpoons [\text{Cr–(OH)–L}]^+ \quad (K_2) \qquad (6)$$

$$[\text{Cr–(OH)–L}]^+ + \text{CrOH}_2^{\,3+} \rightleftharpoons [\text{Cr–(OH)–LH–(OH)–Cr}]^{4+} \quad (K_3) \qquad (7)$$

$$[\text{Cr–(OH)–LH–(OH)–Cr}]^{4+} \xrightarrow{\text{rds}} 2\text{Cr(IV)} + \text{IO}_3^- + \text{H}_3\text{O}^+ \quad (k_4) \qquad (8)$$

$$\text{Cr(IV)} + \text{I(VII)} \xrightarrow{\text{fast}} \text{Cr(VI)} + \text{IO}_3^- \qquad (9)$$

The rate law given in eq 10 is derived from the above

$$d[\text{Cr(VI)}]/2dt = \frac{k_4K_2K_3K_h[\text{Cr(III)}]^2[\text{I(VII)}]}{[\text{H}^+](1 + K_1[\text{H}^+])} \qquad (10)$$

mechanism on the assumption that $[\text{Cr(III)}] \approx [\text{Cr}^{3+}]$ and is consistent with the experimental results. The dependence of k_3 on $[\text{H}^+]$ is given by eq 11.

$$k_3 = k_4K_2K_3K_h/([\text{H}^+] + K_1[\text{H}^+]^2) \qquad (11)$$

An alternative mechanism that is also consistent with the rate law is given by Scheme II.[16]

Scheme II

$$\text{L}^- + \text{H}^+ \rightleftharpoons \text{LH} \quad (K_1) \qquad (12)$$

$$\text{Cr}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{CrOH}^{2+} + \text{H}^+ \quad (K_h) \qquad (13)$$

$$\text{CrOH}^{2+} + \text{L}^- \rightleftharpoons [\text{Cr–(OH)–L}]^+ \quad (K_2) \qquad (14)$$

$$[\text{Cr–(OH)–L}]^+ + \text{CrOH}^{2+} \rightleftharpoons [\text{Cr–(OH)–L–(OH)–Cr}]^{3+} \quad (K_4) \qquad (15)$$

$$[\text{Cr–(OH)–L–(OH)–Cr}]^{3+} + \text{H}^+ \xrightarrow{\text{rds}} 2\text{Cr(IV)} + \text{IO}_3^- + \text{H}_3\text{O}^+ \quad (k_5) \qquad (16)$$

$$\text{Cr(IV)} + \text{I(VII)} \rightarrow \text{Cr(VI)} + \text{IO}_3^- \qquad (17)$$

The rate law is given by eq 18. The variation of k_3 with

$$d[\text{Cr(VI)}]/2dt = \frac{k_5K_2K_4K_h^{\,2}[\text{Cr(III)}]^2[\text{I(VII)}][\text{H}^+]}{[\text{H}^+]^2(1 + K_1[\text{H}^+])} \qquad (18)$$

$[\text{H}^+]$ is described in eq 19.

$$k_3 = k_5K_2K_4K_h^{\,2}/([\text{H}^+] + K_1[\text{H}^+]^2) \qquad (19)$$

From a comparison of eq 3, 10, and 19 one obtains $a = k_4K_2K_3K_h$, or $a = k_5K_2K_4K_h^{\,2}$, $b = K_1$, and $c = 1$. The values of a and b were determined as 12.8 ± 2.2 M^{-1} s^{-1} and 770 ± 26 M^{-1}, respectively. The magnitudes of k_4 and k_5 can be estimated as $>(1.29 \pm 0.22) \times 10^5$ and $>(1.29 \pm 0.22) \times 10^9$ M^{-1} s^{-1}, respectively, by substituting $K_h = 10^{-4}$ M and assuming K_2, K_3, and K_4 are small. If K_3 and K_4 are of comparable magnitudes, the high value of k_5 may favor the mechanism in Scheme I. The kinetically determined value of K_1 at $I = 0.25$ M and $T = 25$ °C is reasonable compared to its thermodynamic value of $\sim 10^3$ M^{-1}.

An inner-sphere mechanism is proposed by both schemes. They differ, however, in the mode of entry of the second chromium(III). Scheme I proposes that the second chromium(III) is the hexaaquochromium(III) ion whose bridging to $[\text{Cr–(OH)–L}]^+$ is facilitated by a proton transfer from a coordinated water molecule to an unprotonated oxygen atom of I(VII). Scheme II assumes that hydroxochromium(III) is the second entering chromium(III) ion and that electron transfer is proton activated. In both mechanisms intramolecular electron transfer within the dichromium(III)–iodine(VII) species is considered rate determining.

The I(VII) involved in the formation of the dibridged species is either the labile octahedral H_4IO_6^-[17] and/or the tetrahedral IO_4^-. The H_4IO_6^- ion reacts with the loss of two water molecules, and IO_4^- extends its coordination number to 6.

It is the held view that, in the oxidation of Cr(III) and the reduction of Cr(VI), the change over from Cr(IV) to Cr(V) or vice versa is rate determining.[18] The proposed mechanisms for this reaction assume that the formation of Cr(IV) is the slow step. The mechanisms also claim a rate-determining two

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(14) S. H. Laurie, J. M. Williams, and C. J. Nyman, *J. Phys. Chem.*, **68**, 1311 (1964).

(15) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Wiley, 1972, p 836.

(16) This mechanism was suggested by a reviewer.

(17) I. Pechet and Z. Luz, *J. Am. Chem. Soc.*, **87**, 4068 (1965).

(18) Fred Basolo and Ralph G. Pearson, "Mechanism of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, p 499.

one-electron transfer in a single activated state. Two-electron transfer is commonly proposed for periodate oxidation of organic substrates,[19] for iodide,[20] and for one pathway in the Fe(II)[3] reactions. The transfer of electrons from two chromium(III) ions to I(VII) precludes the formation of a high-energy free-radical I(VI). The formation of I(VI) is probably avoided, in the whole course of this reaction, if Cr(IV) is oxidized in a single step by I(VII) to Cr(VI).

Oxidation of chromium(III) by periodate, based on the validity of the above mechanism, is in accord with the hypothesis that periodate is an inner-sphere oxidant. In this reaction the bridging ligand is supplied by the reductant. An outer-sphere mechanism, on the other hand, may be ruled out on two accounts: (i) the second-order dependence on [Cr(III)] and (ii) the difference in the reactivity between hydroxo- and aquochromium(III) ions. Outer-sphere reactions are generally of the first order in each reactant, and hydroxo and aquo species of a given complex react with comparable rates with a common reactant by an outer-sphere mechanism.[21]

An alternative reaction pathway is to propose that mixed inner- and outer-sphere mechanisms are operative. The inner-sphere electron transfer will be from chromium(III) in $[Cr-(OH)-L]^+$ to I(VII) and a concurrent outer-sphere electron transfer from a second chromium(III) ion.

In conclusion the chromium(III)-periodate reaction exhibited an unusual second-order dependence on [Cr(III)]. The reaction does not contradict the hypothesis that periodate is an inner-sphere oxidant as, at least, one electron is transferred via an inner-sphere pathway to I(VII). Hydroxochromium(III) ion is the first entering chromium(III) as it is capable of bridging the two reactants via its coordinated hydroxide ligand.

Registry No. Cr^{3+}, 16065-83-1; IO_4^-, 15056-35-6.

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(19) B. Sklarz, *Q. Rev., Chem. Soc.*, **21**, 3 (1967).

(20) A. Indelli, F. Ferranti, and F. Secco, *J. Phys. Chem.*, **70**, 631 (1966).

(21) N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1968).

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Complexation Kinetics and Equilibria of Nickel(II) with Vanillomandelic, Mandelic, and Thiolactic Acid Ligands

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The complexation reactions of Ni^{2+} with the monovalent bidentate ligands vanillomandelic, mandelic, and thiolactic acids were studied at 25 °C and ionic strength 0.5 M (KNO_3) by temperature-jump and stopped-flow methods. The formation rate constants determined for the reaction

$$Ni^{2+} + HL^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NiHL^+$$

were $(3.64 \pm 0.39) \times 10^3$, $(4.93 \pm 0.56) \times 10^3$, and $(7.66 \pm 0.52) \times 10^3$ M^{-1} s^{-1} for vanillomandelic acid, mandelic acid, and thiolactic acid, respectively. Stability constants for the formation of the metal mono complexes were determined by utilizing the Bjerrum titration technique. The values obtained for $K_{NiHL} = [NiHL^+]/[Ni^{2+}][HL^-]$ were 32.93 ± 8.66 (Ni^{2+}-vanillomandelic acid), 45.46 ± 8.07 (Ni^{2+}-mandelic acid), and 56.58 ± 10.63 M^{-1} (Ni^{2+}-thiolactic acid). The kinetics of complex formation is discussed in terms of two different rate-determining steps, sterically controlled substitution and internal hydrogen bonding, as the results do not support the more usual dissociative substitution mechanism on nickel(II).

Introduction

In the field of solution kinetics, Ni^{2+} is one of the more extensively investigated transition-metal ions. The attention paid to nickel(II) is due not only to general interest in the kinetics of metal-complexation reactions, but also to the fact that the rate constants for nickelous ion substitution fall within a convenient time range. Few surprises have resulted from these studies; usually the formation of a mono complex follows the multistep Eigen mechanism,[1] in which an incoming ligand replaces one or more coordinated water molecules depending on its denticity. The overall rate is not determined by ligand characteristics but by the rate of loss of the first water molecule from the inner-sphere coordination shell.

Deviations from this "normal" substitution, in which the rate constants obtained are lower than those predicted by the Eigen mechanism, have been attributed to processes involving rate-determining chelate ring closure (sterically controlled substitution),[2,3] steric hindrance,[4,5] protonated ligands,[3,6] and, in some instances, ligands in which the reactive site is blocked due to internal hydrogen bonding.[6,7]

Abnormally low rate constants have been obtained for Ni^{2+} complexation reactions with the monovalent bidentate chelates

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(1) Eigen, M.; Wilkins, R. G. *Adv. Chem. Ser.* **1965**, *No. 49*, 55.

(2) Kowalak, A.; Kustin, K.; Pasternack, R. F.; Petrucci, S. *J. Am. Chem. Soc.* **1967**, *89*, 3126.

(3) (a) Margerum, D. W.; Cayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In "Coordination Chemistry"; Martell, A. E., Ed.; American Chemical Society: Washington, D.C., 1978; Vol. 2, Chapter 1. (b) The reaction between a metal ion and an amino acid ligand has been extensively investigated, especially with regards to the relative reactivities of the amino acid anion and the protonated amino acid (zwitterion). Cf.: Cassatt, J. C.; Wilkins, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 6045. Letter, J. E., Jr.; Jordan, R. B. *J. Am. Chem. Soc.* **1975**, *97*, 2381, and other references in ref 3a. The α-substituted carboxylic acid and ortho-substituted benzoic acid ligands reported on in this paper are not analogous to the amino acid zwitterion ($^+H_3NRCOO^-$) since the α or ortho substituents do not lose their protons upon substitution.

(4) Turan, T. S. *Inorg. Chem.* **1974**, *13*, 1584.

(5) Turan, T. S.; Rorabacher, D. B. *Inorg. Chem.* **1972**, *11*, 288.

(6) Perlmutter-Hayman, B.; Shinar, R. *Inorg. Chem.* **1976**, *15*, 2932.

(7) Mentasti, E.; Pelizzetti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* **1979**, *7*, 2007.