vanadium(III). The observed dependence of k_2 upon the concentration of vanadium(III) is consistent with a decrease in the amount of disproportionation of dichloride ion as the vanadium(III) concentration is increased.

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Kinetics and Mechanism of the Oxidation of Vanadium(III) by Chlorate Ion, Chlorine Dioxide, Chlorous Acid, and Hypochlorous Acid

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The reactions of hypochlorous acid, chlorous acid, and chlorine dioxide with vanadium(III) have been surveyed. The apparent second-order rate constants have been evaluated to be 3, 75, and 22 $M^{-1}\ s^{-1}$, respectively. The rate of the reaction of chlorate ion with vanadium(III) has also been studied and has been found to be independent of the concentration of hydrogen ion. The reaction proceeds predominantly by a one-electron-transfer process with an apparent second-order rate constant of 5.4 $M^{-1}\ s^{-1}$. The similarity of the rate constants for the reactions of all of these chlorine oxidants with vanadium(III) is discussed and contrasted with reactions of the chlorine oxidants with other metal ions.

Introduction

The rates of reaction of the various chlorine oxidants with a given metal ion often differ by several orders of magnitude.[1-3] All of these chlorine species are thermodynamically strong oxidants, and the reasons for the variation in rate are poorly understood. This paper presents the results of a study of the rate of oxidation of vanadium(III) by chlorate ion, chlorine dioxide, chlorous acid, and hypochlorous acid. The kinetics of the reaction between chlorine and vanadium(III) have been described previously.[1]

The selection of vanadium(III) as the reductant for this study allowed for the possibility of either one- or two-electron-transfer processes as the major reaction pathways. In addition, the rates of reaction of chlorate ion and chlorine dioxide[2] and of hypochlorous acid and chlorine[3] with vanadium(IV) have been reported. A knowledge of these rates was anticipated to be useful for comparison or contrast with the results obtained in the present study.

Experimental Section

Vanadium(IV) perchlorate solutions were prepared by electrolysis of a suspension of vanadium pentoxide in 3–5 M perchloric acid.[1,4] The vanadium(IV) concentration was determined by titration with potassium permanganate solution[5,6] at 60 °C, and the hydrogen ion concentration was determined by using an ion-exchange technique.[7] Solutions of vanadium(III) were prepared by the reaction of equal moles of vanadium(II) and vanadium(IV) as described previously.[1]

Reagent grade sodium chlorate was recrystallized from water. Solutions were standardized by passing aliquots through columns of cation-exchange resin in the acid form and by titrating the resulting acid.[7]

Chlorine dioxide was prepared by the general method of Bray.[8,9] A mixture of 10 g of oxalic acid, 25 g of potassium chlorate, and 30 ml of 3 M sulfuric acid was heated to 50 °C by a water bath. The yellow gas produced was carried by a nitrogen stream through two 2 M sodium carbonate bubblers to remove carbon dioxide and then into a cold solution of the desired acidity and ionic strength. The concentration of chlorine dioxide was estimated spectrophotometrically

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from the reported value of 1250 ± 3 M^{-1} cm^{-1} for the molar absorptivity at 358.5 nm.[9]

Sodium chlorite solutions were prepared by dissolving the solid in water. The concentration of chlorite ion was determined by the addition of an aliquot to an acidic solution of potassium iodide. The iodine liberated was titrated with standard sodium thiosulfate solution. In the kinetic studies, neutral solutions of sodium chlorite were mixed with vanadium(III) solutions which contained the appropriate amount of acid.

Hypochlorous acid was prepared by the method of Cady.[10] Chlorine monoxide is produced by the action of mercuric oxide on chlorine dissolved in carbon tetrachloride, and hypochlorous acid results from shaking an aqueous solution with the chlorine monoxide solution. Solutions of hypochlorous acid were prepared fresh daily and were standardized iodometrically using a calibrated drive syringe[11] of the stopped-flow apparatus to deliver an aliquot under the surface of a potassium iodide solution.

Phenol was obtained as crystals which contained approximately 0.15% hypophosphorous acid as a preservative. The crystals were dissolved in water and the concentration of phenol was determined spectrophotometrically at 270 nm where the molar absorptivity[12] is 1474 M^{-1} cm^{-1}.

Sodium perchlorate was prepared from the carbonate and perchloric acid,[7] and solutions were standardized by the method used for sodium chlorate solutions. Sodium chloride solutions were prepared gravimetrically. Perchloric acid solutions were made by dilution of the concentrated acid and were standardized by titration with standard sodium hydroxide solution.

Kinetic studies involving hypochlorous acid, chlorous acid, or chlorine dioxide as reactants were performed at 25.0 ± 0.1 °C by using a Durrum stopped-flow spectrophotometer equipped with a Teflon cell. The volume of the solution which flows through the cell in each experiment was adjusted to be at least 0.68 ml to ensure that all of the reactant solutions came directly from the drive syringes[13] where temperature control is most effective. Kinetic studies involving chlorate ion as a reactant utilized both the stopped-flow apparatus and a rapid-mix syringe[14] in conjunction with a Beckman DU spectrophotometer. The stopped-flow apparatus was used only for experiments at 25 °C. In all experiments, the ionic strength was maintained at 2.0 M using sodium perchlorate.

The rate of the reaction of chlorate ion with vanadium(III) was monitored at 358.5 nm where the initial product which is chlorine dioxide has a molar absorptivity[9] of 1250 ± 3 M^{-1} cm^{-1}. The stoichiometry of the reaction was determined from the change in absorbance at this wavelength. The rates of the other reactions and the stoichiometry of the chlorous acid reaction were determined from absorbance changes at 760 nm where the molar absorptivities of vanadium(III) and vanadium(IV) were measured to be 0.4 ± 0.1 and 17.0 ± 0.1 M^{-1} cm^{-1}.

Hypochlorous acid solutions were thermostated before introduction into the stopped-flow apparatus, as previously described for chlorine solutions,[1] in an attempt to minimize losses due to volatilization.

The reaction between vanadium(III) and chlorous acid was studied in the presence of excess vanadium(III) and in the presence and in the absence of phenol. When phenol was used, it was added to the vanadium(III) solution after the vanadium(II) and vanadium(IV) had reacted. Independent experiments revealed that the visible spectrum of vanadium(III) was not changed by the presence of 0.1 M phenol and that, on the time scale of the vanadium(III)–chlorous acid reaction, no change in absorbance at 760 nm occurred when a vanadium(IV) solution and 0.1 M phenol were mixed. The vanadium(III)–chlorine dioxide reaction was studied only in the presence of excess vanadium(III), and the vanadium(III)–chlorate ion reaction was studied in the presence of excess chlorate ion. These conditions were chosen in order to minimize the effect of consecutive reactions on the observed rates.

The mathematical analyses in this study utilized the nonlinear least-squares program[15] FIT70. For fits of absorbance–time data, unit weights were used, and for fits of observed rate constants at various temperatures to determine activation parameters, $(1/k_{obsd})^2$ weights were used. All rate constants reported in this paper are those appropriate to the equation

$$-\frac{1}{n}\frac{d[V(III)]}{dt} = k_{obsd}[V(III)][oxidant] \qquad (1)$$

where n is the appropriate integral change in oxidation state for the chlorine-containing oxidizing agent.

Table I. Approximate Rate Constants from Initial Rates^a for the Reaction between Vanadium(III) and Hypochlorous Acid in 1.00 M Hydrogen Ion at 25 °C

$[V(III)]_0$, M	$[HOCl]_0$, M	k_{obsd}, M^{-1} s^{-1}
0.007 73	0.003 00	2.6
0.059 6	0.052 4	3.0
0.059 6	0.003 00	7.3

^{a} Stoichiometric coefficient, $n = 2$.

Table II. Effect of Phenol on the Stoichiometry of the Reaction between Vanadium(III) and Chlorous Acid

$[V(III)]_0$, M	$10^4[HClO_2]_0$, M	$[V(IV)]_{obsd}/[HClO_2]_0$
0.006 69^a	5.67	3.57
0.006 69^a	5.67	3.87^c
0.029 7^a	21.2	3.79
0.007 73^b	13.7	1.08
0.006 69^b	21.2	1.05
0.006 69^b	5.67	1.06

^{a} In the absence of phenol. ^{b} With 0.05 M phenol added initially. ^{c} 0.25 M chloride ion present.

Table III. Rate Constants^a for the Reaction between Chlorous Acid and Vanadium(III) in 1.00 M Hydrogen Ion at 25 °C

$[V(III)]_0$, M	$[HClO_2]_0$, M	k_{obsd}, M^{-1} s^{-1}	$[V(III)]_0$, M	$[HClO_2]_0$, M	k_{obsd}, M^{-1} s^{-1}
0.029 7	0.002 10	73.9^b	0.007 73	0.001 37^c	74.2 ± 0.3
0.006 69	0.002 10^c	77.5 ± 1.1	0.029 7	0.002 12^{c,d}	203 ± 1

^{a} Stoichiometric coefficient, $n = 1$. ^{b} In the absence of phenol. Rate constant evaluated by the method of initial rates. ^{c} In the presence of 0.05 M phenol. ^{d} 0.2 M hydrogen ion.

Results

Reaction of Vanadium(III) with Hypochlorous Acid. When solutions of vanadium(III) and hypochlorous acid are mixed, the rate of appearance of vanadium(IV) at first increases as the reaction proceeds. This rate behavior complicates the detailed analysis of the entire reaction curve. Thus, initial rate measurements were used to determine the approximate values for observed rate constants presented in Table I.

Reaction of Vanadium(III) with Chlorous Acid. When the reaction between chlorous acid and excess vanadium(III) is monitored at 760 nm, an initial rapid increase in absorbance is followed by a much slower but larger increase. Phenol, which was used to scavenge chlorine-containing intermediates in two related studies,[16,17] was added to the reaction mixture in an attempt to remove the source of the slower reaction. The result was a change in stoichiometry and a reaction curve which corresponded to only the initial rapid reaction observed in the absence of phenol. Table II presents stoichiometric coefficients for the vanadium(III)–chlorous acid reaction in the presence and in the absence of phenol. In the absence of phenol the stoichiometry approaches that given by eq 2. In

$$4V(III) + HClO_2 = 4V(IV) + Cl^- \qquad (2)$$

the presence of phenol the stoichiometry is approximately 1 mol of vanadium(III) reacting with 1 mol of chlorous acid. The observed second-order rate constants presented in Table III have been determined from experiments in the presence and in the absence of phenol. For those experiments in the presence of phenol, the entire reaction curve was fitted. The method of initial rates was used to derive the rate constants in the absence of phenol. The experimental values of the rate constants can be used as evidence that the presence of phenol

Table IV. Rate Constants[a] for the Vanadium(III)–Chlorine Dioxide Reaction in 1.00 M Hydrogen Ion at 25 °C

$[V(III)]_0$, M	10^5-$[ClO_2]_0$, M	k_{obsd}, M^{-1} s^{-1}	$[V(III)]_0$, M	10^5-$[ClO_2]_0$, M	k_{obsd}, M^{-1} s^{-1}
0.0596	3.71	24.4 ± 0.6	0.0596	19.8	18.6 ± 0.3
0.0298	3.82	23.3 ± 0.3	0.0298	21.1	18.0 ± 0.4

[a] Stoichiometric coefficient, $n = 1$.

Table V. Stoichiometry of the Vanadium(III)–Chlorate Ion Reaction as a Function of Reactant Ratio

$10^5[V(III)]_0$, M	$[ClO_3^-]_0$, M	$[ClO_3^-]_0/[V(III)]_0$	$[ClO_2]_{obsd}/[V(III)]_0$
10.5	0.500	4762	0.99
10.5	0.050 0	476	0.89
19.9	0.018 1	91.0	0.87
8.35	0.002 32	27.7	0.76
16.7	0.002 32	13.8	0.43
10.5	0.005 00	6.2	0.40

has a negligible effect on the initial reaction and that the rate of the vanadium(III)–chlorous acid reaction increases as the concentration of hydrogen ion decreases. From the limited data presented, the apparent order of the reaction with respect to the concentration of hydrogen ion is calculated to be about −0.6.

Reaction of Vanadium(III) with Chlorine Dioxide. Table IV presents rate constants for the vanadium(III)–chlorine dioxide reaction. For the two experiments in the presence of a large excess of vanadium(III), pseudo-first-order plots were linear for all data collected. For those experiments in the presence of a small excess of vanadium(III), the slope of pseudo-first-order plots decreased sharply after about 75% of reaction owing to side reactions of the intermediates. For these latter experiments, only data corresponding to less than 75% of reaction were used in the evaluation of the rate constants. The average value of the apparent second-order rate constant is 22.3 ± 5.4 M^{-1} s^{-1}.

Reaction of Vanadium(III) with Chlorate Ion. An experiment at 5.5 °C in the presence of a 40-fold excess of chlorate ion was used to demonstrate that the initial product of the vanadium(III) reduction of chlorate ion is chlorine dioxide. At this low temperature, a spectrum from 300 to 440 nm taken 45 s after mixing revealed the characteristic fine structure of the chlorine dioxide spectrum.

Table V lists the results of a series of experiments designed to determine the stoichiometry of the reaction between chlorate ion and vanadium(III). The largest yield of chlorine dioxide measured was 99% for an experiment in the presence of nearly a 5000-fold excess of chlorate ion. The stoichiometry for this experiment may be represented by eq 3. Under conditions

$$V(III) + ClO_3^- = V(IV) + ClO_2 \tag{3}$$

of a smaller excess of chlorate ion, the percentage yield of chlorine dioxide decreases. Both the consecutive reaction[2] between the products of reaction 3 and the parallel reaction of vanadium(III) with chlorine dioxide would be expected to reduce the apparent yield of chlorine dioxide under these conditions.

Table VI. Rate Constants[a] for the Reaction between Vanadium(III) and Chlorate Ion in 1.00 M Hydrogen Ion

$10^4[V(III)]_0$, M	$[ClO_3^-]_0$, M	T, °C	k_{obsd}, M^{-1} s^{-1}
1.50	0.002 00	15.8	2.27[b]
1.50	0.002 00	20.2	3.20[b]
2.15	0.018 1	25.0	5.86[c]
77.3	0.500	25.0	5.43
8.08	0.500	25.0	5.25
1.05	0.500	25.0	5.35[d]
74.5	0.077 6	25.0	6.33
1.05	0.050 0	25.0	5.31
8.08	0.050 0	25.0	5.37
2.15	0.018 1	25.0	5.01[e]
2.15	0.018 1	25.0	4.79[e,f]
8.08	0.005 00	25.0	5.34
1.05	0.005 00	25.0	5.60
0.834	0.002 32	25.0	5.90[b]
1.67	0.002 32	25.0	6.14[b]
2.15	0.018 1	25.0	4.39[g]
2.15	0.018 1	25.0	4.85[h]
2.15	0.018 1	25.0	4.75[i]
1.50	0.002 00	30.1	8.39[b]
1.50	0.002 00	35.5	14.4[b]
1.50	0.002 00	40.2	20.4[b]

[a] Stoichiometric coefficient, $n = 1$. [b] Experiments using rapid-mix syringe. [c] $[H^+] = 1.99$ M. [d] Entire reaction curve fitted; standard deviation of the fit ±0.20. [e] $[H^+] = 1.02$ M. [f] 0.25 M chloride ion present initially. [g] $[H^+] = 0.518$ M. [h] $[H^+] = 0.318$ M. [i] $[H^+] = 0.118$ M.

In order that these competing reactions do not affect the observed rate constants, the method of initial rates was used, except for the experiment in the presence of a nearly 5000-fold excess of chlorate ion. For that experiment the entire reaction curve was fitted. Rate constants from experiments over a wide variation in concentration and at six different temperatures are given in Table VI. Variation of the hydrogen ion concentration from 0.12 to 2.0 M had no effect on the value of the rate constant, nor did the presence of 0.25 M chloride ion. The average value of the observed rate constant at 25 °C is 5.4 ± 0.5 M^{-1} s^{-1}. Activation parameters fitted[15] to the observed variation with temperature are $\Delta H^{\ddagger} = 15.9 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = -1.9 \pm 1.5$ eu.

Discussion

The increasing reaction rate observed when vanadium(III) and hypochlorous acid are mixed is consistent with the production of chloride ion which reacts with hypochlorous acid to form chlorine.[3] The chlorine reacts more rapidly with vanadium(III) than does hypochlorous acid.[1] The concentration of chlorine initially present is small but finite. The rate law reported[1] for the vanadium(III)–chlorine reaction exhibits one term which is expressed as independent of chlorine. In view of this rate law, during the experiment reported here a significant fraction of the vanadium(III) may be oxidized by the chlorine present in the hypochlorous acid solutions. This competitive reaction would have the effect of increasing the observed rate constants, and the rate constants presented for the oxidation of vanadium(III) by hypochlorous acid in Table I must therefore be regarded as upper limits.

The observation of a fast reaction followed by a slower process when vanadium(III) reacts with chlorous acid can be understood in terms of an initial reaction in which chlorous acid reacts rapidly with vanadium(III) to form vanadium(IV) and a reduced chlorine species. The chlorine-containing intermediate either could react slowly with vanadium(III) or chlorous acid or could decompose to form other chlorine species which react with vanadium(III) or chlorous acid. The general features of this mechanism are consistent with observations on reactions of chlorous acid with iron(II)[16] and uranium(IV).[17,18] In the presence of phenol, the stoichiometry is approximately 1 mol of vanadium(III) reacting with 1 mol of chlorous acid. This stoichiometry can be taken as evidence that the predominant species scavenged by phenol corresponds to chlorine(II), which would be the product of a one-electron-transfer process.

The reaction between chlorous acid and iron(II) has been found to proceed via a one-electron process.[16] The lifetime

Table VII. Activation Parameters for Reactions of Chlorate Ion with Various Metal Ions

Metal ion	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
Cr(II)	11.2 ± 0.1	−17 ± 0.4	23
V(II)	9.9 ± 0.2	−23 ± 2.0	7
V(III)	15.9 ± 0.5	−1.9 ± 1.5	This work

of the chlorine(II) species resulting from the one-electron reduction of chlorous acid was apparently too short in that system to allow its reaction with phenol. The stoichiometry in the presence of phenol was interpreted in terms of scavenging of chlorine(I). If the same chlorine(II) species is produced in both the vanadium(III) and the iron(II) reduction of chlorous acid, its reaction with vanadium(III) is apparently slower than that with iron(II). This ordering of relative rates would have precedent in the rates of reaction of chlorate ion with vanadium(III) and iron(II).

In the reaction between chlorine dioxide and vanadium(III), the formation of chlorine dioxide by interaction of chlorous acid with chlorine or hypochlorous acid[19] would cause the observed deviation from pseudo-first-order behavior. These last three chlorine species correspond to successive reduction products of chlorine dioxide and after 75% of reaction would be responsible for the formation of chlorine dioxide.[19] The rate of the consecutive reactions of the various intermediates, relative to the rate of the vanadium(III)–chlorine dioxide reaction, is greatest for the experiments with the smallest excess of vanadium(III), which is consistent with the expected deviations from pseudo-first-order behavior.

The stoichiometry of the vanadium(III)–chlorate ion reaction in the presence of a 5000-fold excess of chlorate ion is evidence that the reaction proceeds via a one-electron-transfer process. A two-electron pathway would produce chlorine(III) and reduce the amount of chlorine dioxide observed. A predominant one-electron pathway is not surprising in view of the stability[2] of the products chlorine dioxide and vanadium(IV).

A common basis for distinction between inner- and outer-sphere electron-transfer processes is a comparison of the rates with the rates of substitution reactions. The average value of the observed second-order rate constant at 25 °C for the reaction between vanadium(III) and chlorate ion as reported here is intermediate between rate constants determined for the substitution reactions of azide ion[20] and thiocyanate ion[21,22] on vanadium(III). In the reported rate laws, the rate constants for the terms independent of the hydrogen ion concentration are reported to be 0.39 $M^{-1}\ s^{-1}$ for azide ion[20] and 114 and 104 $M^{-1}\ s^{-1}$ for thiocyanate[21,22] ion. In that the rate of the vanadium(III)–chlorate ion reaction is not faster than the substitution reactions, the rate comparison does not support a conclusion as to whether the reaction of vanadium(III) with chlorate ion proceeds via an inner-sphere or an outer-sphere pathway.

The values of enthalpy and entropy of activation for the reactions of several metal ions with chlorate ion are presented in Table VII. The values of $\Delta S^\ddagger$ for the reactions of chromium(II) and vanadium(II) are considerably smaller than for the reaction of vanadium(III). The chromium(II) reaction is primarily an inner-sphere electron-transfer process in that oxygen from the chlorate ion is retained in the coordination sphere of the chromium(III) product.[23] A more positive value for $\Delta S^\ddagger$ would be expected for systems in which an initial displacement of a coordinated water molecule does not occur. The values in Table VII are thus consistent with inner-sphere mechanisms for the chromium(II) and vanadium(II) reactions and an outer-sphere mechanism for the vanadium(III) reaction.

Table VIII. Rate Constants for the Major Pathways of the Reactions of Chlorine Oxidants with Vanadium(II), Vanadium(III), and Vanadium(IV) in 1.00 M Hydrogen Ion at 25 °C

Chlorine oxidant	Obsd rate const, $M^{-1}\ s^{-1}$		
	V(II)	V(III)	V(IV)
ClO_3^-	3.0[a]	5.4	0.01[b]
ClO_2		22.3	5[b]
$HClO_2$		75.0	
HOCl		(3)	5.5[c]
Cl_2	250.0[d]	20[e]	0.004[c]

[a] 20; ref 7. [b] Reference 2. [c] Reference 3. [d] Reference 24. [e] Reference 1.

The values of the rate constants for reactions of the chlorine oxidants chlorate ion, chlorine dioxide, chlorous acid, hypochlorous acid, and chlorine with vanadium(III) exhibit a striking similarity. A summary of these rate constants appears in Table VIII. The available results for the same reactions with vanadium(II)[7,24] and vanadium(IV)[2,3] are included in the table for comparison. The largest and smallest rate constants for the redox reactions with vanadium(III) differ by a factor as small as 25. For vanadium(IV) the factor is greater than 10^3. The latter factor is more typical for the reactions of the chlorine oxidants with metal ions. It is interesting to speculate that all of the reactions of these chlorine oxidants with vanadium(III) might proceed via outer-sphere pathways or possibly pseudo-inner-sphere reactions in which the oxidant attacks the trigonal face of the vanadium(III) species. The observed small variations in rate are consistent with either mechanism as are the activation parameters determined for the reaction between vanadium(III) and chlorate ion.

The dependences of the rates of the reactions of chlorate ion and chlorous acid with vanadium(III) upon the concentration of hydrogen ion have been determined. Both of these dependences are consistent with the observations of Newton and Baker[25] that the order with respect to the acid concentration is between zero and the number of hydrogen ions gained in the overall reaction. The reaction of chlorine[1] with vanadium(III) has also been noted to be in agreement with this general observation. These results are further support for the relationship between the hydrogen ion dependence of the rate and the hydrogen ion stoichiometry of the overall reaction.

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Registry No. V, 7440-62-2; HOCl, 7790-92-3; $HClO_2$, 13898-47-0; ClO_2, 10049-04-4; ClO_3^-, 14866-68-3.

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Kinetic Study of the 1:1 Equilibration of Thiocyanate with the Molybdenum(IV)–Aquo Ion

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The kinetics of the equilibration of thiocyanate with the molybdenum(IV)–aquo ion

$$MoO^{2+} + NCS^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} MoO(NCS)^+$$

have been studied by conventional spectrophotometry in perchloric acid, $[H^+] = 0.75–2.0$ M, $I = 2.00$ M ($LiClO_4$), at temperatures in the range 10–25 °C. The equilibrium constant K_1 for (i) has been determined spectrophotometrically and has a value 405 ± 35 M^{-1} at 25 °C in 2 M $HClO_4$, with $\Delta H_1 = -6.7 \pm 0.9$ kcal mol^{-1} and $\Delta S_1 = -10.5 \pm 3.0$ cal K^{-1} mol^{-1}. First-order rate constants, k_{obsd}, for equilibration i can be expressed as $k_{obsd} = (k_1 + k_2[H^+]^{-1})([NCS^-] + K_1^{-1})$. At 25 °C, rate constants for the forward reaction are $k_1 \approx 0.23$ M^{-1} s^{-1} and $k_2 = 1.25$ s^{-1}. Activation parameters for the dominant $[H^+]^{-1}$-dependent pathway k_2 are $\Delta H_2^{\ddagger} = 14.9 \pm 0.25$ kcal mol^{-1} and $\Delta S_2^{\ddagger} = -8.1 \pm 0.9$ cal K^{-1} mol^{-1}.

Souchay et al.[1] first prepared the aquomolybdenum(IV) ion in 1966 by heating solutions containing Mo(III) and Mo(V) species. The same ion has been obtained from Mo(III) and Mo(VI).[2] Evidence in favor of a mononuclear divalent cationic structure, MoO^{2+}, in noncomplexing aqueous media has been reported.[3] Ardon and Pernick[4] in 1973 suggested that the structure was dimeric. More recent studies in these laboratories have provided conclusive evidence that the ion is monomeric.[5] A formula MoO^{2+}, or less likely $Mo(OH)_2{}^{2+}$, has been assigned in agreement with Souchay et al.[3] The first full kinetic study aimed at evaluating the substitution properties of the molybdenum(IV)–aquo ion is described in this paper. A spectrophotometric study of the reaction of Mo(IV) with thiocyanate has previously been reported.[6] However the conditions used, sulfate buffer pH 1.9, were very different from those in this study, and no kinetic data were presented.

Experimental Section

Reagents. Sodium thiocyanate (GPR, Hopkin and Williams) was recrystallized once from ethanol. Thiocyanate solutions were standardized by titration against mercury(II) with iron alum as indicator or against silver(I) with eosin (tetrabromofluorescein) as indicator. Sodium molybdate, $Na_2MoO_4 \cdot H_2O$ (Analar, BDH), was used without further purification. The complex $(NH_4)_2[MoCl_5(H_2O)]$ was prepared as described previously,[7] and $K_3[MoCl_6]$ was generously provided by the Molybdenum Climax Co. Lithium perchlorate was prepared from 72% perchloric acid (Analar, Hopkin and Williams) and lithium carbonate (Reagent grade, BDH) and purified by recrystallization. *p*-Toluenesulfonic acid (HPTS) (Aldrich Chemical Co.) was purified by recrystallization from water.

Aquomolybdenum(IV). A solution of $Na_2MoO_4 \cdot H_2O$ in 2 M HCl (25 ml, 0.3 M) was added to a solution of $K_3[MoCl_6]$ or $(NH_4)_2[MoCl_5(H_2O)]$ in 2 M HCl (50 ml, 0.3 M). Both solutions were deoxygenated by passing nitrogen through them for 30 min prior to mixing. The reaction mixture was kept for 1 h at 90 °C under N_2, and the resultant stock solution stored in the refrigerator. For normal purposes 5–10 ml of this stock was diluted ca. 50 times with 0.5 M HPTS and left to stand at room temperature for at least 1 day to allow aquation of coordinated chloride. To isolate the aquo ion the solution was transferred to a Dowex 50W-X2 cation-exchange column (12 cm × 1.2-cm diameter). A red band was held on the column and a diffuse yellowish brown band of Mo(V) dimer formed below this. Elution of the Mo(V) was achieved with 0.5 M HPTS. The red band moved slowly under these conditions and in some cases split into two, the first of which was eluted with 1.0 M HPTS and was shown to contain chloride ions. The second band, the aquomolybdenum(IV) ion, was eluted with 2.0 M HPTS. To obtain Mo(IV) in perchlorate medium the HPTS solution was again ion exchanged on Dowex 50W-X2 resin, but this time with a very short (ca. 0.5 cm) column and by eluting with 2 M $HClO_4$ after first moving the band to the bottom of the column with 1 M $HClO_4$. The Mo(IV) was determined by titration against cerium(IV), when oxidation to Mo(VI) occurs, using ferroin indicator.

Stability and Spectrum of Mo(IV). Solutions of Mo(IV) in 2 M HPTS were quite stable to aerobic oxidation, and the loss of Mo(IV) was less than 10%/day. In the absence of oxygen such solutions appear to be stable indefinitely. Molybdenum(IV) in perchlorate is generally very much less stable and aerobic oxidation of such solutions can be quite rapid. The stability of Mo(IV) in deoxygenated perchlorate solutions is variable since solutions were often stable for over 1 day at room temperature, but at other times only for 1 h or so. Such solutions were much more stable when maintained at <0 °C and with $[H^+]$ as high as possible (ca. 2.0 M). With such precautions small amounts of oxygen could even be tolerated, and in this study it was not always necessary to work in strictly anaerobic conditions.

Attempts were made to determine the acid dissociation constant K_a for the 2+ molybdenum(IV)–aquo ion by measuring absorption changes of solutions $[HClO_4] = 0.02–0.20$ M, $I = 2.00$ M ($LiClO_4$), at 250 nm. However these changes were not always rapidly established and it seems unlikely that protonation alone is important. For example, small (6%) changes in absorbance ($t_{1/2}$ = ca. 3 min) were observed on changing the $[H^+]$ from 0.65 to 0.055 M. Over short time intervals the changes appeared to be reversible. These absorbance changes may reflect polymerization processes in solution, a phenomenon which is not perhaps too surprising in view of the behavior exhibited by some other tetravalent transition metal ions such as Zr(IV) and Hf(IV). To avoid such changes $[H^+]$ values were restricted to ≥0.75 M, although this probably represents an overcautious approach. For such a range of $[H^+]$ values it is assumed that $K_a << [H^+]$.

The absorption spectrum of Mo(IV) in 1 M $HClO_4$, Figure 1, has two absorption maxima, λ 303 nm (ε 265 M^{-1} cm^{-1}) and 505 nm (ε 63 M^{-1} cm^{-1}). Solutions in 1 M HPTS give additional absorption < ca. 300 nm due to the PTS^- ion. The visible spectrum reported here is in good agreement with spectra reported elsewhere.[3,4]

Equilibrium Constants. Absorbance changes for a series of solutions at constant $[H^+]$, constant [Mo(IV)], and varying $[NCS^-]$, $I = 2.00$