Volume 15
Number 5
May 1976

Inorganic Chemistry

Contribution from the Departments of Chemistry, University of Iowa, Iowa City, Iowa 52242, and Miami University, Oxford, Ohio 45056

Kinetics and Mechanism of the Oxidation of Vanadium(III) by Chlorine in Aqueous Solution

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Received July 18, 1975

AIC504741

The stoichiometry of the reaction of chlorine with vanadium(III) is dependent upon which reactant is in excess. In the presence of excess vanadium(III), vanadium(III) is oxidized to vanadium(IV), while in the presence of excess chlorine, vanadium(V) is also formed. The rate of the reaction has been measured at 400 and 760 nm. In the presence of excess vanadium(III) this rate can be expressed by the equation $-d[V(III)]/2dt = d[V(IV)]/2dt = k_a'[V(III)] + k_b'[V(III)][Cl_2]$, in which the values of k_a' and k_b' depend upon the inverse of the hydrogen ion concentration. At 25 °C in 1.0 M perchloric acid $k_a' = 0.044 \pm 0.014\ s^{-1}$ and $k_b' = 19.9 \pm 2.1\ M^{-1}\ s^{-1}$. In the presence of excess chlorine, the nonintegral stoichiometry necessitates a more complex expression of the rate. The rate of appearance of vanadium(V), measured at 292 nm, and the induced oxidation of cobalt(II) are given as evidence that the reaction proceeds predominantly by a one-electron-transfer process.

Introduction

The reaction between vanadium(III) and chlorine is of interest because both reactants can potentially react via either one- or two-electron-transfer processes. The equilibria[1-5] and rates of reaction[5-7] which determine the relative amounts of the species chlorine, chloride ion, trichloride ion, and hypochlorous acid in acidic aqueous "chlorine" solutions have been well characterized. Flash photolysis[8-10] and pulse radiolysis[11,12] have been used to investigate selected reactions of the dichloride radical anion. The rate of the reaction between vanadium(III) and vanadium(V) to form vanadium(IV) has also been studied in detail.[13] The understanding of these reactions provides the requisite background for a thorough study of the oxidation of vanadium(III) by chlorine.

This reaction is of further interest in view of investigations[14-20] of the reactions of chlorine and hypochlorous acid with metal ions or metal ion complexes. For a given reductant, the ratio of the rate constant for the chlorine reaction to that for the hypochlorous acid reaction varies[16,19,20] from 10^{-3} for vanadium(IV) to 10^2 for $Fe(phen)_3^{2+}$. A determination of the rate constant for the vanadium(III)–chlorine reaction can be compared to that for the vanadium(III)–hypochlorous acid reaction[21] with the goal of understanding the relative rates of these two oxidants for a series of reductants.

Experimental Section

Vanadium(IV) perchlorate solutions were prepared by electrolytically reducing a suspension of vanadium pentoxide at a platinum electrode in 3–5 M perchloric acid. The vanadium(IV) concentration was determined by titration with standard potassium permanganate solution[22,23] at 60 °C. The hydrogen ion concentration was determined by using an ion-exchange technique.[24] For the majority of experiments vanadium(III) perchlorate solutions were prepared under deoxygenated nitrogen by passing an aliquot of a vanadium(IV) perchlorate solution through a Jones reductor and allowing the vanadium(II) produced to react with a second aliquot of vanadium(IV) perchlorate solution. Vanadium(III) perchlorate solutions were prepared fresh daily.

Vanadium(III) solutions were prepared by three other procedures: (1) using the above Jones reductor technique on a vanadium(IV) chloride solution prepared from vanadium oxysulfate by an ion-exchange method, (2) electrolytic reduction of a vanadium(IV) perchlorate solution, and (3) dissolution of vanadium pentoxide in hydrochloric acid followed by reduction to vanadium(III) and vanadium(II) by mossy zinc. Cation-exchange resin was used to separate vanadium(III) from vanadium(II) and zinc ion. Results obtained using these three methods for vanadium(III) preparation were experimentally indistinguishable from those using the first method.

Aqueous solutions of chlorine were prepared on the day of use by bubbling chlorine gas from a cylinder first through 96% sulfuric acid, then through an aqueous solution of 2 M ionic strength, and finally into a solution of the desired concentration of chloride ion and hydrogen ion. The chlorine concentration was determined iodometrically. A drive syringe of the stopped-flow apparatus was calibrated[25] and used to measure aliquots of the chlorine solution, which were delivered under the surface of a potassium iodide solution. In a minority of experiments the chlorine concentration was estimated from the magnitude of the change in absorbance during the vanadium(III)–chlorine reaction under the condition of excess vanadium(III).

Sodium perchlorate was used to maintain 2.0 M ionic strength in all experiments. The salt was prepared from sodium carbonate and perchloric acid[24] and was standardized by titrating the acid released when aliquots of the solution were placed on a cation-exchange solumn.

Kinetic studies were performed at 25.0 °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 solution in the cell came directly from the drive syringes[26] where temperature control is most effective.

Chlorine solutions were brought to 25.0 ± 0.1 °C in a 50-ml water-jacketed glass syringe.[27] The water circulating through the water jacket was drawn from the same bath as used to maintain the temperature of the drive syringes of the stopped-flow apparatus. The vanadium(III) solutions were allowed to reach the desired temperature in one of the drive syringes, but the chlorine solutions were not introduced into the other drive syringe until immediately before use. This procedure was used in an attempt to minimize possible losses of chlorine by volatilization.

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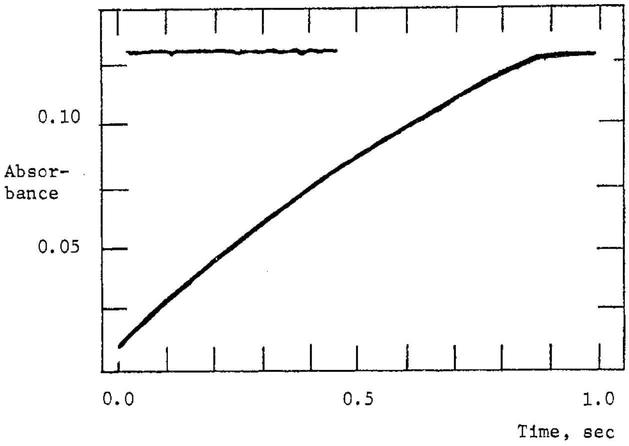

Figure 1. Representation of typical reaction curve for vanadium(III)-chlorine reaction under conditions of excess vanadium(III): $[V(III)] = 0.0321$ M, $[Cl_2] = 0.00198$ M.

The stoichiometry was determined from the absorbance change at 760 nm where the molar absorptivities of vanadium(III) and vanadium(IV) were measured to be 0.4 ± 0.1 and 17.0 ± M^{-1} cm^{-1}, respectively. Kinetic data are reported for experiments monitored at this same wavelength. The results of complementary experiments at 400 nm where vanadium(III) has an absorption maximum were in complete agreement with the results at 760 nm. At 292 nm the molar absorptivity of vanadium(IV) is very nearly equal to the sum of the molar absorptivity of vanadium(III) and half that of chlorine. Any absorbance change observed at this wavelength was attributed to vanadium(V), which has a molar absorptivity measured to be about 1250 M^{-1} cm^{-1} at 292 nm. The induced oxidation of cobalt(II) was followed at 602 nm where the spectra of vanadium(III) and vanadium(IV) exhibit an isosbestic point. The spectrum of cobalt(III) is reported to have an absorption maximum at 605 nm where the molar absorptivity[28] is 35.3 M^{-1} cm^{-1}.

The analyses in this work used the nonlinear least-squares program[29a] FIT70. For fits of absorbance-time data to rate laws, unit weights were used, and for fits of observed rate constants to concentration dependences, $(1/k_{obsd})^2$ weights were used.

Results

The stoichiometry of the reaction between vanadium(III) and chlorine varies with the relative concentrations of the reactants. In the presence of excess vanadium(III), at 25 °C in 1.00 M hydrogen ion and 0.50 M chloride ion, the average value of $[V(IV)]_{obsd}/[Cl_2]_0$ is 1.96 ± 0.05. This stoichiometry is consistent with the equation

$$2V(III) + Cl_2 = 2V(IV) + 2Cl^- \tag{1}$$

In the presence of excess chlorine the yield of vanadium(IV), as given by ratio $[V(IV)]_{obsd}/[V(III)]_0$, is near unity for a small excess of chlorine but decreases toward values as small as 0.76 for ratios of $2[Cl_2]_0/[V(III)]_0$ up to 27. This change in stoichiometry is consistent with the formation of vanadium(V) as one product.

In the presence of a tenfold stoichiometric excess of chlorine, the rate of the vanadium(III)-chlorine reaction is well described by pseudo-first-order kinetics for more than 5 half-lives. In the presence of excess vanadium(III) the rate of the reaction does not decrease as rapidly as predicted by a simple first- or second-order rate law. Under this condition, the reaction rate maintains this unusual behavior until greater than 90% of the reaction has occurred. For a typical experiment in the presence of an eightfold excess of vanadium(III) a graphical representation of the absorbance vs. time trace observed appears in Figure 1.

Due to the lack of a known simple mathematical description of the rate of change of absorbance with time in the presence of excess vanadium(III), the method of initial rates was used to determine the dependence of the rate upon the concentrations of reactants. Table I presents values of the initial rate for experiments at 1.0 M hydrogen ion and 0.5 M chloride ion at 25 °C. The apparent orders with respect to the concentrations of vanadium(III) and chlorine as defined by the equation

Table I. Initial Rate Data for the Vanadium(III)-Chlorine Reaction in 0.50 M Chloride Ion and 1.00 M Hydrogen Ion at 25 °C

$[Cl_2]_0$, M	$[V(III)]_0$, M	Initial rate, M s^{-1}	$k_{1\,obsd}$, s^{-1}
0.024 2	0.008 40	0.006 94	0.413
0.023 6	0.003 41	0.002 35	0.345
0.022 5	0.064 8	0.056 7	0.438
0.018 2	0.032 4	0.021 7	0.335
0.013 8	0.083 4	0.047 1	0.282
0.010 2	0.064 8	0.035 2	0.272
0.006 11	0.004 20	0.001 16	0.138
0.005 54	0.032 4	0.010 5	0.162
0.005 54	0.004 20	0.000 998	0.119
0.003 05	0.064 8	0.013 3	0.102
0.002 70	0.032 4	0.006 27	0.0968
0.002 63	0.004 20	0.000 653	0.0777
0.002 54	0.012 6	0.002 23	0.0884
0.002 07	0.020 8	0.003 85	0.0925
0.002 05	0.064 2	0.012 3	0.0958
0.001 98	0.032 1	0.004 57	0.0712
0.001 86	0.064 2	0.014 0	0.109
0.001 74	0.008 32	0.000 817	0.0491
0.001 54	0.004 26	0.000 475	0.0558
0.001 33	0.064 8	0.008 49	0.0655

$$\frac{d[V(IV)]}{2dt} = k_{obsd}[V(III)]_0^{\,a}[Cl_2]_0^{\,b} \tag{2}$$

have been determined to be $a = 1.0_7 \pm 0.0_2$ and $b = 0.7_1 \pm 0.0_2$. The fitted value of k_{obsd} is 8.0 ± 0.9.

For purposes of determining the form of the predominant term in the rate law, the order with respect to the concentration of vanadium(III) is approximated as 1.00. This adjustment appears to be reasonable in view of the fit to first-order behavior in the presence of a large excess of chlorine. Values of $k_{1_{obsd}}$ were calculated by dividing the initial rate by twice the initial concentration of vanadium(III) and were fit to eq 3 and 4. Typical values of $k_{1_{obsd}}$ and initial concentrations

$$k_{1\,obsd} = k_a + k_b[Cl_2]_0 \tag{3}$$

$$k_{1\,obsd} = \frac{k_c[Cl_2]_0}{1 + k_d[Cl_2]_0} \tag{4}$$

are given in Table I. By using all 43 of the initial rate experiments,[21] the following values were obtained: $k_a = 0.038 \pm 0.004$ s^{-1}, $k_b = 17.4 \pm 1.1$ M^{-1} s^{-1}, $k_c = 38.1 \pm 2.1$ M^{-1} s^{-1}, and $k_d = 57.6 \pm 10.8$ M^{-1}. The average deviation for all 43 of the observed values of $k_{1_{obsd}}$ from those calculated using the above parameters is 18% for eq 3 and 20% for eq 4.

Although either eq 3 or 4 could be used to represent initial rate data, eq 5, which incorporates the chlorine dependence

$$d[V(IV)]/2dt = k_a'[V(III)] + k_b'[V(III)][Cl_2] \tag{5}$$

of eq 3, gives better fits to absorbance-time data than the analogous differential equation corresponding to eq 4. For fits to a typical reaction curve[29b] in the presence of excess vanadium(III), the average differences between the observed and calculated absorbance values differ by a factor of 4 for the two equations. The average values of rate constants obtained by fitting[29b] absorbance-time traces from experiments in the presence of excess vanadium(III) at 1.0 M hydrogen ion and 0.5 M chloride ion to eq 5 are $k_a' = 0.044 \pm 0.014$ s^{-1} and $k_b' = 19.9 \pm 2.1$ M^{-1} s^{-1}. These numbers agree well with the values of k_a and k_b which resulted from a treatment of initial rate data.

To determine the dependence of the rate upon the concentration of hydrogen ion, experiments were run in 0.1, 0.2, 0.5, and 1.0 M acid. For the rate constants in eq 5, the apparent orders with respect to the concentration of hydrogen ion have been determined to be -1.01 ± 0.24 for k_a' and -1.21 ± 0.12 for k_b'. From these results it is concluded that the predominant term in the rate law is inverse first order in the concentration of hydrogen ion. The large uncertainty in the data rules out a more detailed formulation of the dependence of the rate on the acid concentration.

The presence of significant initial concentrations of vanadium(IV) noticeably affects the shape of the reaction curve observed at 760 nm. The initial rate of appearance of vanadium(IV) is less than expected for experiments in the absence of added vanadium(IV). After an induction period, the reaction curve assumes the general form expected in the initial absence of vanadium(IV).

In an attempt to create a mathematical description which encompasses the rate behavior under conditions of excess vanadium(III), the effect of added vanadium(IV), and the nonintegral stoichiometry in the presence of excess chlorine, reaction steps 6–9 were considered. The rate of the process

$$\mathrm{V(III)} + \mathrm{Cl_2} = \mathrm{V(IV)} + \mathrm{Cl_2^-} + 2\mathrm{H^+} \tag{6}$$

$$\mathrm{V(III)} + \mathrm{Cl_2^-} = \mathrm{V(IV)} + 2\mathrm{Cl^-} + 2\mathrm{H^+} \tag{7}$$

$$\mathrm{V(IV)} + \mathrm{Cl_2^-} = \mathrm{V(V)} + 2\mathrm{Cl^-} + 2\mathrm{H^+} \tag{8}$$

$$\mathrm{V(III)} + \mathrm{V(V)} = 2\mathrm{V(IV)} \tag{9}$$

or processes represented by eq 6 is formulated to be that given by eq 10. For mathematical simplicity reactions 7 and 8 are

$$\frac{d[\mathrm{V(IV)}]}{dt} = \frac{k_1[\mathrm{V(III)}]}{[\mathrm{H^+}]} + \frac{k_2[\mathrm{V(III)}][\mathrm{Cl_2}]}{[\mathrm{H^+}]} \tag{10}$$

considered to be very rapid relative to the other reactions. The ratio of the rate constant for reaction 7 to that for reaction 8, k_3/k_4, and the rate constants k_1 and k_2 from eq 10 are the parameters which were used to fit the data. Equation 9 represents the reproportionation of vanadium(III) and vanadium(V) which has been reported[13] to have a rate law for which the predominant term is first order in each reactant and inverse first order with respect to hydrogen ion concentration. The value of the second-order rate constant at 25 °C and 1.0 M hydrogen ion was given as 243 M^{-1} s^{-1} and was experimentally reproduced to within 10% during the present study.

Data from reaction curves for the vanadium(III)–chlorine reaction at 1.0 M hydrogen ion were fitted[21,29b] to a pair of differential equations formulated on the basis of the reactions and rate laws described. For each experiment an attempt was made to fit those parameters most sensitive to the shape of the reaction curve, and the remaining parameters were fixed at the average values from experiments for which they were fitted. By making use of this mathematical model, data from experiments both in the presence of excess vanadium(III) and in the presence of excess chlorine could be fitted. The average values of the fitted parameters are $k_1 = 0.042 \pm 0.019$ M s^{-1}, $k_2 = 18.3 \pm 3.5$ s^{-1}, and $k_3/k_4 = 5 \pm 3$ at 0.5 M chloride ion.

Values of k_2 obtained are slightly higher at higher concentrations of vanadium(III). For experiments in the presence of greater than 0.03 M vanadium(III) the average value of k_2 is 20.5 ± 2.2 s^{-1}, while for experiments in the presence of less than 0.01 M vanadium(III), $k_2 = 15.4 \pm 2.6$ s^{-1}. A similar dependence of k_1 upon the concentration of chlorine is observed. Average values of k_1 are 0.066 ± 0.018 M s^{-1} for experiments in the presence of greater than 0.005 M chlorine and 0.031 ± 0.014 M s^{-1} for experiments at less than 0.003 M chlorine.

Due to the possibility of complexation of vanadium(III) by chloride ion, the dependence of the rate of reaction on the concentration of chloride ion was investigated. The possible effect of changing the net chloride ion concentration was considered, as well as were differences in the location of chloride ion before mixing. The latter possibility was ruled out by the agreement of experiments for which the chloride ion was present only in the chlorine solution with those for which it was present only in the vanadium(III) solution. In this second experiment, the "chlorine" solution contained hypochlorous acid and chlorine was formed upon mixing. For a series of experiments in which the net concentration of chloride ion was varied, no trend as a function of chloride ion concentration can be observed in k_2. For k_1, values as small as 0.06 s^{-1} are observed for experiments at 0.015 M chloride ion. Experiments at chloride ion concentrations from 0.1 to 2.0 M do not show variation with chloride ion concentration.

Cobalt(II) is known to be oxidized rapidly by dichloride ion,[9] and cobalt(III) is reduced more slowly by vanadium(III) and vanadium(IV),[30] as well as by chloride ion.[31,32] If dichloride ion is an intermediate in the vanadium(III)–chlorine reaction, it should be possible to show the appearance and subsequent disappearance of cobalt(III). At 602 nm the spectra of vanadium(III) and vanadium(IV) exhibit an isosbestic point, and at 605 nm the spectrum of cobalt(III) has a maximum.[28] When the vanadium(III)–chlorine reaction proceeded in the presence of cobalt(III), the induced oxidation of cobalt(II) was monitored at 602 nm. The conditions of this experiment were 0.0100 M vanadium(III), 0.0500 M cobalt(II), 0.0221 M chlorine, and 1.0 M hydrogen ion at 0.35 M chloride ion. The absorbance was observed to increase during the vanadium(III)–chlorine reaction and to decrease after about 3 s. In the absence of cobalt(II), the reaction under otherwise identical conditions had reached 85% of completion after 3 s. The absorbance in the induced oxidation experiment reached a maximum of 0.211 above the initial value. This absorbance change in a 2-cm cell corresponds to a cobalt(III) concentration of 0.003 M and is given as evidence for the presence of dichloride ion as an intermediate.

To understand further the processes which occur in this system, the appearance and subsequent disappearance of vanadium(V) in the presence of excess vanadium(III) were monitored at 292 nm. The shape of the reaction curve at this wavelength is qualitatively described by the scheme presented even though only a small part of the reaction proceeds by forming vanadium(V). The same solutions used for experiments at 292 nm were also used for observation of the change in absorbance at 760 nm. The time at which the absorbance at 292 nm suddenly drops is the same as the time at which the rate of increase in absorbance at 760 nm drops drastically. The magnitude of the maximum absorbance change at 292 nm is also in agreement with the equations used to fit the data at 760 nm. The values of k_1 and k_2 determined from the reaction curve at 760 nm and an assumed value of k_3/k_4 of 1.5 give the observed magnitude for the maximum absorbance change.

A measure of the relative amounts of one- and two-electron pathways can be obtained by comparing the initial rate of appearance of vanadium(V) at 292 nm with the initial rate of appearance of vanadium(IV) at 760 nm. For an experiment at 292 nm the initial rate of appearance of vanadium(V) is 3.0×10^{-5} M s^{-1}. The portion of the reaction curve used for this calculation corresponds to less than 0.5% of the reaction as measured by the amount of chlorine consumed. Under the same conditions the total rate of appearance of vanadium(IV) measured at 760 nm is 6.9×10^{-4} M s^{-1} after 0.5% of the chlorine is consumed. The initial rate of appearance of vanadium(V) is greater than predicted using the scheme of reactions presented, but much less than the rate of production of vanadium(IV). These observations and rate comparisons are taken as evidence of a very minor two-electron pathway.

Discussion

One goal of the research reported here is to gain insight into whether the reaction of vanadium(III) with chlorine proceeds via one- or two-electron-transfer processes. Three experiments allow a definitive answer: the determination of the effect of added vanadium(IV) on the rate, the direct observation of vanadium(V), and the induced oxidation of cobalt(II).

In the first experiment vanadium(IV) was added to the reaction mixture. Vanadium(IV) reacts much more slowly[16] with chlorine than does vanadium(III). The presence of large amounts of vanadium(IV) decreased the initial rate of appearance of vanadium(IV). This observation is consistent with a one-electron reduction of chlorine by vanadium(III) to form vanadium(IV) and a reactive chlorine-containing intermediate. This intermediate could further react with either vanadium(III) or vanadium(IV) to form chloride ion. In the presence of a large excess of vanadium(IV) the intermediate would react predominantly with vanadium(IV) to form vanadium(V). Thus, initially vanadium(IV) would be consumed nearly as rapidly as it is produced. As the concentration of vanadium(V) increased, the rate of formation of vanadium(IV) from the vanadium(III)–vanadium(V) reaction would be fast enough to raise the net rate of vanadium(IV) production to near the rate expected in the absence of significant initial concentrations of vanadium(IV).

The second experiment is the induced oxidation of cobalt(II). Chlorine is too weak an oxidizing agent to oxidize cobalt(II) to cobalt(III). Dichloride ion is a strong oxidant, and the rate constant for its oxidation of cobalt(II) has been reported[9] to be 1.4×10^6 M^{-1} s^{-1} at 25 °C. Taube[33] has indirectly observed the oxidation of cobalt(II) by a chlorine-containing intermediate which today would be interpreted as dichloride ion. He noted the effect of the presence of cobalt(II) on the iron(II) induced oxidation of oxalic acid by chlorine. Experiments reported here at 602 nm in the presence of cobalt(II) can be used as conclusive evidence for the presence in the vanadium(III)–chlorine reaction of a highly reactive chlorine-containing intermediate.

Assuming the molar absorptivity[31,34] of cobalt(III) at 602 nm to be 35.3 M^{-1} cm^{-1}, the maximum concentration of cobalt(III) observed is 0.003 M for an experiment which had 0.01000 M vanadium(III) as the limiting reagent. Cobalt(III) is known to be reduced[30] by vanadium(III) and vanadium(IV), and by chloride ion,[31,32] all of which are present in the reaction mixture. The observed concentration of cobalt(III) is therefore a lower limit of the total concentration formed. The maximum concentration of cobalt(III) expected if all of the vanadium(III)–chlorine reaction proceeded by a one-electron pathway and if all of the chlorine-containing intermediate reacted with cobalt(II) would be 0.005 M. On the basis of the experiment reported here, it is possible to say that greater than 60% of the chlorine is reduced by a one-electron-transfer process.

Flash photolysis[8,9] and pulse radiolysis[11,12] studies of aqueous solutions have demonstrated the existence of dichloride ion. The kinetic studies reported here are given as evidence that dichloride ion exists as an intermediate in the vanadium(III)–chlorine reaction. Spectrophotometric detection of this intermediate at 340 nm, the absorption maximum for dichloride ion, is complicated by the presence of at least six absorbing species. However, in the absence of evidence for a different species, the chlorine-containing intermediate is concluded to be dichloride ion.

The third experiment is the monitoring of the vanadium(III)–chlorine reaction at 292 nm. In the presence of excess vanadium(III), reactants and ultimate products absorb equally at this wavelength. The magnitude of the change in absorbance is consistent with the formation and disappearance of vanadium(V) predicted by the scheme used to fit the data at 760 and 400 nm. The small absorbance changes at 292 nm are further evidence that the oxidation of vanadium(III) by chlorine occurs predominantly by a one-electron-transfer process.

The fractions of reaction occurring by one- and two-electron-transfer processes can be determined by comparing the initial rate of appearance of vanadium(V) with the initial rate of appearance of vanadium(IV) at 760 nm. In the absence of any initial concentration of vanadium(IV), the initial rate of appearance of vanadium(V) would be zero if no reaction occurred by a two-electron transfer. Only as the concentration of vanadium(IV) increased could the formation of vanadium(V) be detected. Over the first 0.5% of reaction, the rate of appearance of vanadium(V) was 4% of the rate of appearance of vanadium(IV) under identical conditions. Thus, initially approximately 4% of the reaction occurs by a two-electron-transfer process, and the predominant pathway is a one-electron-transfer process.

The presence of a major one-electron pathway and a very minor two-electron pathway is consistent with results reported for the iron(II)–chlorine[15] and chromium(II)–chlorine[14] reactions, in which less than 5% polymeric products were observed. It should be noted that the presence of polynuclear products for these two reactions can alternatively be attributed to successive one-electron-transfer processes. Also, the chemistry of chlorine is complex and the apparent existence of a two-electron pathway could possibly be due to the presence of an unrecognized reaction. The similarity of the three systems, however, is striking.

An interesting feature of the vanadium(III)–chlorine reaction is its rapid rate compared to the vanadium(III)–hypochlorous acid reaction.[21] These relative rates are in contrast to the relative rates for the reactions of chlorine and hypochlorous acid with iron(II)[15] and with vanadium(IV),[16] which most likely also proceed via a one-electron transfer process. Hypochlorous acid reacts much more rapidly with each of these reductants than does chlorine. It is interesting to compare the relative rates of these reactions with the oxidation potentials[35] for the reductants, i.e.

$$\mathrm{V(III)} = \mathrm{V(IV)} + e^- \quad E^\circ = -0.36 \text{ V}$$

$$\mathrm{Fe(II)} = \mathrm{Fe(III)} + e^- \quad E^\circ = -0.77 \text{ V}$$

$$\mathrm{V(IV)} = \mathrm{V(V)} + e^- \quad E^\circ = -1.0 \text{ V}$$

The reduction potential for reducing chlorine to chloride ion is 1.36 V. Clearly, each reductant above is thermodynamically strong enough to achieve this reduction. For these metal ions, however, it is probable that the reaction with chlorine occurs predominantly by a one-electron process. Only a very strong reductant can readily reduce chlorine to dichloride ion. The potential for that reduction has been estimated[9] to be 0.43 V. Of the three metal ions considered, only vanadium(III) is a strong enough reductant for the first one-electron step to be thermodynamically favored, and for vanadium(III), the chlorine reaction is faster than the hypochlorous acid reaction. For the two weaker reductants, reduction of chlorine to dichloride ion is not thermodynamically favored, and the chlorine reaction is slower than the hypochlorous acid reaction. Thus, if the rate of reaction of hypochlorous acid with a metal is considered to be a standard, the relative rate of the corresponding chlorine reaction can be correlated on the basis of oxidation potentials.

The value of k_2 was observed not to vary with changes in the concentration of chloride ion. As the concentration of chloride ion was varied from 0.015 to 2.0 M, the fraction of chlorine present as the trichloride ion varied from less than 1% to nearly 30%. Although the internal agreement of the data is not sufficient to allow a definitive statement, it appears most likely that chlorine and trichloride ion react at comparable rates in the mechanistic pathway which gives rise to k_2.

The dependence of the predominant term of the rate law for the vanadium(III)–chlorine reaction upon the reciprocal of the concentration of hydrogen ion has precedent in a large number of other redox reactions of vanadium(III), including those with bromine[36] and iodine.[37] Newton and Baker[38] have noted that the number of hydrogen ions lost or gained in the formation of an activated complex is usually between zero and the number of hydrogen ions lost or gained in the overall reaction. The hydrogen ion stoichiometry for the vanadium(III)–chlorine reaction and order with respect to the hydrogen ion concentration are consistent with the general observation of Newton and Baker.

Most probably the form of the hydrogen ion dependence arises from the hydrolysis of one of the reactants. The independent study of the oxidation of vanadium(III) by hypochlorous acid[21] discounts the possibility of a chlorine hydrolysis product leading to the observed rate law. The inverse dependence of the rate on the concentration of hydrogen ion most probably arises from hydroxovanadium(III) being the reactive species. If this assumption is valid, the value of the microscopic rate constant, k_{2m}, can be related to k_2 by K_h, the hydrolysis constant for vanadium(III). From the values $K_h = 0.002$ M reported in the literature[39] and $k_2 = 20\ s^{-1}$, k_{2m} is calculated to be $10^4\ M^{-1}\ s^{-1}$.

The magnitude of the rate constant k_{2m} can be used as a basis for a conclusion as to whether the vanadium(III)–chlorine reaction proceeds via an outer- or inner-sphere electron-transfer process. On the basis of a comparison with estimated substitution rates, Adegite and Ford-Smith[36] concluded that the vanadium(III)–bromine reaction proceeds via an outer-sphere process. The faster vanadium(III)–chlorine reaction therefore, by the arguments of Adegite and Ford-Smith, would also be concluded to be outer sphere.

The rates of very few substitution reactions of vanadium(III) have been studied in aqueous solution. Of those which have been studied as a function of hydrogen ion concentration, only the substitutions by hydrazoic acid[40] and oxalic acid[41] were found to be faster at lower hydrogen ion concentrations. For the oxalic acid substitution, the near equality of the hydrolysis constant of vanadium(III) and the first acid dissociation constant for oxalic acid makes a distinction between possible sets of reactive species difficult. For the substitution by hydrazoic acid, Espenson and Pladziewicz[40] used a comparison of the entropy of activation with that for the formation of the isothiocyanato complex[42] as support for a conclusion that hydrolyzed vanadium(III) was the reactive species. The resulting value for the microscopic rate constant is $30\ M^{-1}\ s^{-1}$ and is much smaller that the value of k_{2m} reported here. This comparison can be taken as strong evidence that the vanadium(III)–chlorine reaction proceeds *via* an outer-sphere pathway.

The distinction between inner- and outer-sphere reactions is based on the assumption that penetration into the inner coordination sphere cannot occur faster than the loss of a coordinated water molecule. Recently, the suggestion has been made[43] that a reactant could enter the first coordination sphere of a metal to form a short-lived seven-coordinate intermediate and that a "pseudo-inner-sphere" electron-transfer process could occur while the coordination sphere remained otherwise intact. In the system discussed here, the data do not form a basis for a distinction between this "pseudo-inner-sphere" process and an outer-sphere process.

The mechanistic pathway which corresponds to a term independent of the concentration of chlorine in the rate law is not readily apparent. One species which has been postulated[44,45] as a product of the hydrolysis of vanadium(III) is VO^+, which might be termed oxovanadium(III). A possible structural similarity of such an ion to oxovanadium(IV) could allow it to be relatively rapidly oxidized. If the formation of oxovanadium(III) were slow due to the necessary rearrangement of the coordination sphere, its formation could be the rate-determining step corresponding to the k_1 term. Unfortunately, results which have been used as evidence for a slow hydrolysis reaction[44,46] for vanadium(III) are from experiments in the presence of complexing ions. Although no direct evidence can be presented to confirm that the formation of oxovanadium(III) is the rate-determining step responsible for the k_1 term, this explanation must be regarded as the most plausible.

The limiting form of the rate law for inner-sphere substitution is independent of the concentration of the entering ligand at high concentrations of that ligand. The rate constant for substitution thus approaches the value for the rate constant for water exchange. The water-exchange rate constant[47] for vanadium(III) is $300\ s^{-1}$ at 25 °C. This value differs substantially from the observed value of k_1, and provides additional evidence that the observed k_1 term is not due to a pathway limited by the rate of substitution.

The values of k_2 have been noted to be slightly higher for experiments in the presence of larger concentrations of vanadium(III) than for those at lower concentrations. A possible explanation for this variation lies in differences in the contribution of the disproportionation reaction of dichloride ion. This intermediate may be considered to react via three pathways (eq 11–13). Reaction 13 may be thought of as

$$V(III) + Cl_2^- = V(IV) + 2Cl^- \tag{11}$$

$$V(IV) + Cl_2^- = V(V) + 2Cl^- \tag{12}$$

$$Cl_2^- + Cl_2^- = Cl_3^- + Cl^- \tag{13}$$

counter productive: it regenerates reactants. To the extent that this reaction is important the observed rate is diminished. The rate constant for reaction 13, k_{Cl}, has been measured[10] to be $5.2 \times 10^9\ M^{-1}\ s^{-1}$ at 25 °C. From the results of Taube[33] on the effect of vanadium(IV) on the iron(II)-induced oxidation of oxalic acid by chlorine, the rate constant for reaction 12 is estimated to be on the order of $3 \times 10^5\ M^{-1}\ s^{-1}$. The value of k_3/k_4 obtained from experiments on the vanadium(III)–chlorine reaction indicates that the rate constant for reaction 11, k_V, is close to $10^6\ M^{-1}\ s^{-1}$. These approximate numbers may be used to show that partitioning of the consumption of dichloride ion among the above reactions changes as the concentration of vanadium(III) changes. The ratio of the amount of dichloride ion consumed by reaction 11 to that consumed by reaction 13 is given by $k_V[V(III)][Cl_2^-]:k_{Cl}[Cl_2^-]^2$. These terms can be evaluated using the given values of rate constants and the steady-state concentration of dichloride ion calculated from a treatment of reactions 6, 11, and 13. At 0.02 M chlorine, 2% of the dichloride is consumed by reaction 13 at the highest vanadium(III) concentration used in experiments reported here and 26% at the lowest vanadium(III) concentration. Although the rate constants used in this calculation are somewhat uncertain, changes in their values do not change the conclusion that the reactions suggested are strongly competitive for dichloride ion and that at higher concentrations of vanadium(III) the disproportionation of dichloride ion occurs less than at lower concentrations of 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.

Acknowledgment. The authors wish to express their appreciation to the Graduate School at the University of Iowa for financial support of this research and to Miami University for the advantages of a research fellowship for R.D.C.

Registry No. V(III), 7440-62-2; Cl_2, 7782-50-5.

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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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Received July 18, 1975 AIC50511O

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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