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Kinetic Studies on the Reduction of the Tantalum Cluster Ion $(Ta_6Br_{12})^{3+}$ by Chromium(II)[1a]

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The reduction of $(Ta_6Br_{12})^{3+}$ to $(Ta_6Br_{12})^{2+}$ by Cr^{2+} occurs at a rate given by $-d[(Ta_6Br_{12})^{3+}]/dt = (k + k_X[X^-])[Cr^{2+}] \cdot [(Ta_6Br_{12})^{3+}]$ where $[X^-]$ represents the concentration of a halide or pseudohalide ion. At 25.0° and $\mu = 0.100$ *M*, $k = (2.7 \pm 0.4) \times 10^5$ M^{-1} sec^{-1}, and various $10^{-7}k_X$ values are 0.7 (Cl^-), 1.0 (Br^-), 9.0 (I^-), and 21 M^{-2} sec^{-1} (SCN^-). The product in perchlorate solution is $Cr(H_2O)_6^{3+}$, whereas some $(H_2O)_5CrX^{2+}$ is produced in the presence of other anions. The yields of the two Cr(III) products were evaluated for $X^- = Cl^-$ and Br^-. In the case of thiocyanate ion, one product is the less stable linkage isomer, $CrSCN^{2+}$, suggesting a mechanism involving the anion-bridged reduction of $(Ta_6Br_{12})^{3+}$-NCS^- by Cr^{2+}.

Introduction

Several kinetic studies on electron-transfer reactions involving polynuclear metal complexes have been reported in recent years. The most extensively studied species is $(Ta_6Br_{12})^{2+}$, whose oxidations by Fe^{3+},[2] VO_2^+,[3] $HCrO_4^-$,[4] and Co(III) complexes[5] and other substances[5] proceed at easily measured rates. The electrode potentials *vs.* nhe interrelating the different cluster ions are[6]

$$(Ta_6Br_{12})^{4+} + e^- = (Ta_6Br_{12})^{3+} \quad E° = 0.85 \text{ V}$$

$$(Ta_6Br_{12})^{3+} + e^- = (Ta_6Br_{12})^{2+} \quad E° = 0.55 \text{ V}$$

The higher oxidation states can be reduced with reagents having appropriate $E°$ values, as in the reduction of the 4+ cluster with Fe^{2+}.[2] The M_6X_{12} cluster framework is not affected by repeated cycles of oxidation and reduction. Because Fe^{2+} is not as strong a reducing agent as $(Ta_6Br_{12})^{2+}$, it reduces the cluster ion no farther than the 3+ form. We have undertaken a study of the continued reduction using Cr^{2+} ($E° = -0.41$ V), which reacts according to

$$(Ta_6Br_{12})^{3+} + Cr^{2+} = (Ta_6Br_{12})^{2+} + Cr^{3+} \qquad (1)$$

The kinetic inertness of Cr(III) can be used to good advantage to separate and identify the products formed in the presence of anions. Large rate increases were noted with even very small concentrations of halide or pseudohalide ions (X^-). Product studies were carried out in conjunction with the rate measurements to study the mechanism of anion catalysis and to evaluate the relative yield of $(H_2O)_5CrX^{2+}$ and $Cr(H_2O)_6^{3+}$.

Experimental Section

Materials.—$(Ta_6Br_{12})Br_2$ was prepared by the method of Kuhn and McCarley;[7] the solid was recrystallized from water before use. Solutions of $Ta_6Br_{12}^{3+}$ were prepared shortly before use by oxidizing a solution of $(Ta_6Br_{12})^{2+}$ in dilute perchloric acid with bromine water, iron(III) perchlorate solution, or chromium(VI). To avoid any of the 4+ cluster ion, the oxidizing agent was always stoichiometrically deficient so that at least a small amount of the 2+ cluster remained.

Solutions of Cr^{2+} were prepared from solutions of chromium(III) perchlorate in dilute perchloric acid, using electrochemical reduction or amalgamated zinc. The solution was diluted under oxygen-free conditions immediately before use in a kinetic run; the dilute solution was kept in contact with amalgamated zinc to preserve the very low Cr^{2+} concentrations. Analysis for its Cr^{2+} content was made during the course of the run to avoid any error from partial oxidation during the transfer and dilution steps. The dilute Cr^{2+} solutions, typically 3×10^{-4} *M*, were analyzed spectrophotometrically using the decrease in absorbance of $Co(NH_3)_5Br^{2+}$ at λ 253 nm (ε 1.67×10^4 M^{-1} cm^{-1}).[8-10]

Reagent grade hydrobromic acid was purified by treatment with a small amount of Cr^{2+} to destroy traces of bromine; the $CrBr^{2+}$ so generated was removed by cation-exchange chromatography on Dowex 50W-X8. A solution of tetramethylammonium thiocyanate was prepared by treating the hydroxide with ammonium thiocyanate, the resulting ammonia being removed by aspiration.

Some other materials were prepared by methods already described: iron(III) perchlorate,[11] chromium(III) perchlorate,[12] lithium perchlorate,[12] and $[Co(NH_3)_5Br]Br_2$.[13] The remaining substances were used as the reagent grade chemicals. Conductivity water was used throughout.

Rate Measurements.—The rate studies were carried out by the stopped-flow method, mostly with the instrument described by Dulz and Sutin.[14] A Durrum stopped-flow spectrophotometer was also used in a few instances. In most experiments the reaction was monitored at λ 637 nm when $(Ta_6Br_{12})^{2+}$ absorbs strongly (ε 7200 M^{-1} cm), compared to the 3+ cluster (ε ~200) and the chromium ions. A few measurements were also made at λ 870 nm, where $(Ta_6Br_{12})^{3+}$ has an absorption maximum. Ionic strength was maintained at 0.10 *M* by addition of perchloric acid and/or lithium perchlorate.

Most rate experiments were carried out with Cr^{2+} in excess; $[Cr^{2+}]$ was sufficiently large in most cases to be considered approximately constant. The usual first-order rate plots were found to be linear, and the values of k_{app} derived from their slopes were converted to second-order rate constants by dividing k_{app} by the average Cr^{2+} concentration. A few experiments were carried out under conditions where the excess of Cr^{2-} was not as great or where $(Ta_6Br_{12})^{3+}$ was the reagent in excess; these kinetic data were fit to the integrated second-order equation using a least-squares computer program.[15] Three or four determinations were

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[1] (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 3159. (b) Fellow of the Alfred P. Sloan Foundation. (c) National Science Foundation predoctoral fellow.

[2] J. H. Espenson and R. E. McCarley, *J. Amer. Chem. Soc.*, **88**, 1063 (1966).

[3] J. H. Espenson, *Inorg. Chem.*, **7**, 631 (1968).

[4] J. H. Espenson and R. J. Kinney, *ibid.*, **10**, 376 (1971).

[5] J. H. Espenson and D. J. Boone, *ibid.*, **7**, 636 (1968).

[6] N. E. Cooke, T. Kuwana, and J. H. Espenson, *ibid.*, **10**, 1081 (1971).

[7] P. J. Kuhn and R. E. McCarley, *ibid.*, **4**, 1482 (1965).

[8] J. F. Endicott and H. Taube, *ibid.*, **4**, 437 (1965).

[9] O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 1968 (1969).

[10] Endicott and Taube[8] described the general method, which we have used previously for analyzing Cu^+ solutions.[9] One difference between our Cr^{2+} analysis and the published procedure[8] is that an allowance was made for the absorbance of the product $CrBr^{2+}$ at λ 253 nm (ε 1500). The net molar absorptivity decrease used to calculate Cr^{2+} concentrations is 1.52×10^4 M^{-1} cm^{-1}.

[11] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

[12] J. H. Espenson, *ibid.*, **3**, 968 (1964).

[13] H. Diehl, H. Clark, and H. H. Willard, *Inorg. Syn.*, **1**, 186 (1939).

[14] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[15] We are grateful to Drs. T. W. Newton and R. H. Moore for sending a copy of the computer program based on a report from Los Alamos Scientific Laboratory: LA 2367 + addenda.

usually made with each set of solutions.

Product Yields.—The production of CrX^{2+} complexes was studied by an ion-exchange separation. The reaction solutions were mixed using the stopped-flow mixing chamber to ensure that the reactions occurred only after complete mixing.[16] The solutions of $(Ta_6Br_{12})^{3+}$ were prepared by bromine oxidation, and the cluster rather than Cr^{2+} was in excess in the product studies in contrast to the kinetic runs. In this way, one avoids products resulting from air oxidation of Cr^{2+} in solutions containing potentially coordinating anions. The reaction solutions were first treated with Fe^{3+} to oxidize $(Ta_6Br_{12})^{2+}$ and then with H_2O_2 to reoxidize Fe^{2+}. The CrX^{2+} was separated quantitatively on Dowex 50W-X8 resin, eluting the complex with 1 *F* $HClO_4$. The chromium content of the eluent was determined spectrophotometrically as chromate ion after oxidation with peroxide in alkaline solution.[17]

Blank experiments using known quantities of different CrX^{2+} complexes established that these complexes were stable under the reaction conditions and in the presence of all the other ingredients. Recovery of $\geqslant 95\%$ was achieved for $CrCl^{2+}$ and $CrBr^{2+}$. The S-bonded complex $Cr{-}SCN^{2+}$ could not be recovered quantitatively under the conditions of the work-up and isolation, and yield experiments were thus not done for $X^- = SCN^-$.

Results

Kinetic Studies.—The reaction rate in solutions in which perchlorate is the only anion present are given by the expression

$$-d[(Ta_6Br_{12})^{3+}]/dt = k[Cr^{2+}][(Ta_6Br_{12})^{3+}] \quad (2)$$

These rate measurements at 0.100 *M* H^+ consisted of 41 different solutions covering the following ranges of initial concentrations: $6 \times 10^{-5} \leqslant [Cr^{2+}]_0 \leqslant 4 \times 10^{-4}$ and $3 \times 10^{-6} \leqslant [(Ta_6Br_{12})^{3+}]_0 \leqslant 1 \times 10^{-4}$ *M*. The average rate constant at 25.0° and $\mu = 0.100$ *M* is $k = (2.7 \pm 0.4) \times 10^5\ M^{-1}\ sec^{-1}$, where the indicated uncertainty here and elsewhere represents one standard deviation. In six of the runs included in the average, Cr^{2+} was limiting: $[Cr^{2+}] = 1.8 \times 10^{-5}$ and $1.6 \times 10^{-4} \leqslant [(Ta_6Br_{12})^{3+}] \leqslant 2.2 \times 10^{-4}$ *M*. The relatively large number of experiments carried out was to locate the source of the scatter in the rate constant. The data showed no systematic dependence upon the choice of reagent used to prepare the 3+ cluster, the method of Cr^{2+} preparation, the reagent in excess, or the wavelength used to follow the reaction. Ultimately, the difficulty of handling and preserving the air-sensitive Cr^{2+} solutions at the very dilute concentration levels was thought to be responsible for the relatively wide error limits.

The effect of hydrogen ion concentration on the reaction rate was examined in an additional four experiments covering the range 0.004–0.10 *M*. There is a small rate increase with decreasing $[H^+]$, corresponding to a value of $a = 7 \times 10^2\ sec^{-1}$ if the data are fit to the relation

$$k = 2.7 \times 10^5\ M^{-1}\ sec^{-1} + a[H^+]^{-1} \quad (3)$$

The rate constant in 0.1 *M* H^+ at 15.8° was only slightly smaller (~4%) than the value at 25°. The variation was small enough that, considering the precision we could attain in the rate determination, further study was not undertaken. This information was sufficient to provide approximate activation parameters for *k*; $\Delta H^{\ddagger} \approx 0$ and $\Delta S^{\ddagger} \approx -30$ cal mol^{-1} deg^{-1}.

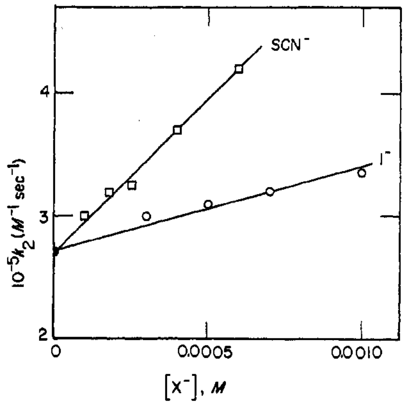


Figure 1.—The linear effect of iodide and thiocyanate ions on the apparent second-order rate constant in accord with eq 4.

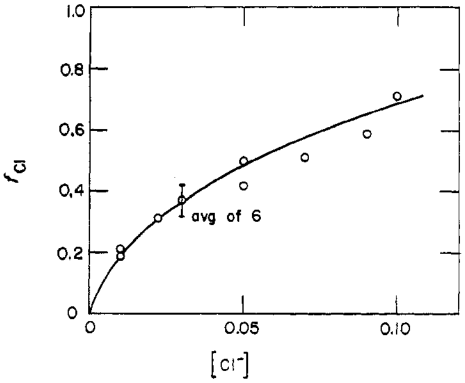


Figure 2.—A plot of the fraction of the Cr(III) product which is the complex $CrCl^{2+}$ as a function of $[Cl^-]$.

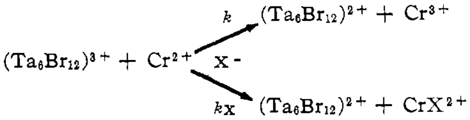
The rate is greatly increased by relatively low concentrations of anions such as Cl^-, Br^-, I^-, and NCS^-. The apparent second-order rate constant was evaluated at 25°, $[H^+] = 0.10$ *M*, $\mu = 1.00$ *M*; it proved to be a linear function of $[X^-]$

$$k_2 = k + k_X[X^-] \quad (4)$$

The values derived from the rate plots for $10^{-7}k_X$ (M^{-2} sec^{-1}) are as follows: Cl^-, 1.1 ± 0.4; Br^-, 1.5 ± 0.8; I^-, 9.0 ± 1.0; SCN^-, 21 ± 3. Plots for I^- and SCN^- are shown in Figure 1.

Product Studies.—The yield of the kinetically inert $CrCl^{2+}$ and $CrBr^{2+}$ complexes was evaluated as described in the Experimental Section. The yield of CrX^{2+} generally increased as $[X^-]$ increased; Figure 2 shows a plot of f_{Cl} ($= [CrCl^{2+}]/[Cr]_{tot}$) *vs.* $[Cl^-]$.

The qualitative nature of this dependence is in accord with the assumption that each of the two paths in the rate expression given in eq 5 produces a different Cr(III) product



$$(Ta_6Br_{12})^{3+} + Cr^{2+} \begin{cases} \xrightarrow{k} (Ta_6Br_{12})^{2+} + Cr^{3+} \\ \xrightarrow[k_X]{X^-} (Ta_6Br_{12})^{2+} + CrX^{2+} \end{cases} \quad (5)$$

in which case

$$f_X = k_X[X^-]/\{k + k_X[X^-]\} \quad (6)$$

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[16] Product yields must be determined in solutions that are well mixed before substantial reaction occurs. Conventional addition with stirring is not sufficiently rapid for these very fast reactions: see D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 599 (1969); *Inorg. Chem.*, **8**, 575 (1969).

[17] G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

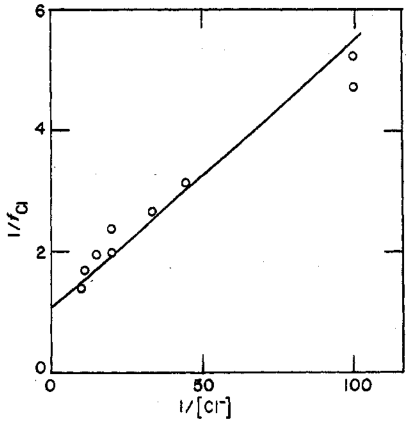

Figure 3.—A double-reciprocal plot of yield and concentration as suggested by eq 7.

which can be rearranged to the form

$$1/f_X = 1 + (k/k_X)[X^-]^{-1} \qquad (7)$$

Equation 7 indicates that plots of $1/f_X$ *vs.* $[X^-]^{-1}$ should be linear if the above mechanism represents the product distribution correctly. The plot for $X^- = Cl^-$ is shown in Figure 3. This plot and that for Br^- are linear, considering the experimental error. The values of the rate constant ratios determined from the slopes of these plots are $k/k_{Cl} = 0.041$ and $k/k_{Br} = 0.026$, in comparison with the ratios computed from the kinetic data which are 0.025 ± 0.010 and $0.018 \pm 0.006\ M$. Considering the large errors associated with the kinetic determinations for these anions, the agreement appears satisfactory.

Product Studies with $X^- = SCN^-$.—The reduction of $(Ta_6Br_{12})^{3+}$ with Cr^{2+} in solutions containing free thiocyanate ions appears to produce both the linkage isomers of the CrX^{2+} complex, $CrNCS^{2+}$ and $CrSCN^{2+}$, when the tantalum cluster is present in stoichiometric excess. The production of $CrSCN^{2+}$ is a particularly striking observation because the S-bonded isomer is markedly less stable than the N-bonded form (the equilibrium constant is $\sim 10^6$).[18] The conclusion that $CrSCN^{2+}$ is a major product[19] of the reaction is based upon the following observations: (1) The elution of the product solutions with 1.0 *F* $HClO_4$ removed a CrX^{2+} fraction having a band with a maximum at λ 262 nm and a shoulder at 294 nm, compared to the reported[20] λ_{max} 262 nm for $CrSCN^{2+}$ and 292 nm for $CrNCS^{2+}$. (2) The absorbance decreased at both wavelengths upon addition of $Hg(ClO_4)_2$ but the 294-nm band reappeared upon addition of Cl^-. These observations agree with those of Orhanović and Sutin[20] for $CrSCN^{2+}$. (3) The CrX^{2+} product reacts with V^{2+}. Under appropriate conditions two reactions may be studied: at λ 262 nm a second-order reaction occurs at a rate $9.4[CrX^{2+}]\cdot[V^{2+}]\ M\ sec^{-1}$ (25°, $[H^+] = 1.0\ M$, $\mu = 1.0\ M$) followed by a slower first-order reaction seen at λ 350 nm with a rate constant of $\sim 1\ sec^{-1}$. The first stage is identified as the reaction[21] of $CrSCN^{2+}$ with V^{2+} for which k_2 is $9.8\ M^{-1}\ sec^{-1}$ and the second as the aquation of $VNCS^{2+}$ (λ_{max} 350 nm, $k_{aq} = 1.03\ sec^{-1}$).[22]

Of interest in this context is a precipitate which forms when $(Ta_6Br_{12})^{3+}$ and SCN^- are mixed at higher concentrations. Its insolubility prevented purification, although by analogy with known materials it might correspond to a member of the family $K_y(Ta_6Br_{12})X_{3+y}$ (with $X^- = SCN^-$; $0 \leqslant y \leqslant 3$). The ir spectrum of the impure solid showed absorption bands at 2090 (s), 740 (w), and 780 (w) cm^{-1}. The frequencies suggest the coordination Ta–NCS rather than Ta–SCN.[23]

Interpretation and Discussion

The reaction in the absence of anions other than perchlorate proceeds largely by a pathway independent of $[H^+]$. The data do suggest a single electron is transferred, which is consistent with the observation that $(Ta_6Br_{12})^{2+}$ is the most reduced species of the cluster ion that can be prepared. The large negative value of $\Delta S^{\ddagger}$ is similar to values found in most redox reactions between positively charged metal ions. A very small enthalpy of activation is consistent with a process requiring little rearrangement of the primary or secondary hydration spheres prior to electron transfer.

The slight increase in rate with decreasing $[H^+]$ may represent a medium effect of the sort encountered in earlier studies.[24] Reliance has been placed on activity coefficients remaining constant while $HClO_4$ and $LiClO_4$ are traded at constant ionic strength; this is not necessarily quantitatively correct. The small magnitude of the rate effect and the imprecision of the kinetic data lead us to feel that it may be unwarranted to ascribe the effect to a genuine parallel pathway of composition $[Ta_6Br_{12}OHCr^{4+}]^{\ddagger}$ rather than to a medium effect. If this term does represent a genuine pathway, its contribution is so small that it could not be assessed with any accuracy.

The mechanism shown in eq 5 appears to account satisfactorily for the effect of the added anions on the rate as well as on the yield of CrX^{2+} complexes. The yield data, in fact, are probably considerably more reliable than the kinetic parameter k_X for Cl^- and Br^-. The rate constants derived from a plot of f_X^{-1} *vs.* $[X^-]^{-1}$ as in eq 7 leads to the values $k_{Cl} = 6.6 \times 10^6$ and $k_{Br} = 1.0 \times 10^7\ M^{-2}\ sec^{-1}$.

The results in the case of thiocyanate ions served to provide some additional information about the nature of the anion catalysis. The ways in which one might envisage an anion leading to a significant rate enhancement involve the reduction either of an ion pair[25]

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(18) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 4210 (1965); **88**, 434 (1966).

(19) The relative concentration of the two isomers could not be determined because a separation from the reaction mixture was first required owing to the intense uv absorptions of the cluster ions. The separation procedure, particularly the addition of H_2O_2 and the ion-exchange step, causes loss of $CrSCN^{2+}$. The highest isolated yield of $CrSCN^{2+}$ appeared to be about 50% of the CrX^{2+} fraction.

(20) M. Orhanović and H. N. Sutin, *J. Amer. Chem. Soc.*, **90**, 4386 (1968).

(21) M. Orhanović, H. N. Po, and N. Sutin, *ibid.*, **90**, 7224 (1968).

(22) B. R. Baker, N. Sutin, and T. J. Welch, *Inorg. Chem.*, **6**, 1948 (1967).

(23) J. Lewis, R. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

(24) O. J. Parker and J. H. Espenson, *J. Amer. Chem. Soc.*, **91**, 1313 (1969), and references therein.

(25) The structure of Ta_6Br_{12} leaves six positions in which a group can coordinate directly to each of the six tantalum atoms. For example, compounds $(Et_4N)_3[(Ta_6Cl_{12})Cl_6]$ and $[(Ta_6Cl_{12})Cl_3(H_2O)_3]\cdot 3H_2O$ are known: B. G. Hughes, J. L. Meyer, P. B. Fleming, and R. E. McCarley, *Inorg. Chem.*, **9**, 1343 (1970). Direct structural data are available only for $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$, in which four water molecules and two chloride ions are coordinated to the cluster unit: R. D. Burbank, *Inorg. Chem.*, **5**, 1491 (1966). Little doubt remains, however, that the other derivatives are similarly constituted. The poorly characterized thiocyanate derivative may have a similar structure, and the reactive "$(Ta_6Br_{12})^{3+}NCS^-$" may as well.

$(Ta_6Br_{12})^{3+}X^-$ by Cr^{2+} or of the cluster ion by the Cr(II) complex CrX^+. Since the latter for chromium(II) thiocyanate would almost certainly involve the $Cr-NCS^+$ isomer, production of substantial quantities of $Cr-SCN^{2+}$, far in excess of the equilibrium values, suggests at least partial involvement of $(Ta_6Br_{12})^{3+}\text{-}NCS^- + Cr^{2+}$. In such a reaction the ion-paired thiocyanate ion would serve as a bridging group,[26] and the less stable $CrSCN^{2+}$ linkage isomer would result solely from the stereochemistry of such a transition state. Whether the $CrNCS^{2+}$ which is produced results from a parallel path or from isomerization of the S-bonded product could not be determined.

[26] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **8**, 575 (1969).

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The Mechanism of Inhibition of the Vanadium(IV)–Chlorate Reaction by Chloride Ion

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The reduction of chlorate ion by oxovanadium(IV) was studied at 25° and an ionic strength of 2.0 *M* under a variety of hydrogen ion concentrations from 0.40 to 1.9 *M* and chloride ion concentrations from 3.4×10^{-3} to 1.50 *M*. When the concentration of oxovanadium(IV) is in excess relative to the concentration of chlorate ion in the presence of initially added chloride ion, the stoichiometry is 4. In the absence of initially added chloride ion, the stoichiometry is 5. The kinetics of the reduction of chlorate ion by oxovanadium(IV) in the presence and absence of chloride ion are consistent with the following rate law: $\text{rate} = \{(k_1 + k_2[H^+])/(1 + K[Cl^-])\}[VO^{2+}][ClO_3^-]$. The parameters k_1 and K are independent of the hydrogen ion concentration and correspond to the values $(9.47 \pm 0.10) \times 10^{-3}\ M^{-1}\ sec^{-1}$ and $0.235 \pm 0.010\ M^{-1}$, respectively. The rate constant, k_2, for the hydrogen ion dependent term is calculated to be $(3.21 \pm 0.090) \times 10^{-3}\ M^{-2}\ sec^{-1}$. The change in stoichiometry, as a function of the chloride ion concentration, is due to differences in the rate of reaction between hypochlorous acid and chloride ion to form chlorine or hypochlorous acid and vanadium(IV) to form vanadium(V). The moderate inhibition of the vanadium(IV)–chlorate reaction by added chloride ion is discussed in terms of complex ion formation between vanadium(IV) and chloride ion.

Introduction

The reactions between various oxychlorine species and transition metal ions have been shown[1-6] to undergo both one- and two-electron-transfer processes. In an attempt to obtain more meaningful comparisons between one- and two-electron-transfer reactions, several kinetic studies of the reaction between vanadium(IV)[7] and chlorate ion were initiated[8-11] since vanadium(IV) is limited to a single electron oxidation. These investigations were complicated by the lack of availability of exact stoichiometric data. This complication arose in that the rates of reaction between vanadium(IV) and hypochlorous acid and chlorine were unknown. A recent report[12] indicates chlorine oxidizes vanadium(IV) only slowly but that the hypochlorous acid–vanadium(IV) reaction is relatively fast. A number of inherent kinetic complications were noted in the vanadium(IV)–chlorate reaction by Rosseinsky and Zlotnick[8] but the preliminary nature of their report precluded the possibility of a complete mechanistic interpretation. The kinetic data reported here are now sufficient to suggest a detailed rate law and reaction mechanism.

Experimental Section

Reagents.—Vanadium(IV) perchlorate solutions were prepared by electrolytic reduction of vanadium(V) oxide suspensions at platinum electrodes in perchloric acid media.[13] The vanadium(V) oxide was Fisher Certified reagent grade vanadium pentoxide. The electrolytic reduction was terminated when all of the vanadium(V) was reduced. Oxygen was bubbled through the vanadium(IV) solution to oxidize small amounts of vanadium(III). The purity of a vanadium(IV) solution was checked[14] by spot testing for vanadium(III) and vanadium(V). This procedure was sensitive to $10^{-5} M$ vanadium(III) and 10^{-4} *M* vandium(V) in 0.2 *M* vanadium(IV). Chloride ion[15] concentrations were below the 10^{-5} *M* level in the vanadium(IV) solutions as detected by the addition of aqueous silver nitrate. The vanadium(IV) solutions were standardized by using potassium permanganate.[16] The hydrogen ion concentration of the vanadium(IV) solutions was determined by the method described earlier.[4]

Sodium perchlorate was prepared by neutralizing reagent grade sodium carbonate with perchloric acid. Solid sodium perchlorate was obtained[4] by precipitation of sodium perchlorate, followed by three recrystallizations. J. T. Baker reagent grade sodium chlorate was used without further purification.

Chlorine dioxide was generated from the oxalic acid reduction of potassium chlorate in a method similar to that reported by Bray.[17] The chlorine dioxide was collected in water after being passed through a 2 *M* sodium carbonate wash solution. The vessel which contained the chlorine dioxide was sealed tightly

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[1] (a) E. Grimley, R. Buchacek, and G. Gordon, *Inorg. Chem.*, **10**, 873 (1971); (b) M. Ondrus and G. Gordon, *ibid.*, **10**, 474 (1971).

[2] (a) R. Thompson and G. Gordon, *ibid.*, **5**, 562 (1966); (b) B. Z. Shakhashiri and G. Gordon, *J. Amer. Chem. Soc.*, **91**, 1103 (1969).

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[6] A. M. Azzam and I. A. W. Shimi, *Z. Phys. Chem. (Frankfurt am Main)*, **33**, 190 (1962).

[7] The vanadium(IV) species present in aqueous perchloric acid solution is the $[(H_2O)_4VO^{2+}]$ species which will be termed vanadium(IV) in this paper.

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[16] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **6**, 48 (1934).

[17] W. C. Bray, *Z. Phys. Chem.*, **54**, 569 (1906).