but solvent isotope effects of this type are frequently difficult to interpret with confidence.

One plausible interpretation of the marked difference between the rate parameters of the decomposition of the $U^V \cdot Cr^{III}$ complex and those of the two Np(V) complexes is that it indicates the importance of the f electrons in the bonding of these species. It may be noted that replacing Cr(III) (a 3d ion) by Ru(III) (a 4d ion) in the Np(V) complex has little effect on the magnitude of the rate parameters. However, replacing the $5f^2$ Np(V) ion by the $5f^1$ U(V) ion has a marked effect on the kinetic behavior.[15] A study of the rates of decomposition of the analogous $Pu^V \cdot Cr^{III}$ complex would clearly be of considerable interest in this respect.

(b) **Reaction of Cr(II) with $U^V \cdot Cr^{III}$.** The results obtained for this reaction support the conclusion of Gordon[2] that the intermediate reacts with excess Cr(II) before either disproportionating or dissociating.

Although the net reaction (eq 3) requires the consumption of four protons for each molecule of $U^V \cdot Cr^{III}$ reduced, the rate law for the reduction of $U^V \cdot Cr^{III}$ does not contain any acid concentration term. Analogous results have been obtained for the reduction of the $Pu^V \cdot Cr^{III}$ complex by Pu(III)[16] and Fe(II)[17] and since the rate laws for the disproportionation or reduction of the actinide(V) ions usually contain a positive acid dependency, it has been suggested[17] that the Cr(III) ion plays a role similar to that of the proton in the reduction mechanism. This conclusion is supported by the observation that the reduction of $Pu^V \cdot Cr^{III}$ by either Pu(III) or Fe(II) is much faster than the reduction of uncomplexed Pu(V) by these reagents. Unfortunately the rate constant for the reduction of uncomplexed U(V) by Cr(II) cannot easily be determined, but preliminary experiments suggest that the reduction of U(V) by Eu(II), which has virtually the same redox potential as Cr(II), is much slower than the disproportionation of U(V) in 1 *M* $HClO_4$ at 20°.[18] It would thus appear that the general mechanism of the reduction of $U^V \cdot Cr^{III}$ by Cr(II) is similar to that operating in the reduction of the $Pu^V \cdot Cr^{III}$ complex.

The lack of an acid dependency in the rate law also indicates that the major activation process is the reaction

$$\mathrm{Cr(II)} + \mathrm{U^V \cdot Cr^{III}} \rightarrow [\mathrm{Cr \cdots O\text{-}U\text{-}O \cdots Cr}]^* \qquad (18)$$

where the activated complex may well have a linear structure as suggested by Gordon.[2] However, the possibility that the perchlorate ion may be involved in the formation of the activated complex cannot be entirely excluded.

Comparison of the rate parameters of the $U^V \cdot Cr^{III}$–Cr(II) and $Pu^V \cdot Cr^{III}$–Pu(III) reactions (Table VII) shows that the higher rate for the former reaction is almost entirely the result of a slightly smaller ΔH^* value, the ΔS^* values being nearly the same for the two reactions. For a series of similar reactions it is frequently found that the ΔS^* value becomes more negative as the charge on the activated complex increases.[19] It would thus be expected that the ΔS^* value for the Cr(II)–$U^V \cdot Cr^{III}$ reaction would be less negative compared to that found for the Pu(III)–$Pu^V \cdot Cr^{III}$ reactions. The observation that the two values are in fact almost identical could indicate that the $[\mathrm{Cr \cdots O\text{-}U\text{-}O \cdots Cr}]^*$ activated complex has a higher charge density when compared to the one formed in the Pu(III)–$Pu^V \cdot Cr^{III}$ reaction.

Acknowledgment. The authors wish to thank Mr. J. M. Barry (Applied Mathematics and Computing Section, AAEC) for writing the computer programs used for the nonlinear least-squares analysis of the rate curves and Dr. T. W. Newton for his helpful advice on this problem.

Registry No. Uranium(VI), 22541-40-8; chromium(II), 22541-79-3.

[15] The author wishes to thank Dr. J. C. Sullivan for suggesting this interpretation of the results.

[16] C. Lavallee and T. W. Newton, *Inorg. Chem.*, 11, 2616 (1972).

[17] T. W. Newton and M. J. Burkhart, *Inorg. Chem.*, 10, 2323 (1971).

[18] A. Ekstrom, unpublished data; see also ref 12.

[19] (a) J. Halpern, *Quart. Rev., Chem. Soc.*, 15, 220 (1961); (b) T. W. Newton and F. B. Baker, *Advan. Chem. Ser.*, No. 71, 268 (1967).

Contribution from the Department of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174

Mechanism of the Reduction of Bromate Ion by Hexacyanoferrate(II) and by Bromide Ion in Acidic Aqueous Solution

JAMES P. BIRK* and STEPHEN G. KOZUB

Received March 13, 1973

The reaction between ferrocyanide and bromate ions follows partially autocatalytic kinetics, with the autocatalysis arising from the bromide–bromate reaction. The rate equation is given by $-d[\mathrm{Fe(CN)_6}^{4-}]/dt = 6k_1[\mathrm{Fe(CN)_6}^{4-}][\mathrm{BrO_3}^-] + 6k_3[\mathrm{Br}^-][\mathrm{BrO_3}^-][\mathrm{H}^+]^2$, with $k_1 = c + d[\mathrm{H}^+]^2$. Values of the parameters at 25.0° and 0.50 *M* ionic strength are $c = (1.25 \pm 0.12) \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, $d = 0.193 \pm 0.005\ M^{-3}\ \mathrm{sec}^{-1}$, and $k_3 = 2.86 \pm 0.06\ M^{-3}\ \mathrm{sec}^{-1}$. A detailed mechanism is presented to explain these results.

Introduction

The rates of both oxygen exchange and oxidation–reduction reactions of many oxy anions depend very strongly on acid concentration. For a number of oxy anions (*e.g.*, SO_4^{2-}, NO_3^-, ClO_3^-, BrO_3^-, CO_3^{2-}, and NO_2^-) the rate laws for oxygen exchange and for reduction by a species R generally have major rate terms of the form $k[XO_m^{n-}][H^+]^2$ and $k[XO_m^{n-}][R][H^+]^2$, respectively. On the basis of close correlations between rates of exchange and redox reactions as well as other evidence (*e.g.*, isotope effects) which has been discussed extensively elsewhere,[1,2] it has been proposed

---

* Author to whom inquiries should be addressed at the Department of Chemistry, Arizona State University, Tempe, Ariz. 85281.

that the oxidation-reduction reactions occur by a mechanism involving replacement of an oxo group prior to electron transfer, *i.e.*, an inner-sphere process.[1]

We have previously developed rate correlations, based on the Marcus theory, for the reductions of chromium(VI)[3] or vanadium(V)[4,5] by $Fe(CN)_6^{4-}$, $Fe(bipy)(CN)_4^{2-}$ (bipy = 2,2'-bipyridyl), $Fe(bipy)_2(CN)_2$, and $Fe(bipy)_3^{2+}$, which appear to provide a viable criterion for a distinction between inner-sphere and outer-sphere mechanisms, at least for this series of reducing agents. We hope to examine these rate correlations for the reduction of oxy anions by the above series of iron(II) complexes to determine whether an inner-sphere mechanism is indeed operative in such systems.

We wish to report here a kinetic study of the $Fe(CN)_6^{4-}$-BrO_3^- reaction, which exhibits rather novel partially autocatalytic kinetic behavior. In order to interpret this system completely, it was also necessary to carry out kinetic studies of the Br^--BrO_3^- and $Fe(CN)_6^{4-}$-Br_2 reactions.

These systems are of further interest since the bromate oxidation of metal ions has been studied in only a few systems, these having VO^{2+},[6] Np(V),[7,8] Ce(III),[7] Mn(II),[7] or Fe^{2+} [9] as the reducing agent. In the first and last systems, a simple mixed second-order rate equation was observed, while the other three systems exhibited an induction period followed by conformance to a rate equation second-order in bromate and independent of the reducing agent. Mechanisms consistent with these observations have been proposed,[7b] and it has been suggested that the rate behavior can be correlated with the strength of the reducing agent, the stronger (VO^{2+} and Fe^{2+}) having the simpler behavior. Thus it was of interest to determine whether this correlation would hold with $Fe(CN)_6^{4-}$ which is an even stronger reducing agent than VO^{2+} or Fe^{2+}. Studies have also been carried out previously with the two-electron reductants U(IV)[10] and Sb(III).[11]

Experimental Section

Solutions of potassium ferrocyanide, lithium perchlorate, and perchloric acid were prepared and analyzed as previously described.[3] A lithium bromide solution was prepared from reagent grade material and was analyzed by ion-exchange titration. Reagent grade sodium bromate was recrystallized from distilled water and dried at 120°. Solutions were standardized by reaction with excess sodium iodide in acid. The liberated iodine was titrated with sodium thiosulfate solution previously standardized against dried potassium iodate. Solutions of bromine were prepared immediately before use by reaction of BrO_3^- with excess Br^- in acidic solution, allowing sufficient time for this reaction to reach a state of equilibrium.

The kinetics of the $Fe(CN)_6^{4-}$-BrO_3^- and Br^--BrO_3^- reactions were determined at 25.0° and 0.50 *M* ionic strength (maintained with lithium perchlorate) using a Cary 14 recording spectrophotometer with previously described techniques.[3] Bromate ion was always present in at least a tenfold excess over ferrocyanide or bromide ions. Most measurements were made at 420 nm for the $Fe(CN)_6^{4-}$ reaction and at 395 nm for the Br^- reaction, but measurements at several other wavelengths gave identical results. Bromate was added to the acidic solutions immediately before reaction was initiated because spurious results were sometimes noted when BrO_3^- was in contact with H^+ over a long period, presumably due to oxidation of water. The kinetics of the $Fe(CN)_6^{4-}$-Br_2 reaction were determined at 25.0° and 0.50 *M* ionic strength with a Durrum stopped-flow spectrophotometer at 420 nm.

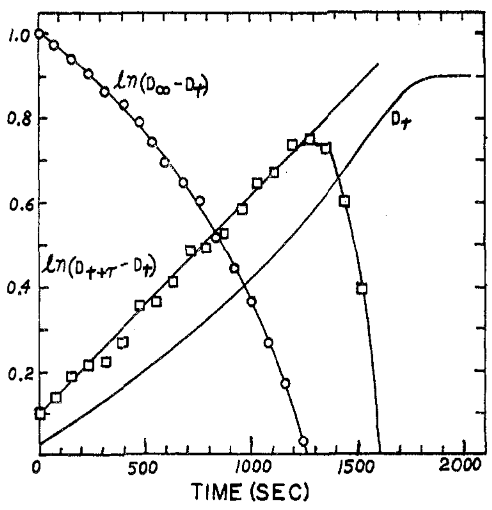

Figure 1. Plots of various functions of absorbance *vs.* time for the $Fe(CN)_6^{4-}$-BrO_3^- reaction. Reaction conditions were 1.0×10^{-4} *M* Fe(II), 1.0×10^{-3} *M* BrO_3^-, 0.50 *M* $HClO_4$, and 25°.

Results

The Bromate-Ferrocyanide Reaction. With BrO_3^- in excess, spectral measurements indicated the overall stoichiometry given in eq 1. Absorbance-time traces for this reaction showed increasing rather than decreasing slope with time and leveled off fairly abruptly at the end of the reaction, suggestive of autocatalysis.

$$BrO_3^- + 5Fe(CN)_6^{4-} + 6H^+ = {}^1/_2Br_2 + 5Fe(CN)_6^{3-} + 3H_2O \qquad (1)$$

As expected, first-order plots of ln $(D_\infty - D_t)$ *vs.* time (where *D* is absorbance at the indicated time) showed downward curvature (Figure 1). Various plots derived for simple autocatalytic rate equations generally gave S-shaped curves. However, Guggenheim plots[12] of ln $(D_{t+\tau} - D_t)$ *vs.* time (where τ is a constant time interval) gave straight lines of positive slope over a large fraction of reaction, followed by a rather abrupt change of slope with a limiting negative value similar to that expected from the Br^--BrO_3^- reaction (Figure 1). These results are reminiscent of the behavior of the VO_2^+-$Ta_6Br_{12}^{2+}$ reaction,[13] which followed a rate equation containing one normal term and one autocatalytic term. The following sequence of reactions was considered as a model which might give rise to partially autocatalytic behavior in the present system

$$Fe(II) + BrO_3^- \xrightarrow[2H^+]{k_1} Fe(III) + BrO_2 + H_2O \qquad (2)$$

$$4Fe(II) + BrO_2 + 4H^+ \overset{fast}{=\!=} 4Fe(III) + {}^1/_2Br_2 + 2H_2O \qquad (3)$$

$$Fe(II) + {}^1/_2Br_2 \overset{k_2,\ fast}{=\!=} Fe(III) + Br^- \qquad (4)$$

$$Br^- + BrO_3^- + 2H^+ \xrightarrow{k_3} \xrightarrow[4H^+]{4Br^-} 3Br_2 + 3H_2O \qquad (5)$$

The combination of reactions 4 and 5 is responsible for the autocatalysis. The identity of the rate-determining step in eq 5 was established in earlier kinetic studies of the Br^--

---

[1] E. Chaffee and J. O. Edwards in "Inorganic Reaction Mechanisms," J. O. Edwards, Ed., Wiley, New York, N. Y., 1970, pp 216-220.

[2] J. O. Edwards, *Chem. Rev.*, 50, 455 (1952).

[3] J. P. Birk, *J. Amer. Chem. Soc.*, 91, 3189 (1969).

[4] J. P. Birk, *Inorg. Chem.*, 9, 125 (1970).

[5] J. P. Birk and S. V. Weaver, *Inorg. Chem.*, 11, 95 (1972).

[6] R. C. Thompson, *Inorg. Chem.*, 10, 1892 (1971).

[7] (a) R. C. Thompson, *J. Amer. Chem. Soc.*, 93, 7315 (1971); (b) R. M. Noyes, R. J. Field, and R. C. Thompson, *ibid.*, 93, 7315 (1971).

[8] G. C. Knight and R. C. Thompson, *Inorg. Chem.*, 12, 63 (1973).

[9] J. P. Birk, *Inorg. Chem.*, 12, 2468 (1973).

[10] A. G. Rykov, V. Ya. Vasil'ev, and G. N. Yakovlev, *Radiokhimiya*, 8, 33 (1966); *Chem. Abstr.*, 64, 18950 (1966).

[11] E. Bishop, J. M. Ottaway, and G. D. Short, *Anal. Chim. Acta*, 27, 528 (1962).

[12] E. A. Guggenheim, *Phil. Mag.*, [7] 2, 528 (1926).

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

Table I. Values of the Rate Parameter $(-b)$ for the Reaction of $Fe(CN)_6^{4-}$ with BrO_3^- [a]

$10^3[BrO_3^-]$, M	$10^3(-b)$, sec^{-1}	$-b/[BrO_3^-]$, M^{-1} sec^{-1}	$10^3[BrO_3^-]$, M	$10^3(-b)$, sec^{-1}	$-b/[BrO_3^-]$, M^{-1} sec^{-1}
1.02	0.325	0.319	10.0[b]	3.46 ± 0.015	0.346
1.96	0.666	0.340	15.0	4.81	0.321
4.01	1.38	0.344	20.0	6.66	0.333
6.99	2.36	0.337	30.0	9.63	0.321
9.98	3.11	0.311			Av 0.330 ± 0.010

[a] $[Fe(CN)_6^{4-}]_0 = 1.00 \times 10^{-4}$ M, $[H^+] = 0.450$ M. [b] $[Fe(CN)_6^{4-}]_0 = (1.00\text{–}5.00) \times 10^{-4}$ M.

BrO_3^- reaction[14-17] and is verified below. If reaction 4 is fast compared to reaction 5, as indicated by a preliminary kinetic study of reaction 4 described below, then Br_2 is maintained at steady-state concentrations until the Fe(II) concentration becomes very small, so that during most of the reaction the stoichiometry is actually 6:1 and becomes 5:1 only when Br_2 starts to accumulate. A rate equation for this system when this condition is met is given by eq 6.

$$-d[Fe(II)]/dt = 6k_1[Fe(II)][BrO_3^-] + 6k_3[Br^-][BrO_3^-][H^+]^2 \qquad (6)$$

The stoichiometric factor of 6 in this equation holds as long as the bromine concentration does not build up to significant levels and this factor in the second term is valid even if Fe(II) intercepts some of the intermediate oxidation states of bromine produced in reaction 5, as long as such reactions are fast compared to reaction 5. Using the stoichiometric relation $[Br^-]_t = ([Fe(II)]_0 - [Fe(II)]_t)/6$ (where the subscript indicates the time) and integrating eq 6 yield the expression for $[Fe(II)]_t$

$$[Fe(II)]_t = (a/b + [Fe(II)]_0)e^{-bt} - a/b \qquad (7)$$

with $a = k_3[H^+]^2([Fe(II)]_0 + [Br^-]_0)[BrO_3^-]$ and $b = (6k_1 - k_3[H^+]^2)[BrO_3^-]$, which is valid whenever the conditions discussed above are met. Subtraction of a similar equation for $[Fe(II)]_{t+\tau}$ from eq 7 and taking the natural logarithm of this difference yields the equation

$$\ln([Fe(II)]_t - [Fe(II)]_{t+\tau}) = \ln\{(a/b + [Fe(II)]_0)(1 - e^{-b\tau})\} - bt \qquad (8)$$

Thus the Guggenheim plots should have slopes of $-b$, *i.e.*, of $(k_3[H^+]^2 - 6k_1)[BrO_3^-]$. The first-order dependence of $-b$ on $[BrO_3^-]$ is shown by a series of experiments at 0.450 M H^+ given in Table I. Variation of the $Fe(CN)_6^{4-}$ concentration in the range $(0.50\text{–}5.00) \times 10^{-4}$ M indicated a first-order dependence on $[Fe(CN)_6^{4-}]$ as demanded by the model (eq 2-5) and no dependence on $[K^+]$ in the range $(2\text{–}20) \times 10^{-4}$ M. Values of b were also determined with $[H^+]$ in the range 0.050-0.488 M, primarily with 0.010 M BrO_3^- but with some experiments having concentrations in the range 0.01-0.04 M. Values of k_1 were extracted from values of b using the relation $k_1 = (k_3[H^+]^2 + b/[BrO_3^-])/6$, with the value of $k_3 = 2.86$ M^{-3} sec^{-1} determined below. The values of k_1 which are summarized in Table II vary with the acidity according to the equation

$$k_1 = c + d[H^+]^2 \qquad (9)$$

Values of the parameters determined with a nonlinear least-squares computer program[18] with each point weighted as k_1^{-2} are $c = (1.25 \pm 0.12) \times 10^{-3}$ M^{-1} sec^{-1} and $d = 0.193 \pm 0.005$ M^{-3} sec^{-1}.

Table II. Values of k_1 for the Reaction of $Fe(CN)_6^{4-}$ with BrO_3^- as a Function of $[H^+]$[a]

$[H^+]_0$, M	10^2k_1, M^{-1} sec^{-1} Obsd[b]	10^2k_1, M^{-1} sec^{-1} Calcd[c]	$[H^+]_0$, M	10^2k_1, M^{-1} sec^{-1} Obsd[b]	10^2k_1, M^{-1} sec^{-1} Calcd[c]
0.488	4.83	4.71	0.250	1.20	1.33
0.450	4.17 ± 0.19 (9)	4.02	0.200	0.830 ± 0.079 (5)	0.895
0.400	3.29 ± 0.24 (2)	3.21	0.150	0.577	0.558
0.350	2.85	2.48	0.100	0.340 ± 0.018 (4)	0.318
0.300	1.88	1.86	0.050	0.168	0.173

[a] Reactant concentrations are given in the text. [b] Where uncertainties are given, these are average deviations for a number of determinations. The number of experiments is given in parentheses. [c] Calculated from eq 9 and the parameters given in the text.

In further support of our interpretation, the limiting initial slopes of the first-order plots of $\ln(D_\infty - D_t)$ *vs.* t, although difficult to evaluate accurately, did resemble the values of k_1 extracted from the slopes of the Guggenheim plots. The abrupt change in slope of the Guggenheim plots near the end of the reaction is attributed to a failure of the assumptions outlined above. In particular, during this time the concentration of Br_2 is building up to non-steady-state levels and the absorbance change is primarily due to the Br^--BrO_3^- reaction.

An experiment was carried out with excess $Fe(CN)_6^{4-}$ under the conditions 1.0×10^{-3} M $Fe(CN)_6^{4-}$, 2.0×10^{-5} M BrO_3^-, and 0.50 M H^+. Since the reaction under these conditions was 6 times slower than under comparable conditions with excess BrO_3^-, a more extensive series of experiments was not carried out because of the possibility of decomposition of BrO_3^- in acidic solutions which we had experienced earlier. Using an initial rate method for this experiment, the value of the pseudo-first-order rate constant was found to be 4.3×10^{-5} sec^{-1}, in good agreement with the value of 4.9×10^{-5} sec^{-1} calculated from k_1. In agreement with the proposed mechanism, autocatalysis was not observed under these conditions. Several other experiments with excess $Fe(CN)_6^{4-}$ are discussed below.

The Bromate-Bromide Reaction. The kinetics of the reaction between BrO_3^- and Br^- (eq 10) were studied at 25.0°

$$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O \qquad (10)$$

and 0.50 M ionic strength. The stoichiometry was confirmed by attainment of the correct final absorbance at 395 nm, a wavelength of maximum absorbance for Br_2. Previous kinetic studies[12-15] of this reaction have shown the primary term in the rate equation to be of the form

$$-d[Br^-]/dt = 5k_3[Br^-][BrO_3^-][H^+]^2 \qquad (11)$$

This equation is confirmed by the data summarized in Table III, which followed pseudo-first-order kinetics for ≥95% reaction and which gives a value of $k_3 = 2.86 \pm 0.06$ M^{-3} sec^{-1}. Previously determined values of k_3 under similar conditions,

---

(14) W. C. Bray and H. A. Liebhafsky, *J. Amer. Chem. Soc.*, 57, 51 (1935).

(15) M. Sclar and S. C. Reisch, *J. Amer. Chem. Soc.*, 58, 667 (1936).

(16) H. A. Young and W. C. Bray, *J. Amer. Chem. Soc.*, 54, 4248 (1932).

(17) J. R. Clarke, *J. Chem. Educ.*, 47, 775 (1970).

(18) The programs used are based on reports from Los Alamos Scientific Laboratory (LA-2367 + addenda) and were modified to operate on the IBM 360/75 computer.

Table III. Values of the Rate Constant for the Reaction of Br^- with BrO_3^- [a]

$10^3 \times [BrO_3^-]_0$, M	$[H^+]$, M	k_3,[b] M^{-3} sec^{-1}	$10^3 \times [BrO_3^-]_0$, M	$[H^+]$, M	k_3,[b] M^{-3} sec^{-1}
10.0	0.489	2.76, 2.83	10.0	0.300	2.85
10.0	0.400	2.89, 2.89	10.0	0.200	2.80
5.00	0.400	2.94	10.0	0.100	2.89
2.00	0.400	2.78	10.0	0.050	2.99
				Av	2.86 ± 0.06

[a] $[Br^-]_0 = 0.1[BrO_3^-]_0$, 25.0°, 0.50 M ionic strength. [b] $k_3 = {}^1/_5(-d \ln [Br^-]/dt)[BrO_3^-]_0^{-1}[H^+]_0^{-2}$.

but with $NaClO_4$ as the inert electrolyte, are 1.78 M^{-3} sec^{-1} using an initial rate method,[14] 2.60 M^{-3} sec^{-1} with allyl alcohol as a scavenger for hypobromous acid,[15] and 2.52 M^{-3} sec^{-1} with hydrogen peroxide as a scavenger.[16] The significant discrepancy between the first value and the last two values does not appear in our data in spite of the absence of a scavenger.[14]

The Bromine-Ferrocyanide Reaction. Preliminary experiments on the kinetics of the reaction between Br_2 and $Fe(CN)_6^{4-}$ indicate that this reaction is indeed sufficiently rapid to conform with the assumptions made for the proposed mechanism, eq 2-5. In the concentration ranges (1-8) × 10^{-4} M Br_2, (0.5-4) × 10^{-5} M Fe(II), 10^{-3}-10^{-1} M Br^-, and 0.025-0.3 M H^+ at 25.0° and 0.50 M ionic strength, the second-order rate constants fell in the range 10^3-10^5 M^{-1} sec^{-1}, which is a factor of $\gtrsim 10^4$ greater than that for the Fe(II)-BrO_3^- or the Br^--BrO_3^- reaction.

Preliminary interpretation of the data suggests that this reaction occurs *via* parallel paths involving Br_2 and HOBr as active oxidizing species.

Discussion

The acid dependence (eq 9) of the first step (eq 2) in the $Fe(CN)_6^{4-}$ reduction of BrO_3^- can be interpreted in terms of parallel inner-sphere (eq 12-14) and outer-sphere (eq 15-16)

$$BrO_3^- + 2H^+ \rightleftharpoons H_2BrO_3^+ \qquad (K_a << 1) \tag{12}$$

$$H_2BrO_3^+ + Fe(CN)_6^{4-} \xrightarrow{k_1'} (NC)_5Fe\text{-}CN\text{-}BrO_2^{3-} + H_2O \tag{13}$$

$$(NC)_5Fe\text{-}CN\text{-}BrO_2^{3-} \overset{\text{fast}}{=\!=} Fe(CN)_6^{3-} + BrO_2 \tag{14}$$

$$BrO_3^- + Fe(CN)_6^{4-} \xrightarrow{k_1''} BrO_3^{2-} + Fe(CN)_6^{3-} \tag{15}$$

$$BrO_3^{2-} + 2H^+ \overset{\text{fast}}{=\!=} BrO_2 + H_2O \tag{16}$$

type paths, with $k_1 = k_1'' + k_1'K_a[H^+]^2$. The postulated binuclear intermediate may indeed exist only in the transition state and the rate-determining step (eq 13) may be a simple substitution reaction producing Fe^{II}-Br^{V}, or it may involve electron transfer as well, producing Fe^{III}-Br^{IV}. A possible precedent for this situation is found in the Fe^{2+}-BrO_3^- reaction,[9] where one of the mechanistic interpretations consistent with the rate equation was suggestive of parallel inner-sphere and outer-sphere paths, and the binuclear intermediate formed in the inner-sphere path probably contained Fe^{III}-Br^{IV}. If both paths should persist for the other Fe(II) complexes, rate correlations[3,5] should provide further evidence regarding these tentative mechanistic details. Identification of the Br(IV) product as either BrO_3^{2-} or BrO_2 is not certain, but both are known forms of Br(IV).[19]

The proposed inner-sphere path (*i.e.*, the path second order in $[H^+]$) can be examined in more detail with respect to the mechanism of displacement of the water molecule from $H_2BrO_3^+$—dissociative forming BrO_2^+ as a distinct intermediate or associative in which the displacement of H_2O is assisted by the incoming $Fe(CN)_6^{4-}$. If a few assumptions can be made, it is possible to calculate rate constants under conditions of excess Fe(II) for the two limiting types of mechanism. If the mechanism is of the associative type with no formation of BrO_2^+, the rate constants should be directly related by the ratio of stoichiometric coefficients to the rate constants with excess BrO_3^-. Several experiments were carried out with excess Fe(II) where rate constants evaluated from initial slopes show deviations from the expected values (Table IV). Values for the H_2O exchange rate constant of BrO_3^- (assumed first order in $[H_2O]$) are 1.4×10^{-4}[20] or 8.0×10^{-5} M^{-3} sec^{-1}[21] at 25° and 0.9-1.0 M ionic strength. If it is assumed that both H_2O exchange and $Fe(CN)_6^{4-}$ reduction involve BrO_2^+, a general mechanism can be developed, where X = H_2O (W) or $Fe(CN)_6^{4-}$ (Fe), as eq 12 followed by

Table IV. Observed and Calculated Rate Constants with Excess Ferrocyanide[a]

$[Fe(CN)_6^{4-}]$, M	$[H^+]$, M	Rate constant × 10^5, sec^{-1}: Obsd	Calcd for no BrO_2^+ [b]	Calcd for BrO_2^+ [b]: Anbar[c]	Hoering[d]
0.0010	0.50	4.3	4.95	4.84	4.76
0.010	0.40	10	32.4	26.9	23.0
0.020	0.30	14	37.2	26.5	21.2

[a] 2×10^{-5}-2×10^{-4} M BrO_3^-. [b] Corrected for the acid-independent path. [c] Exchange rate constant from ref 20. [d] Exchange rate constant from ref 21.

$$H_2BrO_3^+ \underset{k_5}{\overset{k_4}{\rightleftarrows}} H_2O + BrO_2^+ \qquad (K << 1) \tag{17}$$

$$BrO_2^+ + X \xrightarrow{k^X{}_6} XBrO_2^+ \tag{18}$$

Under conditions such that eq 17 approximates a rapid equilibrium (*e.g.*, low [Fe(II)]) and eq 18 is rate determining, rate $= k^X{}_6KK_a[BrO_3^-][X][H^+]^2/[H_2O]$. Since the observed equation is rate $= k^X[BrO_3^-][X][H^+]^2$, $k^X = k^X{}_6KK_a/[H_2O]$ and $k^{Fe}/k^W = k^{Fe}{}_6/k^W{}_6$ with $k^W{}_6 = k_5$, giving $k^{Fe}{}_6 = 1360k_5$[20] or $2400k_5$.[21] If this mechanism is correct, at sufficiently high [Fe(II)], deviations from a first-order [Fe(II)] dependence should be observed: $k^{Fe} = k_4k^{Fe}{}_6K_a/(k^{Fe}{}_6[Fe(II)] + k_5[H_2O])$. Using the excess BrO_3^- data, it is possible to calculate a value for k_4K_a of 8.08×10^{-3}[20] or 4.48×10^{-3} M^{-2} sec^{-1}.[21] It is then possible to calculate values of k^{Fe} for the appropriate conditions (Table IV). The observed values clearly do not match those calculated for a mechanism not involving BrO_2^+. Although the agreement is still not very good for the BrO_2^+ mechanism, it is better and would be improved if the exchange rate constant were actually smaller. Likely experimental errors might be expected to give a value which is too large.

One final point should be made concerning the $[H^+]$ dependence. Over the range of $[H^+]$ covered by these experiments, the fraction of Fe(II) present in different states of protonation ($Fe(CN)_6^{4-}$, $HFe(CN)_6^{3-}$, and $H_2Fe(CN)_6^{2-}$) should vary somewhat.[22] Since this situation would normally result in a sum of terms in the denominator of the rate equation, it must be true that these various species react

---

(19) M. Anbar and P. Neta, *J. Inorg. Nucl. Chem.*, **28**, 1645 (1966).

(20) M. Anbar and S. Guttman, *J. Amer. Chem. Soc.*, **83**, 4741 (1961).

(21) T. C. Hoering, R. C. Butler, and H. O. McDonald, *J. Amer. Chem. Soc.*, **78**, 4829 (1956).

(22) J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

with BrO_3^- at about the same rate. A similar situation was observed in the $Fe(CN)_6^{4-}$-VO_2^+ reaction.[5]

The bromate oxidations of one-electron metal ion reducing agents which have been studied so far appear to fall into mechanistic classifications which depend on the strength of the reducing agent. With the very weak reducing agents Ce(III)[7] ($E^\circ = -1.61$ V[23]), Mn(II)[7] (−1.51 V[23]), and Np(V)[7,8] (−1.15 V[23]), there is very little direct reduction of BrO_3^-. The mechanism involves an autocatalytic production of $HBrO_2$ in competition with the disproportionation of $HBrO_2$. The metal ion is oxidized primarily by BrO_2. With the somewhat stronger reducing agent VO^{2+} (−1.00 V[23]), there is a direct reaction of VO^{2+} with BrO_3^-.[6] However the mechanism is complicated by the fact that the reducing agent is sufficiently weak that $HBrO_2$ disproportionation occurs in competition with the VO^{2+} reduction of $HBrO_2$. With Fe^{2+} (−0.77 V[23]), there is a direct reduction of BrO_3^- with no apparent complexities.[9] Apparently Fe^{2+} is a sufficiently strong reducing agent to reduce $HBrO_2$ faster than it can disproportionate, but is not sufficiently strong to reduce Br_2 fast enough to cause the autocatalysis noted with $Fe(CN)_6^{4-}$. With $Fe(CN)_6^{4-}$ (−0.69 V[23]) there is a direct reduction of BrO_3^- and an autocatalytic reduction due to the $Fe(CN)_6^{4-}$-Br_2 and Br^--BrO_3^- reactions, with a significant portion of the reaction being carried by the autocatalytic path. In this case the reduction of $HBrO_2$ is faster than disproportionation but the overall reaction is not sufficiently fast to eliminate the competition between $Fe(CN)_6^{4-}$ and Br^- for BrO_3^-. It is expected that with stronger reducing agents, the kinetics will be quite straightforward once the reduction of BrO_3^- becomes sufficiently fast compared to the Br^--BrO_3^- reaction. Any future entries in this correlation may of course be modified by any peculiarities in the chemical behavior of the metal ion reducing agent.

Acknowledgment. Support of this work by the Advanced Research Projects Agency and by the National Science Foundation (Grant GH-33633) is gratefully acknowledged.

Registry No. $Fe(CN)_6^{4-}$, 13408-63-4; BrO_3^-, 15541-45-4; Br^-, 24959-67-9; Br_2, 7726-95-6.

[23] W. L. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd ed, Prentice-Hall, New York, N. Y., 1952.

Contribution from the Department of Chemistry and the Laboratory for Research on
the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174

Mechanism of the Reduction of Uranium(VI) by Titanium(III) and of the Induced Reduction of Vanadium(IV)

THOMAS P. LOGAN[1] and JAMES P. BIRK*

Received March 29, 1973

The reduction of uranium(VI) by titanium(III) in acidic chloride or perchlorate media was studied at 25.0° and 0.500 *M* ionic strength. The reaction followed the rate equation $-d[U(VI)]/dt = k_1K_a[Ti(III)][U(VI)]/(K_a + [H^+])$ with K_a being the acid dissociation constant of Ti^{3+}. Values of the parameters were $k_1K_a = 13.7 \pm 0.5\ sec^{-1}$ and $K_a = 0.0136 \pm 0.0035$ *M*. The reaction is inhibited by vanadium(IV), according to the rate equation $-d[U(VI)]/dt = k_1k_2K_a^2k_3^{-1}[Ti(III)]^2[U(VI)](K_a + [H^+])^{-2}/\{[VO^{2+}] + k_2K_ak_3^{-1}[Ti(III)](K_a + [H^+])^{-1}\}$ with $k_1k_2K_a^2k_3^{-1} = 0.446 \pm 0.014\ M\ sec^{-1}$ and $k_2K_ak_3^{-1} = 0.0324 \pm 0.0011\ M$. The inhibition is interpreted in terms of a competition for U(V) between V(IV) and Ti(III), which is verified by the observed production of V(III).

Introduction

As part of a series of kinetic studies of oxidations by d^0 metal oxy ions such as Cr(VI),[2-4] V(V),[5-7] and Mn(VII), to determine the kinetic consequences of the substitution inertness of the reducing agent, we have now studied the reduction of U(VI) by the labile reductant[8] Ti(III). It has been possible to elucidate the mechanism of this reaction in considerable detail by studying the inhibition of the reaction by VO^{2+}. The oxidation of Ti^{3+}, which has been studied in only a few cases,[7] has now been extended to the entire series of d^0 metal ion oxidants—VO_2^+,[7] $HCrO_4^-$,[4] MnO_4^-,[9] and UO_2^{2+}—making it possible to examine the common features of all these reactions to determine those factors which affect the mechanistic behavior of Ti^{3+}.

Experimental Section

Solutions of uranium(VI) were prepared by dissolving weighed amounts of Alfa Inorganics UO_3 in a known excess of $HClO_4$. The solutions were analyzed by reducing U(VI) to U(IV) with zinc amalgam under N_2 and titrating aliquots in 1 *M* H_2SO_4 with 0.1 *M* Ce(IV) to a blue ferroin end point at 50°. The reduced uranium solution was shaken well with air before titration to oxidize any U(III) to U(IV). Results agreed well with the weight of UO_3 taken. Acid concentration was obtained by difference. All other materials were prepared and analyzed as described earlier.[5,7] The handling of solutions and the procedures for kinetic measurements have been described.[7] The acid concentrations in the two reactant solutions to be mixed in the stopped-flow apparatus were controlled appropriately to suppress dissociation of the Ti(III) dimer.[7] Data were obtained principally at 648 nm, a wavelength of maximum absorbance for U^{4+}, but no difference in results was noted upon variation of the wavelength over the small ranges in which reasonable absorbance changes could be obtained. First-order plots of ln $(D_\infty - D_t)$ *vs.* time (D = absorbance) were generally linear to ≥90% reaction under pseudo-first-order conditions. With the slower reactions, infinity readings were sometimes in doubt, due to diffusion of reactants into the observation

---

* Author to whom inquiries should be addressed at the Department of Chemistry, Arizona State University, Tempe, Ariz. 85281.

[1] Taken in part from the Ph.D. thesis of T. P. L., University of Pennsylvania, 1972.

[2] J. P. Birk, *J. Amer. Chem. Soc.*, 91, 3189 (1969).

[3] J. P. Birk and J. W. Gasiewski, *Inorg. Chem.*, 10, 1586 (1971).

[4] J. W. Gasiewski and J. P. Birk, unpublished experiments.

[5] J. P. Birk, *Inorg. Chem.*, 9, 125 (1970).

[6] J. P. Birk and S. V. Weaver, *Inorg. Chem.*, 11, 95 (1972).

[7] J. P. Birk and T. P. Logan, *Inorg. Chem.*, 12, 580 (1973).

[8] A. M. Chmelick and D. Fiat, cited in D. J. Hewkins and R. H. Prince, *Coord. Chem. Rev.*, 5, 45 (1970).

[9] T. P. Logan and J. P. Birk, unpublished experiments.