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(19) This value leads to $\Delta G^{**} = 6.0$–$7.0$ kcal mol$^{-1}$ for $H_2Q^{+}\cdot/H_2Q$ exchange, that is, the rate constant of $7 \times 10^5$–$4 \times 10^6$ L mol$^{-1}$ s$^{-1}$ for the self-exchange rates. Since these values seem low with respect to other exchange rates between radicals and parent molecules,[14] it must be noted that the $\lambda$'s for benzenediol oxidation were derived by setting the deprotonation constant of semiquinone of parent quinol ($H_2Q^{+}\cdot \rightleftharpoons HQ\cdot + H^+$) equal to 10 mol L$^{-1}$.[15b] If the effective value is higher, then $\Delta G°_{12}'$ is higher, and consequently the $\lambda$'s which fit the data are lower. For example, by setting this deprotonation constant at 100 mol L$^{-1}$, the $\lambda$'s are decreased by about 4 kcal mol$^{-1}$; then $\Delta G^{**}$ ($H_2Q^{+}\cdot/H_2Q$) = 4.0–5.0 kcal mol$^{-1}$; that is, self-exchange rate constants are $2 \times 10^7$–$1 \times 10^8$ L mol$^{-1}$ s$^{-1}$.
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# Mechanism of the Reduction of Bromate Ion by Cyano(bipyridyl)iron(II) Complexes[1a]

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The kinetics of the $BrO_3^-$ oxidation of $Fe(bpy)(CN)_4^{2-}$, $Fe(bpy)_2(CN)_2$, and $Fe(bpy)_3^{2+}$ have been determined in acidic perchlorate solutions at 25.0 °C and 0.50 M ionic strength. Each reaction is autocatalytic, the first two complexes following the same mechanism as the $Fe(CN)_6^{4-}$ reaction, with the rate law $-\mathrm{d}[Fe(II)]/\mathrm{d}t = 6(c + d[H^+]^2)[Fe(II)][BrO_3^-] + 6k_3[Br^-][BrO_3^-][H^+]^2$ where $k_3 = 2.86$ M$^{-3}$ s$^{-1}$, and $c = (6.2 \pm 1.1) \times 10^{-3}$ M$^{-1}$ s$^{-1}$, $d = 0.227 \pm 0.018$ M$^{-3}$ s$^{-1}$ for $Fe(bpy)(CN)_4^{2-}$, and $c = (2.95 \pm 0.44) \times 10^{-2}$ M$^{-1}$ s$^{-1}$, $d = 0.755 \pm 0.047$ M$^{-3}$ s$^{-1}$ for $Fe(bpy)_2(CN)_2$. A different rate law and mechanism were found for the autocatalytic $Fe(bpy)_3^{2+}$ reaction, with the slope ($-b$) of Guggenheim plots being given by $-b = g[BrO_3^-][H^+] + h[BrO_3^-]^2[H^+]^2$, where $g = 12.8 \pm 0.3$ M$^{-2}$ s$^{-1}$ and $h = 964 \pm 56$ M$^{-4}$ s$^{-1}$. Rate correlations based on Marcus theory suggest that all these reactions proceed by outer-sphere mechanisms.

## Introduction

One of the predictions of the Marcus theory for oxidation–reduction reactions[2,3] is that the relative rates of oxidation of a series of reducing agents by two different oxidants should be independent of the identity of the reducing agent if both sets of reactions are outer sphere. Comparison of the rates of the Cr(VI) oxidations[4] of $Fe(CN)_6^{4-}$, $Fe(bpy)(CN)_4^{2-}$ (bpy = 2,2′-bipyridyl), $Fe(bpy)_2(CN)_2$, and $Fe(bpy)_3^{2+}$ with the rates of the corresponding outer-sphere oxidations by Ce(IV)[5] suggested that the first three Fe(II) complexes reacted by an inner-sphere mechanism while the last system was outer sphere. These conclusions were supported by examination of the corresponding V(V) oxidations,[6,7] where the predictions of the relative rate comparisons were confirmed by observation of binuclear successor complexes with the cyanide-containing Fe(II) complexes. These rate comparisons thus appear to be

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viable criteria for distinguishing between inner-sphere and outer-sphere mechanisms and have been successful in confirming the outer-sphere nature of the V(V) oxidation of $IrCl_6^{3-}$.[8]

A comparison of rate laws, variation of central atom charge or oxidation state, variation of central atom size, and hydrogen isotope effects for substitution and oxidation–reduction reactions of many oxyanions[9] suggests that substitution occurs prior to or coincident with the electron-transfer step in the redox processes. Since this mechanistic description so closely resembles that of the inner-sphere process commonly applied to transition-metal redox reactions, we decided to develop the appropriate rate comparisons to determine whether the oxyanion redox reactions can indeed properly be classified as inner sphere. Bromate ion was chosen as the oxidizing agent to be reacted with the same series of Fe(II) complexes, because $BrO_3^-$ reacts more rapidly than $ClO_3^-$, while it is not complicated by the formation of significant amounts of a protonated species, as is $IO_3^-$, and because these systems are also of interest to the study of oscillating reactions involving bromine species. We have previously reported the results of a study of the reaction between $Fe(CN)_6^{4-}$ and $BrO_3^-$.[10]

The $BrO_3^-$ oxidation of $Fe(CN)_6^{4-}$ followed partially autocatalytic kinetics:

$$-d[Fe(CN)_6^{4-}]/dt = 6k_1[Fe(CN)_6^{4-}][BrO_3^-] + 6k_3[Br^-][BrO_3^-][H^+]^2 \qquad (1)$$

with $k_1 = 0.0125 + 0.193[H^+]^2\ M^{-1}\ s^{-1}$ and $k_3 = 2.86\ M^{-3}\ s^{-1}$ at 25.0 °C and 0.50 M ionic strength. This rate law was interpreted in terms of the coupled reactions:

$$Fe(II) + BrO_3^- \xrightarrow[2H^+]{k_1} \xrightarrow[4H^+]{4Fe(II)} 5Fe(III) + {}^1/_2Br_2 + 3H_2O \qquad (2)$$

$$Fe(II) + {}^1/_2Br_2 \xrightarrow{\text{fast}} Fe(III) + Br^- \qquad (3)$$

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

Reaction 2 initiates the process and reactions 3 and 4 become increasingly important as the reaction proceeds.

We report here on the bromate oxidation of the remaining three iron(II) complexes in the series, all of which reactions involve autocatalysis.

## Experimental Section

The preparation and analysis of solutions of $LiClO_4$,[4] $HClO_4$,[4] $NaBrO_3$,[10] $K_2Fe(bpy)(CN)_4$,[7] $Fe(bpy)_2(CN)_2$,[7] $Fe(bpy)_3(ClO_4)_2$,[7] and the analogous Fe(III) complexes[7] were previously described. The kinetics of the Fe(II) reductions of $BrO_3^-$ were determined under pseudo-first-order conditions with $[BrO_3^-]_0 \geq 5[Fe(II)]_0$, at 25.0 °C and 0.50 M ionic strength maintained with $LiClO_4$. Data were obtained with a Cary 14 recording spectrophotometer using thermostating and solution handling techniques described earlier.[4] Bromate was added to the acidic solutions immediately before reaction was initiated since spurious results, possibly due to oxidation of water, had been noted occasionally in the $BrO_3^-$–$Fe(CN)_6^{4-}$ system when $BrO_3^-$ was in contact with $H^+$ for long times.[10] The Fe(II) solutions were prepared just prior to use with thermally equilibrated components and were shielded from light at all times. Most data were collected at 450 nm for $Fe(bpy)(CN)_4^{2-}$ and 520 nm for $Fe(bpy)_2(CN)_2$ and for $Fe(bpy)_3^{2+}$, but results were within experimental error at other wavelengths.

## Results

**Stoichiometry.** Agreement between observed and calculated absorbance changes was not a useful criterion for the determination of the reaction stoichiometry. Due to limited solubility of the Fe(II) and Fe(III) complexes, the contribution to the absorbance change from any $Br_2$ formed was within experimental error at all wavelengths. The production of $Br_2$ was confirmed by addition of the Fe(II) complex as a solid to an acidic solution containing excess $BrO_3^-$. The reaction was allowed to proceed to completion, the precipitated Fe(III) complex was removed by filtration, the solution was extracted with carbon tetrachloride to remove any $Br_2$ from other possible bromine species, and the $CCl_4$ extract was reacted with aqueous sodium iodide solution. The $CCl_4$ layer turned purple, confirming the presence of $Br_2$. Similar results were obtained when the Fe(II)–$BrO_3^-$ mixture was extracted before completion of the redox reaction. With $BrO_3^-$ in excess, the stoichiometry of each reaction appears to be given by

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

However, it is not possible, in the absence of spectral confirmation, to rule out the possibility that the initial reaction product could be HOBr which could undergo separation-induced disproportionation to $Br_2$ and $HBrO_2$. In that case, the stoichiometry would be of the form

$$BrO_3^- + 4Fe(II) + 5H^+ = HOBr + 4Fe(III) + 2H_2O \qquad (6)$$

Considering the kinetic results to be described, eq 5 appears to accurately represent the stoichiometry for the $Fe(bpy)(CN)_4^{2-}$ and $Fe(bpy)_2(CN)_2$ reactions, as it did for the $Fe(CN)_6^{4-}$ reaction,[10] while there is some uncertainty about the $Fe(bpy)_3^{2+}$ reaction.

**The Bromate–Tetracyano(2,2′-bipyridyl)iron(II) Reaction.** This reaction behaved in a manner similar to that of the bromate oxidation of ferrocyanide.[10] Absorbance–time traces showed increasing rather than decreasing slope with time and leveled off fairly abruptly at the end of the reaction, indicative of autocatalysis. First-order plots of ln $(A_t - A_\infty)$ vs. time (where $A$ is absorbance at the indicated time) showed downward curvature as expected. However, Guggenheim plots[11] of ln $(A_t - A_{t+\tau})$ vs. time ($\tau$ = constant time interval) were linear with positive slopes through most of the reaction. Near the end of the reaction, the slope abruptly changed to a negative value similar to that expected for the $Br^-$–$BrO_3^-$ reaction.[10]

This general behavior is obtained in systems which are partially autocatalytic, i.e., systems for which the rate law contains at least one term dependent on product but not reactant and usually one or more terms independent of product. Linear Guggenheim plots for pseudo-first-order systems (A → B) can be obtained for the rate laws, $k_a[B]$, $k_b + k_b'[B]$, $k_c[A] + k_c'[B]$, and $k_d + k_d'[A] + k_d''[B]$, with slopes of $k_a$, $k_b'$, $k_c' - k_c$, and $k_d'' - k_d'$, respectively. Note that only a rate law containing a term first order in reactant can give rise to a negative Guggenheim slope. Any rate law having a term with a mixed dependence on reactant and product, such as $k[A][B]$, $k + k'[A][B]$, $k[A] + k'[A][B]$, or $k + k'[A] + k''[A][B]$, will give nonlinear Guggenheim plots. This indicates that the minimal behavior for linear Guggenheim plots in autocatalytic systems is a rate law with one term first order in product, with a term first order in reactant being possible but not essential.

The observance of a limiting final Guggenheim slope corresponding to the $Br^-$–$BrO_3^-$ reaction suggested the following sequence of reactions[10] which can accommodate partial autocatalysis:

$$Fe(II) + BrO_3^- \xrightarrow[2H^+]{k_1} Fe(III) + BrO_2 + H_2O \qquad (7)$$

$$4Fe(II) + BrO_2 + 4H^+ \overset{\text{fast}}{=\!=} 4Fe(III) + {}^1/_2Br_2 + 2H_2O \qquad (8)$$

$$Fe(II) + {}^1/_2Br_2 \underset{\text{fast}}{\overset{k_2}{=\!=}} Fe(III) + Br^- \qquad (9)$$

$$Br^- + BrO_3^- + 2H^+ \xrightarrow{k_3} \xrightarrow[4H^+]{4Br^-} 3Br_2 + 3H_2O \qquad (10)$$

**Table I.** Guggenheim Slopes and Rate Constants for the $Fe(bpy)(CN)_4^{2-}$ Reduction of $BrO_3^-$ [a]

| $10^3[BrO_3^-]$, M | $10^3(-b)$, $s^{-1}$ | $k_1$, $M^{-1}$ $s^{-1}$ |
|---|---|---|
| 0.50 | 0.122 | 0.056 |
| 2.00 | 0.370 | 0.066 |
| 3.00 | 0.597 | 0.063 |
| 4.00 | 1.22 | 0.046 |
| 7.00 | 2.18 | 0.045 |
| 10.0 | 2.95 | 0.047 |
| 20.0 | 4.68 | 0.058 |
| 30.0 | 5.04 | 0.069 |
| 40.0 | 11.2 | 0.050 |
| | Av | 0.056 ± 0.007 |

[a] 25.0 °C, $I = 0.50$ M, $1.0 \times 10^{-4}$ M Fe(II), 0.446 M $H^+$.

**Table II.** Dependence of $k_1$ on $[H^+]$ for the Reaction between $Fe(bpy)(CN)_4^{2-}$ and $BrO_3^-$ [a]

| | $10^2k_1$, $M^{-1}$ $s^{-1}$ | |
|---|---|---|
| $[H^+]$, M | Obsd[b] | Calcd[c] |
| 0.487 | 6.28 | 6.00 |
| 0.446 | 5.55 ± 0.74 (9) | 5.14 |
| 0.399 | 4.48 ± 0.72 (5) | 4.24 |
| 0.352 | 3.27 | 3.44 |
| 0.298 | 2.73 ± 0.07 (3) | 2.64 |
| 0.250 | 1.89 | 2.04 |
| 0.203 | 1.37 ± 0.03 (4) | 1.56 |
| 0.149 | 1.07 | 1.13 |
| 0.101 | 0.989 ± 0.020 (3) | 0.856 |

[a] 25.0 °C, $I = 0.50$ M, 0.003-0.04 M $BrO_3^-$. [b] Where uncertainties are given, these are average deviations for a number of determinations at the same or different $[BrO_3^-]$. The number of experiments is given in parentheses. [c] Calculated from eq 13 and the parameters given in the text.

The autocatalysis arises from reactions 9 and 10 which become increasingly important as the reaction proceeds and $Br^-$ accumulates. When the Fe(II) has been completely or almost completely consumed, a change in Guggenheim slope occurs since the absorbance change is then principally due to the formation of $Br_2$ in reaction 10. As developed earlier,[10] the rate law is given by

$$-d[Fe(II)]/dt = 6k_1[Fe][BrO_3^-] + 6k_3[Br^-][BrO_3^-][H^+]^2 \qquad (11)$$

Solving this equation for [Fe(II)] as a function of time and application of the Guggenheim method yield[10]

$$\ln([Fe(II)]_t - [Fe(II)]_{t+\tau}) = \ln\{(a/b + [Fe(II)]_0)(1 - e^{-b\tau})\} - bt \qquad (12)$$

where $a = k_3[H^+]^2[BrO_3^-]([Fe(II)]_0 + 6[Br^-]_0)$[12] and $b = (6k_1 - k_3[H^+]^2)[BrO_3^-]$. Values of the rate constant $k_3$ have been determined,[10] so the rate constant $k_1$ can be extracted from the Guggenheim parameter $-b$.

The $BrO_3^-$ oxidation of $Fe(bpy)(CN)_4^{2-}$ was studied at 25.0 °C and 0.50 M ionic strength over the concentration ranges (0.5–40) × $10^{-3}$ M $BrO_3^-$, 1.0 × $10^{-4}$ M Fe(II), and 0.101–0.487 M $H^+$. Table I gives values of the Guggenheim slopes ($-b$) and the constant $k_1$ extracted from the slopes as a function of $[BrO_3^-]$ at constant $[H^+]$. These results support the expected first-order dependence on $[BrO_3^-]$. Values of $-b$ and $k_1$ were also determined as a function of $[H^+]$, with most data collected at 0.0100 M $BrO_3^-$, but with a number of experiments having other $[BrO_3^-]$ in the range 3.0 × $10^{-3}$–4.0 × $10^{-2}$ M. Data are presented in Table II and are consistent with the equation

$$k_1 = c + d[H^+]^2 \qquad (13)$$

All data were fit to this equation with a nonlinear least-squares computer program[13] with each point weighted as $k_1^{-2}$, giving $c = (6.2 \pm 1.1) \times 10^{-3}$ $M^{-1}$ $s^{-1}$ and $d = 0.227 \pm 0.018$ $M^{-3}$ $s^{-1}$.

**Table III.** Guggenheim Slopes and Rate Constants for the $Fe(bpy)_2(CN)_2$ Reduction of $BrO_3^-$ [a]

| $10^3[BrO_3^-]$, M | $10^3b$, $s^{-1}$ | $k_1$, $M^{-1}$ $s^{-1}$ |
|---|---|---|
| 0.50 | 0.152 | 0.147 |
| 1.00 | 0.352 | 0.156 |
| 2.00 | 0.570 | 0.144 |
| 3.00 | 1.52 | 0.181 |
| 3.00 | 1.35 | 0.172 |
| 4.00 | 1.96 | 0.178 |
| 7.00 | 2.79 | 0.163 |
| 10.0 | 4.76 | 0.176 |
| 20.0 | 7.96 | 0.163 |
| 30.0 | 21.1 | 0.217 |
| 30.0 | 23.3 | 0.226 |
| | Av | 0.181 ± 0.025 |

[a] 25.0 °C, $I = 0.50$ M, $1.0 \times 10^{-4}$ M Fe(II), 0.446 M $H^+$.

**Table IV.** Dependence of $k_1$ on $[H^+]$ for the Reaction between $Fe(bpy)_2(CN)_2$ and $BrO_3^-$ [a]

| | $10^2k_1$, $M^{-1}$ $s^{-1}$ | |
|---|---|---|
| $[H^+]$, M | Obsd[b] | Calcd[c] |
| 0.487 | 23.0 ± 0.3 (2) | 20.9 |
| 0.446 | 18.1 ± 2.5 (12) | 18.0 |
| 0.399 | 17.3 ± 1.0 (2) | 15.0 |
| 0.352 | 14.0 | 12.3 |
| 0.298 | 11.0 ± 3.0 (2) | 9.7 |
| 0.250 | 8.98 ± 0.75 (2) | 7.67 |
| 0.203 | 6.38 | 6.06 |
| 0.149 | 4.68 | 4.63 |
| 0.101 | 3.36 | 3.72 |

[a] 25.0 °C, $I = 0.50$ M, 0.001-0.03 M $BrO_3^-$. [b] Where uncertainties are given, these are average deviations for a number of determinations at the same or different $[BrO_3^-]$. The number of experiments is given in parentheses. [c] Calculated from eq 13 and the parameters given in the text.

**The Bromate–Dicyanobis(2,2′-bipyridyl)iron(II) Reaction.** This system was qualitatively the same as the $Fe(bpy)(CN)_4^{2-}$ system except that absorbance–time traces could show increasing, constant, or decreasing slopes as the reaction proceeded, depending on the $H^+$ concentration. This behavior extends to the linear Guggenheim plots which have corresponding positive, zero, or negative slopes. Since the slope is given by $-b = (k_3[H^+]^2 - 6k_1)[BrO_3^-]$ according to our model, an appropriate $[H^+]$ dependence for the parameter $k_1$ and appropriate values for the various constants allows the difference $k_3[H^+]^2 - 6k_1$ to have positive, zero, or negative values, depending on the range of $[H^+]$ being examined. This reaction was studied at 25.0 °C and 0.50 M ionic strength over the concentration ranges (0.5–30) × $10^{-3}$ M $BrO_3^-$, 1.0 × $10^{-4}$ M Fe(II), and 0.101–0.487 M $H^+$. Table III presents data which show that the Guggenheim slope is indeed first order in $[BrO_3^-]$ as predicted. Values of $k_1$, presented as a function of $[H^+]$ in Table IV, were also found to obey eq 13. Values of the parameters determined by nonlinear least squares are $c = (2.95 \pm 0.44) \times 10^{-2}$ $M^{-1}$ $s^{-1}$ and $d = 0.755 \pm 0.047$ $M^{-3}$ $s^{-1}$. It is the larger values of these parameters for $Fe(bpy)_2(CN)_2$ than for $Fe(bpy)(CN)_4^{2-}$ that give rise to the occurrence of nonpositive Guggenheim slopes in the former system.

**Aquation of $Fe(bpy)_3^{2+}$.** In order to fully interpret the data for the $Fe(bpy)_3^{2+}$–$BrO_3^-$ reaction, it was necessary to have values of the aquation rate constant under our conditions. Values of $k_{aq}$ determined from eq 14 are presented in Table

$$-d[Fe(bpy)_3^{2+}]/dt = k_{aq}[Fe(bpy)_3^{2+}] \qquad (14)$$

**Table V.** Rate Constants for Aquation of $Fe(bpy)_3^{2+}$ [a]

| $[H^+]$, M | $10^4 k_{aq}$, $s^{-1}$ Obsd | Calcd[b] |
|---|---|---|
| 0.500 | 5.31 | 5.53 |
| 0.452 | 5.19 | 5.26 |
| 0.397 | 4.90 | 4.91 |
| 0.348 | 4.70 | 4.56 |
| 0.299 | 4.25 | 4.16 |
| 0.250 | 3.75 | 3.71 |
| 0.202 | 3.40 | 3.21 |
| 0.153 | 2.55 | 2.62 |
| 0.100 | 1.88 | 1.87 |
| 0.0501 | 1.00 | 1.02 |

[a] 25.0 °C, 0.50 M ionic strength, $1.00 \times 10^{-4}$ M $Fe(bpy)_3^{2+}$.
[b] Calculated from eq 15 and the parameters given in the text.

V. The hydrogen ion dependence of $k_{aq}$ was found to be given by eq 15. The parameters were determined with a nonlinear

$$k_{aq} = e[H^+]/(1 + f[H^+]) \qquad (15)$$

least-squares computer program to be $e = (2.26 \pm 0.06) \times 10^{-3}$ $M^{-1}$ $s^{-1}$ and $f = 2.08 \pm 0.16$ $M^{-1}$. These results are in reasonable agreement with those of Baxendale and George[14] and of Basolo, Hayes, and Neumann.[15] Each of these studies suggested the existence of a second numerator term zero order in $[H^+]$ which we were unable to detect. However, these studies did not maintain constant ionic strength and in both studies it proved to be impossible to fit the data exactly to the proposed rate law. Our data suggest the mechanism

$$\mathrm{Fe(bpy)_3^{2+}} \underset{k_5}{\overset{k_4}{\rightleftarrows}} \mathrm{Fe(bpy)_2(bpy^*)^{2+}} \qquad (16)$$

$$\mathrm{Fe(bpy)_2(bpy^*)^{2+} + H^+} \xrightarrow{k_6} \mathrm{Fe(bpy)_2^{2+} + bpyH^+} \qquad (17)$$

followed by rapid decomposition of $Fe(bpy)_2^{2+}$, with bpy* being monodentate bipyridyl. The parameters correspond to $e = k_4k_6/k_5$ and $f = k_6/k_5$.

**The Bromate–Tris(2,2′-bipyridyl)iron(II) Reaction.** This reaction did not behave the same as the other three reactions in the series. Under some conditions the reaction was autocatalytic as expected, while under other conditions aquation of $Fe(bpy)_3^{2+}$ was rate determining. The change in behavior was remarkably abrupt. For example, in 0.5 M $HClO_4$ with $1.0 \times 10^{-4}$ M $Fe(bpy)_3^{2+}$, the reaction was autocatalytic with 0.01 M $BrO_3^-$, but aquation was rate determining with 0.006 M $BrO_3^-$. Figure 1 shows the conditions under which the two types of behavior were observed over the concentration ranges studied at 25.0 °C and 0.50 M ionic strength: $1.0 \times 10^{-4}$ M $Fe(bpy)_3^{2+}$, (0.5–40) $\times 10^{-3}$ M $BrO_3^-$, 0.05–0.494 M $H^+$. Under all conditions where aquation was rate determining, the first-order rate constant for disappearance of $Fe(bpy)_3^{2+}$ agreed well with the appropriate aquation rate constant determined independently, as described above. The shaded area in Figure 1 represents a region in which intermediate behavior was observed. There were induction periods of various lengths depending on conditions, during which the absorbance decreased at the aquation rate. This was followed by an autocatalytic stage which did not correlate well with the autocatalysis observed in the upper right region of Figure 1. Toward the end of the reaction there was considerable tailing-off, much in excess of that observed in the other reactions where it was attributed to the $Br^-$–$BrO_3^-$ reaction. This tailing-off was always accompanied by the occurrence of a layer of orange $Fe(bpy)_3^{2+}$ along the walls of the spectrophotometer cell. This may well be due to a silica-catalyzed reduction of $Fe(bpy)_3^{3+}$ by water, analogous to the hydroxide-catalyzed reaction,[16] but if so, we do not understand the occurrence of this reaction only under the rather limited conditions shown in Figure 1. We suspect that during the inhibition period, aquation of $Fe(bpy)_3^{2+}$ produces $Fe^{2+}$, which reduces $BrO_3^-$ more rapidly than does $Fe(bpy)_3^{2+}$.[17] When a sufficient amount of the autocatalytic product is formed, the autocatalytic mechanism becomes predominant and $Fe(bpy)_3^{2+}$ is then oxidized to $Fe(bpy)_3^{3+}$. The tailing-off at the end of the reaction is due to reduction of $Fe(bpy)_3^{3+}$ at the walls and diffusion of $Fe(bpy)_3^{2+}$ back into the bulk of the solution, thereby apparently slowing down the reaction. We have not fit this model to appropriate mathematical equations to try to reproduce the absorbance–time behavior.

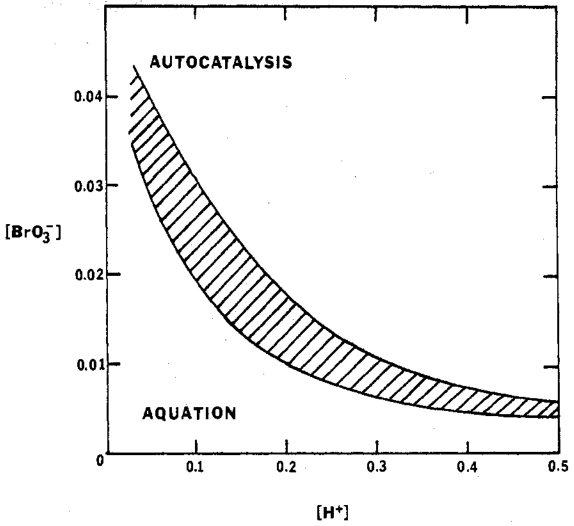

**Figure 1.** Conditions for autocatalytic kinetics or rate determining aquation of $Fe(bpy)_3^{2+}$ in the reaction of $BrO_3^-$ with $Fe(bpy)_3^{2+}$.

Data collected under conditions producing autocatalysis gave good linear Guggenheim plots with positive slopes, indicating that the rate law was of the same type as for the other systems, probably containing one term pseudo-first-order in reactant as well as the required term pseudo-first-order in an accumulating product. Unfortunately when it was assumed that the Guggenheim slope was given by the usual relation, $-b = (k_3[H^+]^2 - 6k_1)[BrO_3^-]$, negative values of $k_1$ were obtained. Apparently the $Br^-$–$BrO_3^-$ reaction coupled with a $Fe(bpy)_3^{2+}$–$Br_2$ reaction is not responsible for the autocatalysis in this case. In the absence of any clue as to the identity of the reactions responsible for autocatalysis, it was necessary to determine the concentration dependences of the Guggenheim slopes without benefit of a model. Table VI presents values of the Guggenheim slopes under conditions where autocatalysis was observed.

The Guggenheim slope decreases with decreasing $[BrO_3^-]$ and with decreasing $[H^+]$, with the order in each case being between first and second. Plots of $-b/[BrO_3^-]$ vs. $[BrO_3^-]$ at constant $[H^+]$ are linear, indicating two terms:

$$-b = k[BrO_3^-] + k'[BrO_3^-]^2 \qquad (18)$$

Similar plots of $-b/[H^+]$ vs. $[H^+]$ at constant $[BrO_3^-]$ are also linear.

$$-b = k[H^+] + k'[H^+]^2 \qquad (19)$$

Consideration of the slopes and intercepts of these plots suggests that the first-order terms in each equation combine together and the second-order terms in each equation combine:

$$-b = g[BrO_3^-][H^+] + h[BrO_3^-]^2[H^+]^2 \qquad (20)$$

Conformance to this equation is shown for all data in a plot of $-b/[BrO_3^-][H^+]$ vs. $[BrO_3^-][H^+]$, given in Figure 2. A linear-least-squares computer fit of the data to eq 20, with each point weighted as $b^{-2}$, yielded the parameters $g = 12.8 \pm 0.3$

**Table VI.** Guggenheim Slopes for the Autocatalytic Reduction of $BrO_3^-$ by $Fe(bpy)_3^{2+}$ at 25.0 °C and 0.50 M Ionic Strength

| $[H^+]$, M | $[BrO_3^-]$, M | $-b$, $s^{-1}$ Obsd | $-b$, $s^{-1}$ Calcd[a] |
|---|---|---|---|
| 0.492 | 0.0080 | 0.0603 | 0.0653 |
| 0.450 | 0.030 | 0.341 | 0.349 |
| | 0.020 | 0.195 | 0.193 |
| | 0.010 | 0.0760 | 0.0772 |
| | 0.0080 | 0.0555 | 0.0586 |
| 0.400 | 0.030 | 0.284 | 0.293 |
| | 0.020 | 0.161 | 0.164 |
| | 0.010 | 0.0676 | 0.0667 |
| | 0.0080 | 0.0470 | 0.0509 |
| 0.350 | 0.030 | 0.236 | 0.241 |
| | 0.020 | 0.140 | 0.137 |
| | 0.010 | 0.0566 | 0.0566 |
| | 0.0080 | 0.0402 | 0.0434 |
| 0.300 | 0.040 | 0.285 | 0.293 |
| | 0.030 | 0.191 | 0.193 |
| | 0.020 | 0.117 | 0.112 |
| | 0.010 | 0.0444 | 0.0471 |
| 0.250 | 0.040 | 0.217 | 0.225 |
| | 0.030 | 0.157 | 0.150 |
| | 0.020 | 0.0924 | 0.0882 |
| | 0.010 | 0.0365 | 0.0380 |
| 0.200 | 0.040 | 0.173 | 0.164 |
| | 0.030 | 0.118 | 0.112 |
| | 0.020 | 0.0730 | 0.0667 |
| 0.150 | 0.040 | 0.116 | 0.112 |
| | 0.030 | 0.0840 | 0.0772 |
| | 0.020 | 0.0499 | 0.0471 |
| 0.100 | 0.040 | 0.0693 | 0.0667 |
| | 0.030 | 0.0474 | 0.0471 |
| | 0.020 | 0.0295 | 0.0295 |
| 0.050 | 0.040 | 0.0315 | 0.0295 |

[a] Calculated from eq 20 and values of the parameters given in the text; the average deviation between observed and calculated values of $-b$ is 4.0%.

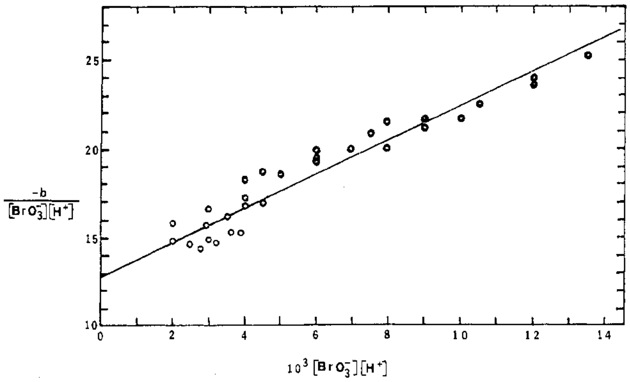

**Figure 2.** Plot of $-b/[BrO_3^-][H^+]$ vs. $[BrO_3^-][H^+]$ for the reaction of $BrO_3^-$ with $Fe(bpy)_3^{2+}$. The line was calculated from eq 20, and the parameters are given in the text.

$M^{-2}\ s^{-1}$ and $h = 964 \pm 56\ M^{-4}\ s^{-1}$.

The change in behavior of this system was unfortunate with respect to our desire to make rate correlations based on the Marcus theory. We had hoped to get values of $k_1 = c + d[H^+]^2$ for each of the four iron(II) complexes in the series. Since there was a wide range of conditions under which aquation of $Fe(bpy)_3^{2+}$ was rate limiting, it can be assumed that the same mechanism as for the other iron(II) complexes might have been followed if a more efficient mechanism had not been available. The pseudo-first-order rate constant for this unobserved redox process, no matter what the mechanism, must be less than the pseudo-first-order aquation rate constant: $nk_1[BrO_3^-] \leq k_{aq}$, where $n = 5$ if the stoichiometry is accurately represented by eq 5 (reduction to $Br_2$). Using this approach, maximum values of $5k_1$ are calculated to be 0.021, 0.033, 0.044, 0.055, 0.062, 0.076, and 0.076 $M^{-1}\ s^{-1}$ at $[H^+] = 0.05$, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.40 M. Then if $k_1 = c + d[H^+]^2$, subtraction of two values of $k_1$ and division by the difference in the square of the two corresponding values of $[H^+]$ give a maximum value of $d$. Using all possible combinations of the $k_1$ values, it was found that $d \leq 0.15 \pm 0.05\ M^{-3}\ s^{-1}$. Using a value of $d = 0.15$, $c$ can be calculated as $c = k_1 - d[H^+]^2$, giving an average value of $c \leq 0.0042 \pm 0.0010\ M^{-1}\ s^{-1}$. Considering the large uncertainties involved and the possibly dubious nature of the assumptions behind these calculations, the values of $c$ and $d$ are remarkably similar to those found for the bromate oxidation of the other iron(II) complexes. The validity of this approach is supported by initial rate studies on the $Fe(bpy)_3^{2+}$ reaction in the autocatalytic range. The observed pseudo-first-order rate constants were corrected by subtracting $k_{aq}$ and then dividing by $[BrO_3^-]$ to give apparent values of $5k_1$. These values were considerably dependent on $[BrO_3^-]$ and $[H^+]$ since they were not corrected for contributions from the autocatalytic path. However, extrapolation to low $[BrO_3^-][H^+]$, where the autocatalysis is minimized, gave an approximate value of $5k_1 \approx 0.03 \pm 0.02\ M^{-1}\ s^{-1}$ in reasonable agreement with the values estimated from the aquation limited data.

## Discussion

The rate law for the direct reduction of $BrO_3^-$ by the Fe(II) complexes is consistent with the first electron transfer step being rate determining, but with parallel paths having different $[H^+]$ dependences:

$$Fe(II) + BrO_3^- \xrightarrow{k_7} Fe(III) + Br(IV) \qquad (21)$$

$$BrO_3^- + 2H^+ \overset{K<<1}{\rightleftharpoons} H_2BrO_3^+ \text{ (or } BrO_2^+ + H_2O) \qquad (22)$$

$$Fe(II) + H_2BrO_3^+ \xrightarrow{k_8} Fe(III) + Br(IV) \qquad (23)$$

followed by rapid reduction of Br(IV) as indicated in eq 7–10. This interpretation has $c = k_7$ and $d = k_8K$. We have previously[10] discussed the possibility that eq 21 may proceed by an outer-sphere path while eq 23 might be inner sphere. This is suggested by the $[H^+]^2$ dependence in the second path, which could give rise to labilization of an oxide bound to Br(V), allowing bonding to the Fe(II) complex. Based on our experience with the Fe(II) complex reduction of Cr(VI)[4] and V(V),[6,7] the intimate mechanism of these two pathways might be determinable by use of rate correlations based on the Marcus theory.[2,3] The basis for this mechanistic criterion has been developed elsewhere[4,7] but briefly consists of examination of the ratios of the rate constants for oxidation of Fe(II) complexes by Ce(IV) compared to the rate constants for oxidation by the oxidant in question. Relatively constant ratios throughout the series of Fe(II) complexes, including the necessarily outer-sphere $Fe(bpy)_3^{2+}$ (since bpy is not known to behave as a bridging ligand), suggest an outer-sphere mechanism for all reactions. A much higher ratio for $Fe(bpy)_3^{2+}$ than for the potentially inner-sphere cyanide complexes and relatively constant values for those complexes suggests an inner-sphere mechanism for each cyanide complex. The values of the rate constants and rate constant ratios are summarized in Table VII. Both paths show reasonably constant ratios of the rate constants for bromate oxidation to those for cerium(IV) oxidation, suggesting that both paths follow an outer-sphere mechanism. A critical point in interpreting these data lies in the reliability of the values of $c$ and $d$ for $Fe(bpy)_3^{2+}$ since this is a reference point for the outer-sphere mechanism. The oxidation of $IrCl_6^{3-}$ by $VO_2^+$[8] and by Ce(IV)[5] gave a ratio of $k_{Ce}/k_V$ in 0.5 M $H^+$ of $5.3 \times 10^6$, while the corresponding ratio for oxidation of $Fe(bpy)_3^{2+}$ was $\leq 6.8 \times 10^6$,[7] which is good agreement for two systems which are highly likely to be outer sphere.[8] The ratio of $k_{Ce}/k_V$

**Table VII.** Rate Constants and Rate Constant Ratios for Oxidation of Iron(II) Complexes by $BrO_3^-$ and by Ce(IV) at 25.0 °C and 0.50 M Ionic Strength

| Complex | $c$,[a] $M^{-1}$ $s^{-1}$ | $d$,[a] $M^{-3}$ $s^{-1}$ | $10^{-6} \times k_{Ce}$,[b] $M^{-1}$ $s^{-1}$ | $10^{-8} \times k_{Ce}/c$ | $10^{-6} \times k_{Ce}/d$ |
|---|---|---|---|---|---|
| $Fe(CN)_6^{4-}$ | 0.00125 | 0.193 | 1.90 | 15 | 9.8 |
| $Fe(bpy)(CN)_4^{2-}$ | 0.0062 | 0.227 | 12.5 | 20 | 55 |
| $Fe(bpy)_2(CN)_2$ | 0.0295 | 0.755 | 8.4 | 2.9 | 11 |
| $Fe(bpy)_3^{2+}$ | $\leq 0.0042$[c] | $\leq 0.15$[c] | 0.196 | $\geq 0.47$ | $\geq 1.3$ |

[a] Obtained from $k_1 = c + d[H^+]^2$ as described in the text. [b] In 0.50 M $H_2SO_4$.[5] [c] Estimated as described in the text.

for known inner-sphere reactions was 1–10.[7] The rate constant for oxidation of $IrCl_6^{3-}$ by $BrO_3^-$ at 25 °C and 0.50 M $HClO_4$ is about 13 $M^{-1}$ $s^{-1}$.[18] Ratios of $10^{-6}k_{Ce}/k_{BrO_3^-}$ for $Fe(CN)_6^{4-}$, $Fe(bpy)(CN)_4^{2-}$, $Fe(bpy)_2(CN)_2$, $Fe(bpy)_3^{2+}$, and $IrCl_6^{3-}$ are 38, 200, 38, >4.7, and 0.7 respectively, at $[H^+] = 0.5$ M. If $IrCl_6^{3-}$ reacts by an outer-sphere path in this system as well, the order of magnitude agreement suggests that the $Fe(bpy)_3^{2+}$ estimates are not so inaccurate as to invalidate the mechanistic conclusions.

The mechanism of the reduction of $BrO_3^-$ by $Fe(bpy)_3^{2+}$ is not consistent with eq 21–23 followed by eq 7–10. Our mathematical derivations (presented above) suggest that the pseudo-first-order rate law must be of the form $-d[Fe(II)]/dt = k_d + k_d'[Fe(II)] + k_d''[product]$, with $k_d = 0$ and $k_d' = 0$ being possible variations. This will then give a Guggenheim slope of $-b = k_d'' - k_d'$. Experimentally, $-b = g[BrO_3^-][H^+] + h[BrO_3^-]^2[H^+]^2$, so $k_d''$ at least must contain terms of this sort and $k_d'$ either must contain at least one such term or must be so small as to not contribute significantly to $-b$. It seems reasonable to assume that the initiating reaction giving rise to $k_d'$ must make a reasonable contribution or lengthy inhibition periods would have been observed under the conditions in which eq 20 was observed. If $Br_2$ is the stable product of the reaction of $BrO_3^-$ with $Fe(bpy)_3^{2+}$, then consideration of eq 20 and the above arguments gives rise to the following mechanism.

$$Fe(II) + BrO_3^- + H^+ \xrightarrow{k_9} Fe(III) + Br(IV) \tag{24}$$

$$4Fe(II) + Br(IV) + 5H^+ \xrightleftharpoons{\text{fast}} 4Fe(III) + {}^1/{}_2Br_2 + 3H_2O \tag{25}$$

$$Br_2 + BrO_3^- + H^+ \xrightarrow{k_{10}} 2BrO + HOBr \tag{26}$$

$$BrO_3^- + 2H^+ \xrightleftharpoons{K<<1} BrO_2^+ + H_2O \tag{27}$$

$$BrO_2^+ + BrO_3^- \xrightleftharpoons{K_d<<1} Br_2O_5 \tag{28}$$

$$Br_2 + Br_2O_5 + H_2O \xrightarrow{k_{11}} 2BrO + 2HBrO_2 \tag{29}$$

The species HOBr, BrO, and $HBrO_2$ are all involved in the fast reactions summarized in eq 25. Equations 26 and 29 are expected to lie far to the left, but are driven to completion by the rapid scavenging of their products by $Fe(bpy)_3^{2+}$. The existence of the dimeric species $Br_2O_5$ has no precedent in aqueous redox reactions of $BrO_3^-$ but has been prepared under anhydrous conditions.[19] The species in solution would undoubtedly be in a hydrated state and would be present only in very small amounts. We made numerous attempts to accommodate the $[BrO_3^-]^2$ dependence by a mechanism analogous to those found for the $BrO_3^-$ oxidations of Ce(III), Mn(II), and Np(V)[20–22] but were unable to find any such mechanism or a variation thereof which could reproduce the entire functional dependence of $-b$ on $[BrO_3^-]$ and $[H^+]$. The autocatalytic oxidation of these metal ions with a second-order dependence on bromate was obtained with a large excess of metal ion, in contrast to the $Fe(bpy)_3^{2+}$ results which were measured with $BrO_3^-$ in large excess.

If the analogous derivation to that described for the $Fe(CN)_6^{4-}$–$BrO_3^-$ reaction[10] is applied to the above mechanism assuming $[Br_2] = 0.1([Fe(II)]_0 - [Fe(II)])$, the Guggenheim slope is given by the equation

$$-b = (0.5k_{10} - 5k_9)[BrO_3^-][H^+] + k_{11}K_dK[BrO_3^-]^2[H^+]^2 \tag{30}$$

Thus $(0.5k_{10} - 5k_9) = 12.8$ $M^{-2}$ $s^{-1}$ and $k_{11}K_dK = 964$ $M^{-4}$ $s^{-1}$.

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**Registry No.** $BrO_3^-$, 15541-45-4; $Fe(bpy)(CN)_4^{2-}$, 17455-56-0; $Fe(bpy)_2(CN)_2$, 14841-10-2; $Fe(bpy)_3^{2+}$, 15025-74-8; $Fe(CN)_6^{4-}$, 13408-63-4.

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