3%, so within the experimental error this term would go unnoticed.

The mechanism proposed for the first step in the Ti(III)-V(V) reaction[7] involves the formation of a binuclear complex $\mathrm{TiOHVO_2^{3+}}$ from $\mathrm{TiOH^{2+}}$ and $\mathrm{VO_2^+}$, with formation constant 5700 M^{-1}. Under similar conditions, a binuclear species $\mathrm{TiOHCrO_4}$ is proposed in the Ti(III)-Cr(VI) reaction,[4] with formation constant $\sim 10^{10}\ M^{-1}$. In the present study of the Ti(III)-U(VI) reaction, attempts to observe an absorbance change corresponding to binuclear complex formation or to observe a term in the redox rate equation resulting from complex formation were unsuccessful. If it is assumed that a species $\mathrm{TiOHUO_2^{4+}}$ is formed in small amounts, an estimate of the formation constant is $<10\ M^{-1}$ based on the limitations of experimental error. A very distinct two-step reaction is observed in the Ti(III)-Mn(VII) reaction,[9] with the first step presumably corresponding to formation of a binuclear complex such as $\mathrm{TiOHMnO_4^+}$. We do not yet have sufficiently quantitative data to assign a value to the formation constant in this system, but preliminary indications are that it will be quite large, probably consistent with the trend in values established with the other d^0 metal ions. It would appear that the value of the formation constant is in large part determined by the charges on the species involved.

The presence of $\mathrm{TiOH^{2+}}$ as the reactive species in each of these systems as well as most of those studied previously may be indicative of an inner-sphere mechanism. Arguments have been developed in the reduction of cobalt(III) complexes for an inner-sphere mechanism when the hydroxy complex has a high reactivity compared to the aquo complex,[22] but whether this increase in reactivity is due to the electron-mediating effect of bridging $\mathrm{OH^-}$ or to a stability imparted to the inner-sphere complex by the $\mathrm{OH^-}$ ligand is still open to question.[23] The Ti(III) systems differ in that the $\mathrm{OH^-}$ ligand is originally bound to the reducing agent, but we have shown that for some Cr(VI)[2] and V(V)[5,6] oxidations, donation of the bridging ligand by the reducing agent is possible. While the general high reactivity of $\mathrm{TiOH^{2+}}$ in the d^0 metal ion systems may be indicative of an inner-sphere mechanism, an argument which is supported but not proved by the formation of binuclear complexes, it would be difficult to extend such arguments to other oxidants, especially those which are substitution inert and do not expand their coordination sphere upon reduction. An alternate reason for the presence of $\mathrm{TiOH^{2+}}$ is that in the process of oxidation, $\mathrm{Ti^{3+}}$ loses two protons to form $\mathrm{TiO^{2+}}$. It is not unusual for one or more protons to be lost in or before the rate-determining step when protons are lost on going from reactants to products, presumably due to lowering of the energy barrier when the transition state more closely resembles the products.

In each of the Ti(III) reductions we have examined, no dependence on the $\mathrm{Cl^-}$ concentration was noted over wide ranges. Unless $\mathrm{Cl^-}$ were to play some specific role, such as that of a bridging ligand, it would be surprising to see a $[\mathrm{Cl^-}]$ dependence, since Ti(III) exists only to a small extent as $\mathrm{TiCl^{2+}}$.[24] In those cases where a $[\mathrm{Cl^-}]$ dependence was noted,[16] the oxidizing agents have a marked tendency to form $\mathrm{Cl^-}$ complexes, which are probably responsible for this effect.

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Notes

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Mechanism of the Bromate Ion Oxidation of Aquoiron(II)

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The bromate ion oxidation of ferrous ion has been studied as part of a series of oxy anion oxidations of intermediate strength reducing agents such as the cyanide,[1] bipyridyl, and mixed-ligand complexes of iron(II). This reaction is also of interest in relation to the metal ion catalyzed oscillating reaction between bromate ion and malonic acid.[2-4] It has been reported that Fe(III) will cause oscillating behavior in this system.[5] This seemed rather surprising in light of recent mechanistic interpretations of these oscillating reactions.[3,4,6] A crucial part of this mechanism is the appropriate pathway for oxidation of the metal ion by $\mathrm{BrO_3^-}$, which is followed only by very weak metal ion reducing agents (*e.g.*, $\mathrm{Ce^{3+}}$,[7] $\mathrm{Mn^{2+}}$,[7] $\mathrm{NpO_2^+}$ [7,8]). We have verified the occurrence of oscillating behavior in the $\mathrm{BrO_3^-}$-malonic acid reaction catalyzed by a number of metal ion-diimine complexes with oxidation potentials less than -1.1 V but were unable to observe any oscillations with $\mathrm{Fe^{2+}}$ or $\mathrm{Fe^{3+}}$ as the catalyst, in agreement with predictions based on the proposed mechanism.[3,4,6] The kinetics of the $\mathrm{Fe^{2+}}$-$\mathrm{BrO_3^-}$ reaction reported here are also inconsistent with $\mathrm{Fe^{2+}}$-$\mathrm{Fe^{3+}}$ giving rise to oscillating behavior.

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Table I. Rate Constants for Reaction of Fe^{2+} with BrO_3^- at 25.0° and 0.500 M Ionic Strength

				k_{ox}, M^{-1} sec^{-1}	
$[H^+]_0$, M	$10^4[Fe^{2+}]_0$, M	$10^3[BrO_3^-]_0$, M	10^3k_{obsd}, sec^{-1}	Obsd^a	Calcd^b
0.00997	3.94	2.57	1.91	0.744	
	3.94	10.3	7.45	0.725	
				Av 0.735 ± 0.010	0.735
0.0100	7.16	10.3	7.37	0.718	0.736
0.0246	3.94	2.57	3.23	1.26	
	3.94	2.57	3.25 ± 0.06^c	1.27 ± 0.02^c	
	3.94^d	2.57	3.18	1.24	
	3.94^e	2.57	3.36	1.31	
	3.94^f	2.57	3.21	1.25	
				Av 1.27 ± 0.02	1.23
0.0393	3.94	2.57	4.56	1.78	1.69
0.0497	3.94	0.998	2.05	2.05	
	3.94	2.57	5.23	2.04	
	3.94	2.57	5.25	2.05	
	3.94	5.13	10.2	1.99	
	3.94	5.13	9.90	1.93	
	3.94	5.13	9.90	1.93^g	
	3.94	10.3	20.3	1.98	
	3.94	20.5	39.4	1.92	
				Av 1.99 ± 0.04	2.00
0.0499	50.1	0.0998	1.52	1.82^g	
	100	0.0998	3.40	2.03^g	
	200	0.0998	6.66	1.99^g	
	386	0.0998	12.0	1.87^g	
				Av 1.93 ± 0.08	2.00
0.0796	3.94	2.57	7.63	2.97	2.80
0.100	3.94	2.57	8.66	3.37	3.30
0.120	3.94	2.57	9.44	3.68	3.71
	3.94	2.57	9.47	3.69	3.71
0.150	3.94	2.57	11.2	4.37	4.30
0.170	3.94	2.57	12.7	4.96	4.65
0.200	3.94	2.57	13.6	5.30	5.13
0.250	3.94	2.57	14.9	5.81	5.81
0.299	3.94	2.57	15.5	6.04	6.39

[a] $k_{ox} = k_{obsd}/[BrO_3^-]$ or $k_{ox} = 6k_{obsd}/[Fe^{2+}]$. [b] Calculated from eq 4 and values of the parameters given in the text. [c] The average of values determined at seven different wavelengths. [d] 5.02×10^{-4} M Fe^{3+} was added initially. [e] 1.00×10^{-3} M Fe^{3+} was added initially. [f] 2.00×10^{-3} M Fe^{3+} was added initially. [g] Reaction solutions were purged with deoxygenated nitrogen.

Experimental Section

Iron(III) perchlorate was prepared by repeated fuming of iron(III) chloride in 70% perchloric acid until chloride tests with silver nitrate were negative, followed by recrystallization from 6 M $HClO_4$. Solutions were analyzed by reduction of aliquots with zinc amalgam, followed by titration with cerium(IV) to a ferroin end point. Acid concentrations were obtained by ion-exchange titrations.[9] Iron(II) perchlorate solutions were prepared by electrolytic reduction of iron(III), stored under nitrogen, and analyzed as above. Bromate ion solutions were prepared from recrystallized sodium bromate and were analyzed by titration with sodium thiosulfate of the iodine produced by reaction with excess sodium iodide. The preparation and analysis of lithium perchlorate and perchloric acid has been previously described.[9]

Kinetics experiments were carried out with a Cary 14 recording spectrophotometer with previously described thermostating arrangements.[9] Most experiments were carried out at 300 nm, but repetition of an experiment in the range 300–360 nm gave rate constants which varied by only ±2%. Reactions were carried out under pseudo-first-order conditions, with plots of ln $(D_\infty - D_t)$ *vs.* time (D = absorbance) being linear for at least 95% reaction. Ionic strength was maintained at 0.500 M by addition of $LiClO_4$. To avoid the possibility of the oxidation of water, especially at high acidities,[1] the sodium bromate was added to the solution within a few minutes before initiation of the reaction. Results were independent of the presence or absence of oxygen, so only solutions with excess Fe^{2+} were purged with deoxygenated N_2 to prevent air oxidation during the experiment.

Results

The stoichiometry of the reaction with excess BrO_3^-, the condition for most experiments, is given by

$$5Fe^{2+} + BrO_3^- + 6H^+ = 5Fe^{3+} + {}^1/_2Br_2 + 3H_2O \qquad (1)$$

This was verified by comparing the spectra of actual reaction products with the spectrum of a simulated mixture which was identical except that Br_2 was absent. The difference corresponded exactly to the spectrum of Br_2, with 0.0984 Br_2 produced per Fe^{2+} reacting. The iron(III) product is actually a mixture of Fe^{3+}, $FeOH^{2+}$, and $Fe(OH)_2Fe^{4+}$,[10] but these species attain equilibrium rapidly compared to the redox process and thus cause no interference. Iron(III) is known to form complexes with BrO_3^-,[11] but under the conditions of the experiments reported here, the fraction of Fe(III) or BrO_3^- present as $FeBrO_3^{2+}$ is never greater than 0.5%. The further reduction of Br_2 to Br^- probably does not occur to any great extent under these conditions. A kinetic study[12] of the Fe^{2+}-Br_2 reaction indicates that it would be much slower than the Fe^{2+}-BrO_3^- reaction under the conditions of our experiments with excess BrO_3^- and results with systems in which reduction of Br_2 is a rapid and important process indicate that autocatalytic rather than first-order kinetics would be observed.[1] With excess Fe^{2+} the reduction of Br_2 is important, the ratio of second-order rate constants with excess BrO_3^- to those with excess Fe^{2+}, uncorrected for

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stoichiometry, implying a ratio of 6 Fe^{2+} per BrO_3^-

$$6Fe^{2+} + BrO_3^- + 6H^+ = 6Fe^{3+} + Br^- + 3H_2O \qquad (2)$$

As shown by the data in Table I, at constant $[H^+]$, the reaction follows a simple mixed second-order rate equation

$$-d[Fe^{2+}]/dt = -6d[BrO_3^-]/dt = k_{ox}[Fe^{2+}][BrO_3^-] \qquad (3)$$

where k_{ox} was calculated from the observed pseudo-first-order rate constant by $k_{ox} = k_{obsd}/[BrO_3^-]$ or $k_{ox} = 6k_{obsd}/[Fe^{2+}]$, depending on which reagent was in excess. Results were independent of added Fe^{3+} in amounts in large excess over those produced in the reaction. Variation of acidity over the range 0.01-0.30 *M* gives the equation

$$k_{ox} = a + b[H^+]/(c + [H^+]) = (d + e[H^+])/(c + [H^+]) \qquad (4)$$

as shown by a plot of k_{ox} *vs.* $[H^+]$ which has a nonzero intercept and curves downward, indicating the necessity of three parameters. Data were fit to this equation using a nonlinear least-squares computer program with each point weighted as k_{ox}^{-2}.[13] Values of the parameters are $a = 0.372 \pm 0.024\ M^{-1}\ sec^{-1}$, $b = 13.0 \pm 1.0\ M^{-1}\ sec^{-1}$, $c = 0.347 \pm 0.036\ M$, $d = 0.129 \pm 0.020\ sec^{-1}$, and $e = 13.3_7 \pm 1.0_1\ M^{-1}\ sec^{-1}$, which reproduce the values of k_{ox} with an average deviation of ±2.7%. Fit of the data to eq 4 is shown by the agreement between calculated and observed values of k_{ox} in Table I.

Discussion

A possible interpretation for an acid dependence with a sum of terms in the denominator (eq 4) would involve an acid dissociation reaction with appreciable amounts of both acid and base forms being present. This would require an acid dissociation constant of 0.35 *M* for either Fe^{2+} or $HBrO_3$. The value of Fe^{2+} is much too small (*ca.* 10^{-7})[14] and the value for $HBrO_3$ is probably too large. While this value is not known, by considering trends in known values[14] of dissociation constants for other oxyhalogen acids, an estimate of ~50 *M* is obtained. Regardless of the accuracy of this estimate, it is unlikely that the value for $HBrO_3$ is as small as 0.35 or similar rate equations should have been observed in other BrO_3^- oxidations, so this interpretation can be ruled out.

An alternate interpretation involves a steady-state mechanism with $FeBrO_3^+$ as an intermediate[15]

$$Fe^{2+} + BrO_3^- \xrightarrow{k_1} Fe(III) + Br(IV) \qquad (5)$$

$$Fe^{2+} + BrO_3^- \underset{k_3}{\overset{k_2}{\rightleftarrows}} FeBrO_3^+ \qquad (6)$$

$$FeBrO_3^+ + H^+ \xrightarrow{k_4} Fe(III) + Br(IV) \qquad (7)$$

$$4Fe^{2+} + Br(IV) + nH^+ \overset{\text{fast}}{=\!=} 4Fe(III) + {}^1\!/\!{}_2Br_2 + 3H_2O \qquad (8)$$

with $k_{ox} = k_1 + k_2k_4[H^+]/(k_3 + k_4[H^+])$, so $a = k_1$, $b = k_2$, and $c = k_3/k_4$. The identity of Br(IV) cannot be deduced from the rate equation since it occurs after the rate-determining step, but it could be BrO_3^{2-} in eq 5 and BrO_2 in eq 7, perhaps with Fe(III) being produced as $FeOH^{2+}$ *via* OH^- transfer. Subsequent steps (eq 8) must be rapid and may involve interactions between various bromine oxidation states as long as these do not affect the BrO_3^- concentration. These results clearly rule out the types of interaction necessary to give rise to oscillating behavior in the bromate oxidation of malonic acid.[3,4,6]

The intermediate $FeBrO_3^+$ could be either Fe^{II}-Br^{V} or Fe^{III}-Br^{IV}. If the configuration is Fe-O-BrO_2^+, formed by substitution of bromate onto Fe^{2+} rather than by a water molecule on Fe^{2+} forming a bridge to BrO_3^- with expansion of the Br(V) coordination shell, the Fe^{III}-Br^{IV} assignment would seem more likely since the rate constants (k_2 or k_5) are much too small for simple substitution on Fe^{2+}. Another possibility which cannot be ruled out is a two-electron transfer with ultimate formation of Fe(IV), which would react with Fe^{2+} to give $Fe(OH)_2Fe^{4+}$ in greater than equilibrium amounts, since relaxation to the equilibrium concentration is faster than the redox reaction.

A second mechanism may be proposed which is indistinguishable from eq 5-8,[15] *i.e.*

$$Fe^{2+} + BrO_3^- \underset{k_6}{\overset{k_5}{\rightleftarrows}} FeBrO_3^+ \qquad (9)$$

$$FeBrO_3^+ \xrightarrow{k_7} Fe(III) + Br(IV) \qquad (10)$$

$$FeBrO_3^+ + H^+ \xrightarrow{k_8} Fe(III) + Br(IV) \qquad (11)$$

followed by appropriate rapid steps (eq 8). This mechanism has $k_{ox} = (k_5k_7 + k_5k_8[H^+])/(k_6 + k_7 + k_8[H^+])$ with $d = k_5k_7/k_8$, $e = k_5$, and $c = (k_6 + k_7)/k_8$. There are also two more indistinguishable mechanisms,[15] but we view these with disfavor since they both involve the formation of $FeBrO_3^+$ with H^+ as both a reactant and a product.

Reductions of BrO_3^- have usually been found to have a second-order dependence on $[H^+]$, which has been interpreted in terms of a displacement of H_2O from $H_2BrO_3^+$ either prior to or in the rate-determining step.[16,17] It has been suggested that this displacement process results in a binuclear species containing the reducing agent and BrO_2^+, *i.e.*, that the reaction is of the inner-sphere type. In the $Fe(CN)_6^{4-}$ reduction of BrO_3^-,[1] a "normal" $[H^+]^2$ path was observed, but an additional path independent of $[H^+]$ also occurred. Although direct evidence is lacking, these observations were tentatively interpreted in terms of parallel inner-sphere and outer-sphere paths. Results of the Fe^{2+}-BrO_3^- reaction provide definite evidence for the occurrence of an inner-sphere path, probably involving substitution on Fe^{2+} rather than on BrO_3^-. Depending on which mechanism is correct, there could also be a parallel outer-sphere path in this system.

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Registry No. Fe^{2+}, 15438-31-0; BrO_3^-, 15541-45-4.

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Rate of Reduction of Cobalt(III) Complexes by $CO_2\cdot^-$ Radicals in Aqueous Solution[1]

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Reduction of cationic cobalt(III) complexes by the hydrated electron, e_{aq}^-, is very fast with diffusion-controlled rates of (4-9) × 10^{10} M^{-1} sec^{-1}.[3] Although the differences in these rates may be due to the charges and radii of the complexes,[4] the very low reduction potential of e_{aq}^- ($E° = -2.8$ V)[3] makes it an indiscriminant reagent and not kinetically selective. Recently, a great deal of interest has been directed toward the reactions of other radicals with Co(III) complexes in an attempt to aid in the elucidation of the mechanism of inter- and intramolecular electron transfer.[5-8] Of particular concern has been the correlation of the rate constant for the electron-transfer reaction of the radical with the complex with the potential of the redox couple and the free energy of the reaction and comparison with outer-sphere reactions involving metal ion reductants (*e.g.*, Cr^{2+}, $Ru(NH_3)_6{}^{2+}$, and V^{2+}).[9,10] We have chosen to examine the rate of reaction of $CO_2\cdot^-$ radicals ($E_{1/2}$ *vs.* sce = −1.3 V)[11] with selected cobalt(III)-pentaammine and -tris(bipyridyl) complexes to see if this milder reductant of 1− charge would show a greater selectivity in its reaction rates and reactivity patterns compared with those of e_{aq}^-.

The technique of pulse radiolysis permits the $CO_2\cdot^-$ radical to be generated conveniently in less than 1 μsec *via* reaction 1 in solutions containing 0.1 M HCO_2^- and 2.5 × 10^{-2} M

$$\text{OH or H} + HCO_2^- \rightarrow CO_2\cdot^- + H_2O \text{ or } H_2 \qquad (1)$$

$$k_1 = 2.5 \times 10^9 \text{ or } 2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$$

N_2O (1 atm partial pressure in order to convert e_{aq}^- to ·OH radicals). However, because of the low absorptivity of the $CO_2\cdot^-$ radical in accessible regions of the spectrum (λ_{max} 235 nm; ϵ_{max} 3000 M^{-1} cm^{-1}),[12] the disappearance of the radical cannot be conveniently observed. Similarly, most simple cobalt(III)-ammine complexes do not absorb appreciably above 280 nm thus restricting the possibility of monitoring the disappearance of the complex upon reduction by the radical. Furthermore, very few Co(III) complexes are known to give reduced intermediates which can be detected by absorption spectrophotometry. We have already reported[6] that *p*-nitrobenzoatopentaamminecobalt(III) ($p\text{-}O_2NC_6H_4CO_2Co^{III}(NH_3)_5{}^{2+}$; PNBPA) reacts rapidly with $CO_2\cdot^-$ to form a strongly absorbing transient intermediate (λ_{max} 330 nm; ϵ_{max} 2.0 × 10^4 M^{-1} cm^{-1}).

$$CO_2\cdot^- + \text{PNBPA} \rightarrow \text{PNBPA}\cdot^- + CO_2 \qquad (2)$$

$$k_2 = 1.9 \times 10^9\ M^{-1}\ \text{sec}^{-1}$$

PNBPA·$^-$ is relatively long-lived with its intramolecular decay to Co^{2+} having a rate constant 2.6 × 10^3 sec^{-1}. From the competition for $CO_2\cdot^-$ between PNBPA and the complex of interest, values of k_3 can be evaluated.

$$CO_2\cdot^- + \text{complex} \rightarrow \text{reduced complex} + CO_2 \qquad (3)$$

Experimental Section

N_2O-saturated neutral solutions containing 0.1 M HCO_2^- and 4 × 10^{-5} M PNBPA and up to 2 × 10^{-4} M of the complex of interest were subjected to 30-nsec pulses of 2.3-MeV electrons (dose/pulse ≃ 1 krad) and the absorbance of PNBPA·$^-$ at 330 nm using a 2-cm optical path length was recorded.[13] Under the conditions of the experiments, the formation of PNBPA·$^-$ was complete within 40 μsec after the pulse and showed very little decay (~10%) during that time. The oscilloscopic traces, recorded on Polaroid film, were extrapolated back to "zero time" to give the absorbance of PNBPA·$^-$ under initial conditions. Solutions were prepared from triply distilled water that had been radiolyzed and photolyzed and were buffered using phosphate. The complexes were prepared using standard inorganic syntheses and were characterized by their absorption spectrum and elemental analysis.

Results and Discussion

Competition for $CO_2\cdot^-$ by a particular complex *via* reaction 3 causes a reduction in the amount of PNBPA·$^-$ generated in reaction 2. This is reflected by a diminution of the absorbance of PNBPA·$^-$ at 330 nm. At constant radiation dose per pulse, simple competition kinetics yields

$$k_3 = \frac{k_2[\text{PNBPA}]}{[\text{complex}]}\left(\frac{A^0 - A}{A}\right)$$

where A^0 is the absorbance of PNBPA·$^-$ at 330 nm in the absence of added complex scavenger and A is the absorbance in the presence of complex. In the case of $p\text{-}O_2NC_6H_4CH_2\text{-}CO_2Co^{III}(NH_3)_5{}^{2+}$, k_3 could be measured directly from the formation kinetics of the resulting transient at 295 nm (in the absence of PNBPA); for $Co(bipy)_3{}^{3+}$, k_3 was obtained from the kinetics of the disappearance of the strong absorption of the complex at 330 nm (in the absence of PNBPA). In none of the other complexes was a reduced species detected; as well, the rate of electron transfer from PNBPA·$^-$ to the other complexes is too slow ($k < 10^7$ M^{-1} sec^{-1}) to interfere with these measurements. Table I summarizes the data.

As expected, the $CO_2\cdot^-$ radical is kinetically more selective than e_{aq}^- and the values of $k(CO_2\cdot^- + \text{complex})$ show a range of over two orders of magnitude depending upon the nature of the ligands. The faster reactions shown by the aromatic nitro complexes are compatible with the strong electrophilic character of the nitro group; $CO_2\cdot^-$ reacts rapidly (>10^9 M^{-1} sec^{-1}) with these free ligands. Thus, the coordination of these ligands does not remove the reactive site for $CO_2\cdot^-$ attack and electron transfer. In the case of all the other complexes which show rate constants in the rather narrow range of 10^7-10^8 M^{-1} sec^{-1}, $CO_2\cdot^-$ does not react with the

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