a second fraction was collected (3.9 g); this proved to be very largely the cis isomer. The remaining solution was discarded. The cis isomer was recrystallized as the $S_2O_6^{2-}$ salt by dissolution of the crude ClO_4^- salt in H_2O at 0 °C (ca. 90 mL/g; 180 mL) and the addition of $Li_2S_2O_6\cdot 3H_2O$ in ice–water (2 g/10 mL). The resulting mixture was kept on an ice–salt bath, and cold acetone (200 mL, 0 °C) was added. After 10 min, the purified orange-pink cis isomer (1.1 g) was collected, washed with ethanol and ether, and dried in air. The crystals analyzed as the monohydrate, *cis*$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)\cdot 2H_2O$. The perchlorate salt was obtained from the dithionate (1 g) by trituration with cold 4 M $HClO_4$ (10 mL); it dissolved readily only to crystallize shortly thereafter as *cis*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ on addition of cold ethanol (15 mL). It was quickly collected, washed with ethanol and ether, and air dried. ϵ_{456}(max) 129.5 in H_2O. ^{13}C NMR (D_2O/D^+): δ −21.22, −21.71, −22.86, −23.05.^{13}C NMR for the aqua salts in 1 M NaOD ($[Co(en)_2(SO_3)OH]$): δ −22.23, −22.39, −23.27 (2).

trans-$[Co(en)_2(SO_3)Cl]$,[15] *trans*-$[Co(en)_2(SO_3)OH]$,[15] *trans*-$[Co(en)_2(SO_3)CN]$,[18] and *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$[15] were prepared by minor modifications to published procedures. Recrystallizations were from H_2O/CH_3OH, H_2O/CH_3OH, and $H_2O/HClO_4$, respectively. *trans*-$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)\cdot 2H_2O$ crystallized as large khaki-colored from a concentrated aqueous solution of the perchlorate containing $Li_2S_2O_6$, on the slow addition of acetone and cooling. The triflate salt was also characterized by using CF_3SO_3H as the precipitant. For *trans*-$Co(en)_2(SO_3)OH_2^+$: ϵ_{467}(max) 164.0, ϵ_{397}(min) 21.6, ϵ_{360} 98.0 in 0.01 M $HClO_4$. ^{13}C NMR (D_2O/D^+) δ −22.73. ^{13}C NMR for the aqua salts in 1 M NaOD ($[Co(en)_2(SO_3)OH]$): δ −23.22. *trans*-$[Co(en)_2(SO_3)N_3]$ was obtained by dissolving *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ in 2 M NaN_3 to the point of saturation, filtering, and carefully adding an equal volume of methanol. Brown needles deposited on standing in a refrigerator overnight; these were filtered, sucked semidry at the pump, washed with methanol and ether, and air dried. ^{13}C NMR (1 M NaN_3): δ −22.97.

trans-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ was dehydrated to a red power by drying it under vacuum over P_2O_5 for 24 h. The same red material, *trans*-$[Co(en)_2SO_3)]_n(ClO_4)_n$, was synthesized by stirring *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ (2 g) for 1 h in methanol (500 mL), in which the reactant is partially soluble. Although the additional possibility of SO_3^{2-} chelation existed, similar experiments on the cis isomer did not lead to any detectable dehydration of the $Co(en)_2(SO_3)OH_2^+$ moiety.

The sparingly soluble dimeric yellow *trans,trans*-$[(en)_2(SO_3)CoCNCo(en)_2(SO_3)]ClO_4$ salt was obtained by adding a solution of *trans*-$[Con(en)_2(SO_3)CN]$ to an equimolar one of *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4\cdot H_2O$ in water. It crystallized immediately and was collected and washed with methanol and ether and dried in air. The same material was obtained less conveniently by dissolving *trans*-$[Co(en)_2(SO_3)CN]$ in 5 M $HClO_4$; the dimer slowly crystallized on standing. [*Caution! Liberated HCN is toxic.*]

The "double salts" *trans,trans*-$[Co(en)_2A(OH)]_2H\cdot(ClO_4)_3$ are known for several A groups.[23,24] The examples A = N_3^- and NCS^- have been structurally characterized by single-crystal X-ray crystallography, and these ions contain the symmetrical H-bonded bridging ion $H_3O_2^-$.[24] Half-neutralization of *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4$ with aqueous NaOH merely solubilized half of the salt, and presumably for the sulfito species the double salt is more soluble than its individual aqua and hydroxo components. The H-bonding structural feature no doubt is weakened by the trans influence of two SO_3^{2-} groups in the dimer, preventing its ready crystallization.

The visible spectra of the *cis*- and *trans*-$Co(en)_2(SO_3)OH_2^+$ ions were measured in both dilute acid (0.01 M $HClO_4$) and dilute base (0.03 M NaOH). The determination of the pure absorption spectra for the *trans*- and especially the *cis*-(sulfito)aqua ions required repetitive scanning and extrapolation to zero time; a slight temperature dependence was noted, particularly for the tail of the UV band, even over the narrow range 10–25 °C. Quoted data refer to 25 °C. The spectra of the generated *cis*- and *trans*-$[Co(en)_2(SO_3)OH]$ species did not change rapidly with time; indeed, neither showed significant change over 2 days at ambient temperature, as shown by ^{13}C NMR and visible absorption spectrometry (trans: ϵ_{467}(max) 180.5, ϵ_{401}(min) 38.0, ϵ_{360} 138.5. cis: ϵ_{461}(max) 177, ϵ_{404}(min) 70, ϵ_{360} 225).

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Registry No. *cis*-$[Co(en)_2(SO_3)N_3]$, 112571-09-2; *trans*-$[Co(en)_2(SO_3)N_3]$, 112459-43-5; *cis*-$[Co(en)_2(N_3)_2]NO_3$, 22651-44-1; *trans*-$[Co(en)_2(SO_3)OH_2]ClO_4$, 49727-17-5; *trans*-$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)$, 112459-42-4; *trans*-$Co(en)_2(SO_3)OH_2^+$, 24458-52-4; *trans*-$[Co(en)_2(SO_3)OH_2]CF_3SO_3$, 112459-44-6; *cis*-$[Co(en)_2(SO_3)OH_2]_2(S_2O_6)$, 112571-10-5; *cis*-$[Co(en)_2(SO_3)OH_2]ClO_4$, 112571-11-6; *cis*-$Co(en)_2(SO_3)OH_2^+$, 112529-94-9; *cis*-$[Co(en)_2(SO_3)OH]$, 112459-40-2; *trans*-$[Co(en)_2(SO_3)OH]$, 112529-92-7; *trans*-$[Co(en)_2(SO_3)Cl]$, 112459-41-3; *trans*-$[Co(en)_2(SO_3)CN]$, 112529-93-8; *trans*-$[Co(en)_2(SO_3)]_n(ClO_4)_n$, 92130-08-0; *trans,trans*-$[(en)_2(SO_3)CoCNCo(en)_2(SO_3)]ClO_4$, 112459-46-8; NO_2^-, 14797-65-0.

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Electron Transfer. 90. Further Oxidations of Vitamin B_{12r} (Cob(II)alamin)[1]

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Vitamin B_{12r} (cob(II)alamin), the Co(II) derivative of vitamin B_{12}, reduces Fe^{III} (to Fe^{II}), V^V (to V^{IV}), and BrO_2^- (to Br^-) in aqueous solution. The rate law for reaction with Fe^{III}(aq) features an inverse-$[H^+]$ term and, in the presence of added Cl^- or Br^-, a sizable halide-proportional term as well. These kinetic dependencies point to specific redox bridging roles for Fe(III)–bound hydroxide and halide. The very high specific rates for oxidations by $Fe(NCS)^{2+}$ (1.1×10^5) and $Fe(N_3)^{2+}$ ($>1 \times 10^7$ M^{-1} s^{-1}) are in accord with this assignment. Oxidation by Fe^{III}(aq) is inhibited by fluoride, reflecting the conversion of Fe(III) to inactive FeF^{2+}. The specific rate pertaining to the $[H^+]$-independent component in the oxidation by Fe^{III}(aq) corresponds to a self-exchange rate for the cob(II,III)alamin couple of $10^{-4.5}$ M^{-1} s^{-1}, or about 10^{-8} times the corresponding value for cob(I,II)alamin. The acidity pattern for oxidation by vanadium(V) is consistent with partition of V(V) into a reactive protonated form ($pK_A = 3.5$) and an unreactive deprotonated species. The limiting specific rate (4.4×10^5 M^{-1} s^{-1}) points to a predominant inner-sphere path for this reaction. Oxidations by bromite (BrO_2^-) exhibit a prominent $[H^+]$-proportional term, attributed to reaction of B_{12r} with $HBrO_2$, proceeding at a specific rate of 4×10^6 M^{-1} s^{-1}, i.e. about as rapidly as the analogous reaction with $HClO_2$. Oxidations of B_{12r} by $IrCl_6^{2-}$, $Fe(CN)_6^{3-}$, and $Fe(bpy)_3^{3+}$ are too rapid to measure ($k > 7 \times 10^6$ M^{-1} s^{-1} at 25 °C and $\mu = 1.0$ M) by our methods.

We have been interested for some time in the redox reactions of the reduced forms of the coenzyme vitamin B_{12}.[2] The cobalt(I) derivative (B_{12s} or cob(I)alamin) reduces an impressive assortment of organic[3] and inorganic[4] species, and its versatility is enhanced

Table I. Stoichiometries of the Reactions of Vitamin B_{12r} (Cob(II)alamin) with $Fe(SCN)^{2+}$, $Fe(N_3)^{2+}$, VO_2^+, and BrO_2^- [a]

oxidant	10^5[Ox]	$10^5[B_{12r}]$	$10^5\Delta[B_{12r}]$	$\Delta[B_{12r}]/\Delta$[Ox]
$Fe(NCS)^{2+}$ [b]	2.27	4.46	2.28	1.01
	1.66	4.50	1.72	1.04
	2.77	8.92	2.83	1.02
	4.52	9.10	4.74	1.04
	1.72	9.10	1.74	1.01
	3.60	7.76	3.69	1.02
$Fe(N_3)^{2+}$ [c]	2.98	4.46	3.00	1.01
	4.76	8.92	5.19	1.09
	5.47	8.92	5.63	1.03
	1.20	8.92	1.13	0.94
VO_2^+ [d]	5.96	10.75	5.57	0.93
	6.87	10.83	5.67	0.83
	7.70	10.79	7.63	0.99
	8.52	9.68	7.65	0.90
	10.15	10.67	9.78	0.96
BrO_2^- [e]	1.35	15.41	4.72	3.49
	1.35	10.31	4.86	3.60
	2.01	15.29	7.15	3.56
	2.64	15.17	10.01	3.79
	3.93	14.94	13.73	3.51

[a] Reactions were monitored at 353 nm. Concentrations are given in molarity. [b] Reactions in 0.11 M $HClO_4$; $[NCS^-]$ = 0.005 M. [c] Reactions in 0.11 M $HClO_4$; $[HN_3]$ = 0.046 M. [d] Reactions in dilute acetic acid, pH 3.0–3.2. [e] Reactions in phthalate buffers, pH 4.7–4.9.

by its capacity to partake in both two-electron[3a,b,4a] and single-electron[4c,d] transactions, as well as by its participation in autocatalytic sequences.[4c,d] Cob(II)alamin (B_{12r}), the formal potential of which is much less negative than that for B_{12s},[5,6] reacts with a more modest array of acceptors. Nevertheless, a number of its reactions may be monitored conveniently,[7] and a duality of the redox mechanism has been demonstrated.[7d]

This report describes the reactions of vitamin B_{12r} with several strongly oxidizing reagents. With these, attack of the corrin ring system, if it occurs at all, is too slow to pose a serious problem.

Experimental Section

Materials. Hydroxocobalamin hydrochloride (a Sigma product), sodium bromite (Aldrich),[8] and other inorganic reagents (Alfa or Mallinckrodt) were used as received. Solutions of V(V) were prepared by dissolving ammonium vanadate in 1 M H_2SO_4. Lithium perchlorate was prepared as described by Dockal[9a] and recrystallized twice before use. Tris(bipyridyl)iron(III) perchlorate was prepared by the method of Nord.[9b] All reactions were carried out under oxygen-free N_2 in distilled water that had been previously boiled and sparged with N_2 for at least 4 h. Cob(II)alamin was generated by reaction of the Co(III) complex hydroxocobalamin hydrochloride with zinc amalgam,[7] a reaction that was generally complete in less than 1 min;[10] solutions could be transferred without difficulty by using syringe techniques.

Stoichiometric Studies. Stoichiometries of the reactions of the more rapid oxidants with excess B_{12r} were determined by addition of a measured deficiency of the oxidant to the Co(II) solution, waiting 2–5 min, and then measuring the increase in absorbance at 353 nm. These changes, after small corrections for the slow loss of reductant in the absence of coreagent, were compared to those observed when B_{12r} was treated with excess oxidant.[11] Representative results appear in Table I.

Kinetic Studies. Rates were estimated from measurements of absorbance changes at 350 nm, using a Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer. Ionic strength was regulated by addition of known concentrations of $LiClO_4$. Reactions were first order each in oxidant and B_{12r} but were carried out under pseudo-first-order conditions with the oxidant in greater than 10-fold excess. Conversions were followed for at least 5 half-lives. Rate constants from successive half-life values within a run generally agreed to within 5%, and average values did not differ significantly from those obtained from slopes of logarithmic plots of absorbance differences against reaction time. Specific rates from replicate runs agreed to better than 7%. In the case of the reaction with bromite, no sharp drop in absorbance occurred immediately after addition of the oxidant, thus ruling out the rapid formation of a partially reduced halogen species.

Except for the oxidations by $Fe(CN)_6^{3-}$, solutions from each of the reactions carried out with the oxidant in excess exhibited spectra corresponding to that of aquocob(III)alamin.[7b] The $Fe(CN)_6^{3-}$ product was quite different, having the following maxima [λ, nm (ϵ)]: at 356 (27 800), 405 (7300), 508 (10 400), 536 (9840).[12]

Oxidations of B_{12r} by $Fe(CN)_6^{3-}$, $Fe(bpy)_3^{3+}$, $Fe(N_3)^{2+}$, and $IrCl_6^{2-}$ were found to be too rapid to measure, even by using stop-flow methods. With these oxidants at the 10^{-4} M level, half-life values were less than 1 ms, corresponding to bimolecular specific rates greater than 7×10^6 M^{-1} s^{-1} (25 °C, μ = 1 M) for these reactions.

Results and Discussion

Results of the stoichiometric experiments (Table I) allow us to represent the predominant reactions of Fe(III) and V(V) schematically as (1) and (2) and the oxidations by bromite as (3).

$$\text{Fe(III)} + \text{Co(II)} \rightarrow \text{Fe(II)} + \text{Co(III)} \quad (1)$$

$$\text{V(V)} + \text{Co(II)} \rightarrow \text{V(IV)} + \text{Co(III)} \quad (2)$$

$$\text{Br(III)} + 4\text{Co(II)} \rightarrow \text{Br}^- + 4\text{Co(III)} \quad (3)$$

The persistent negative deviations (10–20%) from the indicated stoichiometries with VO_2^+ and BrO_2^- suggest some oxidative disruptions of the corrin ring systems by these reagents. With BrO_2^- in particular, the possibility of partial ring bromination, as reported for the B_{12r}–Br_2 reaction,[7b] cannot be excluded, although no major alterations in the product spectra were evident.

Oxidations by Fe(III). Representative data for oxidation of B_{12r} by Fe(III) systems appear in Table II. With no anionic species added aside from ClO_4^- (column A), reactions are seen to be strongly retarded with increasing acidity. Observed rates are in accord with (4), where k_0 = 51 ± 3 M^{-1} s^{-1} and k' = 7.4

$$k_{\text{obsd}} = k_0 + k'/[\text{H}^+] \quad (4)$$

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(8) Analysis of this reagent indicated 0.4% NaOH and 1.6% $NaBrO_3$ but no detectable NaBr. Since BrO_2^- reacts with B_{12r} over 10^3 times as rapidly as BrO_3^-,[7d] the latter contaminant should not affect our results. The difficulty in preparing pure bromite salts has been emphasized: Noszticzius, Z.; Noszticzius, E.; Schelley, Z. A. *J. Phys. Chem.* **1983**, *87*, 510.

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(10) When this reaction was allowed to proceed for 5 min or more, B_{12r} was further reduced to B_{12s}, as shown by the change from yellow to gray, the fading the Co(II) spectral peaks at 470 and 312 nm, and the growth of Co(I) peaks at 387 and 560 nm.[4a]

(11) Stoichiometric determinations of the slower reactions of B_{12r} with Fe(III) in halide-containing and aquo systems were complicated by the consumption of reductant by traces of oxygen slowly leaking into the vessel. In these instances, such loss was competitive with the transformations of interest, and reaction stoichiometry was taken, in analogy with the $Fe(NCS)^{2+}$ and $Fe(N_3)^{2+}$ reactions, as 1:1.

(12) The spectrum of the $Fe(CN)_6^{3-}$ oxidation product was perceptibly different from that of a red species formed rapidly on treating B_{12a} with $Fe(CN)_6^{4-}$. λ_{max}, nm (ϵ): 355 (23 500), 409 (3640), 506 (7490), 538 (7770). Moreover, the B_{12r}–$Fe(CN)_6^{3-}$ product, but not that from B_{12a}–$Fe(CN)_6^{4-}$, yielded a red precipitate on standing. Digestion of the latter with concentrated H_2SO_4 yielded a solution in which the Fe:Co ratio was found to be 1.50. Although these facets were not pursued, the redox behavior clearly does not correspond to that of a straightforward outer-sphere transformation.

Table II. Representative Kinetic Data for Oxidation of Vitamin B_{12r} (Cob(II)alamin) with Fe(III)[a]

A. $Fe^{III}(aq)-B_{12r}$			B. $Fe^{III}-B_{12r}-Cl^-$ [b]		C. $Fe^{III}-B_{12r}-F^-$				
$10^4[Fe^{III}]$	$[H^+]$	$10^{-2}k$[c]	$10^4[Cl^-]$	$10^{-2}k$[c]	$10^4[Fe^{III}]_T$[d]	$[H^+]$	$10^2[F^-]$	$10^5[Fe^{III}(aq)]$[e]	10^3k[f]
2.64	1.00	0.46	0.94	0.74	10.0	0.10	2.06	2.37	3.3
5.28	1.00	0.44	1.88	1.00	5.0	0.10	2.06	1.13	1.42
10.3	1.00	0.47	2.82	1.11	2.5	0.10	1.94	0.60	0.96
2.74	0.80	0.46	3.76	1.27	2.5	0.10	0.121	8.3	13.1
2.74	0.60	0.56	4.71	1.43	2.5	0.10	0.242	5.0	8.2
2.74	0.40	0.71	5.65	1.95	2.5	0.10	0.484	2.8	4.0
2.74	0.20	0.96	11.3	3.1	2.5	0.10	0.97	1.45	1.91
2.74	0.102	1.47			2.5	0.10	4.1	0.22	0.34
2.74	0.050	2.2			2.5	0.050	1.00	0.59	1.20
0.285	0.024	3.6			2.5	0.20	1.00	2.9	2.6
0.285	0.0143	5.7			2.5	0.40	1.00	4.8	3.6
0.285	0.0109	6.7			2.5	0.80	1.00	8.1	3.8
0.285	0.0066	11.5							

[a] Reactions at 25 °C, μ = 1.0 M ($HClO_4-LiClO_4$); $[B_{12r}]_0 = 2 \times 10^{-6}-4 \times 10^{-5}$ M; 350 nm. [b] $[H^+]$ = 0.502 M; $[Fe^{III}] = 3.75 \times 10^{-4}$ M. [c] Bimolecular specific rates (M^{-1} s^{-1}). [d] Total Fe(III) added. [e] Fe(III) not complexed by fluoride. [f] Pseudo-first-order specific rates (s^{-1}).

Table III. Specific Rates for Oxidation of Vitamin B_{12r} (Cob(II)alamin) with Iron(III) Systems[a]

oxidant	k, M^{-1} s^{-1}
$Fe^{III}(aq)$	$(51 \pm 3) + (7.4 \pm 0.1)[H^+]^{-1}$
$Fe(III) + Cl^-$	$(35 \pm 3) + (10.0 \pm 0.5)[H^+]^{-1} + (2.2 \pm 0.1) \times 10^{-5}[Cl^-]$
$Fe(III) + Br^-$	$(24 \pm 5) + (14.1 \pm 0.8)[H^+]^{-1} + (3.3 \pm 0.2) \times 10^{-5}[Br^-]$[b]
$Fe(NCS)^{2+}$	$(1.21 \pm 0.15) \times 10^5$[c]
$Fe(N_3)^{2+}$	$>1 \times 10^7$[d]
$Fe(CN)_6^{3-}$	$>7 \times 10^6$
$Fe(bpy)_3^{3+}$	$>7 \times 10^6$

[a] Reactions at 25 °C, μ = 1.0 M ($LiClO_4-HClO_4$. [b] $[H^+]$ = 0.1–0.5 M; $[Br^-] = 0-4 \times 10^{-4}$ M. [c] Fe(III)] = 1.5×10^{-4}, $[NCS^-] = 4.5 \times 10^{-3}$ M; $[Fe(NCS)^{2+}]$ calculated as 7.1×10^{-5} M (ref 14). Rate was nearly independent of acidity in the range $[H^+]$ = 0.10–1.0 M. [d] [Fe(III)] = 1.5×10^{-4} M, $[N_3^-]_{added}$ = 0.044 M; $[H^+]$ = 0.1 M; $[Fe(N_3)^{2+}]$ calculated as 6.5×10^{-5} M.

± 0.1 s^{-1}. Added chloride and bromide catalyze this transformation (the latter anion somewhat more effectively), and rate laws for both halide-containing systems include a halide-proportional term (Table III).[13] In contrast, addition of fluoride inhibits the reaction (column C).

The acceleration of outer-sphere electron transfers between metal centers by added halides and thiocyanate has been documented,[14a] but such effects are much less pronounced than the Cl^- and Br^- catalysis observed here. Moreover, they appear to be confined principally to reactions between cations of high charge (whereas B_{12r} has no net charge in our media). We therefore attribute these accelerations to partial conversion of Fe(III) to more reactive halide complexes and the inverse-acid term to participation of $Fe(OH)^{2+}$. The trends in reactivity suggest, although they do not prove, that halide and hydroxide have assumed specific bridging roles analogous to those proposed for the $Fe^{III}-Eu^{II}$ and $Fe^{III}-Cr^{II}$ reactions[14b] and that demonstrated[7d] for the reaction of B_{12r} with $(NH_3)_5CoI^{2+}$. The very high rates observed for $Fe(NCS)^{2+}$, $Fe(N_3)^{2+}$, and $Fe(CN)_6^{3-}$ bolster this inference, for these "pseudohalide" ligands would be expected greatly to favor the unusually soft[7d] Co^{II} center of B_{12r} in such inner-sphere conversions.[15] The rapid aquation at the axial positions of B_{12a} derivatives[16] prevents our confirming a bridged route for the chloride and bromide systems, but the modified Co^{III} species detected in the $Fe(CN)_6^{3-}$ reaction[12] is in accord with such a formulation. The same conclusion, however, cannot apply to the very rapid reaction of the substitution-inert oxidant $Fe(bpy)_3^{3+}$.

Table IV. Kinetic Data for Oxidation of Vitamin B_{12r} (Cob(II)alamin) with Vanadium(V)[a]

$10^5[H^+]$, M	$10^{-4}k_{obsd}$, M^{-1} s^{-1}	$10^{-4}k_{calcd}$,[b] M^{-1} s^{-1}	$10^5[H^+]$, M	$10^{-4}k_{obsd}$, M^{-1} s^{-1}	$10^{-4}k_{calcd}$,[b] M^{-1} s^{-1}
0.63	0.68	0.76	11.0	14.8	10.3
1.74	2.2	2.0	23.4	21	17.4
2.82	2.8	3.2	63	25	28
4.07	5.4	4.5	126	35	34
5.37	5.4	5.7			

[a] Reactions at 23.0 °C, μ = 0.20 M ($LiClO_4$); pH regulated by HOAc + OAc^-; $[V(V)] = 1 \times 10^{-4}-4 \times 10^{-4}$ M; $[B_{12r}] = 2 \times 10^{-5}$ M. [b] Specific rates calculated from (7), with k_{lim} taken as 4.4×10^5 M^{-1} s^{-1} and K_{HA} as 3.6×10^{-4} M.

Inhibition by added fluoride doubtless reflects partial conversion of Fe(III) to the slightly dissociated FeF^{2+} complex and indicates that the hard fluoride ligand is ineffective as a redox bridge to B_{12r}, as has been shown[7d] to be the case for the reaction of B_{12r} with $(NH_3)_5CoF^{2+}$. The equilibrium quotient for ligation by HF (reaction 5) may be used to estimate the concentration of Fe(III)

$$Fe^{III}(aq) + HF \rightleftharpoons FeF^{2+} + H^+$$
$$Q_F = 166 \quad (25\ °C, \mu = 1.0\ M)^{14b} \qquad (5)$$

not bound to fluoride ($[Fe^{III}(aq)]$ in column C of Table II) in each flouride mixture.[17] Division of the observed pseudo-first-order specific rates by these concentrations yields the bimolecular specific rates 45, 72, 90, 146, and 240 M^{-1} s^{-1} at $[H^+]$ = 0.79, 0.39, 0.19, 0.099, and 0.040 M, in agreement with (4), confirming the negligible reactivity of the fluoro complex(es).

If oxidation by the hexaaquo cation $Fe(H_2O)_6^{3+}$ be taken as an outer-sphere process, the specific rate for that component (50 M^{-1} s^{-1}) may be used, in conjunction with the approximate relationship (6),[18,19] to estimate $k_{Co(2,3)}$, the rate for electron self-

$$k_{Fe,Co} = (k_{Fe(2,3)}k_{Co(2,3)}K_{Fe,Co})^{1/2} \qquad (6)$$

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(13) In the absence of additional complications, the acid-independent term in the specific rate for oxidation by $Fe^{III}(aq)$ should equal the corresponding terms for oxidations by Fe(III) + Cl^- and by Fe(III) + Br^-, and the same should be true for the respective $[H^+]^{-1}$-proportional terms (for none of these terms involves halide). Although the indicated differences (Table III) exceed the estimated uncertainties in these parameters (3 M^{-1} s^{-1} for k_0, 0.1–0.9 s^{-1} for k'), we remain skeptical of their reality. If not artifacts, such discrepancies suggest the intervention of minor but specific kinetic medium effects, leading to more complicated rate expressions than those tabulated.

(14) (a) See, the example: Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545. (b) Carlyle, D. W.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 599.

(15) If the inverse-acid term in (4) is taken to describe the reaction of $Fe(OH)^{2+}$ with B_{12r}, a bimolecular specific rate 4×10^4 M^{-1} s^{-1} (25 °C, μ = 1.0 M) may be calculated by dividing k′ by the recorded acidity constant of $Fe^{III}(aq)$ (1.2×10^{-3} M). Analogous calculations using the formation constants of $FeCl^{2+}$ (4.3 M^{-1}) and $FeBr^{2+}$ (0.9 M^{-1}) lead to bimolecular specific rates of 5×10^4 and 4×10^5 M^{-1} s^{-1} for these species. Equilibrium constants for Fe(III) systems have been assembled by: Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1976; Vol. 4, pp 7–116.

(16) Thusius, D. *J. Am. Chem. Soc.* **1971**, *93*, 2629.

(17) For these calculations, [HF] at equilibrium was assumed to lie close to $[F^-]_{added}$, and $[H^+]_{eq}$ was taken as $[H^+]_{added}$ – [HF]. Conversions to FeF_2^+ and higher fluoro complexes were neglected.

(18) This stems from the treatment of Marcus[19] but should be applied only to redox systems featuring moderate differences in formal potentials.

Table V. Kinetic Data for Oxidation of Vitamin B_{12r} (Cob(II)alamin) with Bromite[a]

buffer	$10^7[H^+]$, M	$10^{-5}k$, $M^{-1}\ s^{-1}$
$H_2PO_4^- + HPO_4^{2-}$	31	11.8
	23	7.6
	13.8	4.3
	9.8	3.7
	6.8	2.8
	4.6	2.0
	3.1	1.46
	2.69	1.79
	1.23	1.23
	0.79	0.89
$H_3BO_3 + H_2BO_6^-$	0.023	0.57
$HCO_3^- + CO_3^{2-}$	0.159	0.45
	0.0028	0.42
	0.00090	0.40

[a] Reactions at 24.0 °C, $\mu = 0.20$ M ($LiClO_4$); $[BrO_2^-] = 6 \times 10^{-5}$–$1.3 \times 10^{-4}$ M; $[B_{12r}] = 2 \times 10^{-5}$ M.

exchange pertaining to the couple cob(II,III)alamin (B_{12r},B_{12a}). The value of $k_{Fe(2,3)}$, for self-exchange in the system $Fe^{2+/3+}$, has been recorded as 4.0 $M^{-1}\ s^{-1}$,[20] and $\Delta E°$ for the two half-reactions (0.44 V) corresponds to an equilibrium constant, $K_{Fe,Co}$, of $10^{7.3}$. The resulting value for $k_{Co(2,3)}$ is $10^{-4.5}$ $M^{-1}\ s^{-1}$, well below the estimated[4d] rate of self-exchange, $10^{4.8\pm0.5}$, for the related B_{12} couple cob(I,II)alamin (B_{12s},B_{12r}). A similar conclusion results from the electrochemical measurements of Lexa.[22]

Oxidations by Vanadium(V). Data for oxidations by vanadium(V) are summarized in Table IV. Rates are seen to be nearly proportional to $[H^+]$ near pH 5 but approach a limiting value in solutions with pH near 3. Values can be correlated with eq 7,

$$k_{obsd} = \frac{k_{lim}[H^+]}{K_A + [H^+]} \tag{7}$$

which indicates partition of one of the redox partners between a reactive protonated form (with acidity constant K_A and specific rate k_{lim}) and an unreactive deprotonated form. Refinement in terms of (7) yields $k_{lim} = (4.4 \pm 1.1) \times 10^5$ $M^{-1}\ s^{-1}$ and $K_A = (3.6 \pm 1.0) \times 10^{-4}$ M ($pK_A = 3.5$).

The pK_A value lies close to that reported for vanadium(V) ("H_3VO_4", $pK_A = 3.78$),[16] indicating that the acidic form of the oxidant is bearing the burden of oxidation, as is the case for reactions of B_{12r} with oxyhalogen species.[7c]

From the rate constant calculated above for B_{12r},B_{12a} self-exchange, in combination with $\Delta E°$ for this reaction (0.70 V) and the appropriate (outer-sphere) self-exchange rate for vanadium(IV,V) (10^{-3} $M^{-1}\ s^{-1}$),[23,24] we may estimate the specific rate for this reaction, 2×10^2 $M^{-1}\ s^{-1}$, if it were to utilize only an outer-sphere path. This falls well below our value of k_{lim}, indicating a preponderant inner-sphere contribution to this reaction.

Oxidation with Bromite.[25,26] Kinetic data for the reaction of B_{12r} with BrO_2^- in phosphate, borate, and carbonate buffers are gathered in Table V. Reactions are seen to be accelerated by increasing $[H^+]$, with specific rates conforming to the binomial expression (8) with $k_0 = (4.7 \pm 0.3) \times 10^4$ $M^{-1}\ s^{-1}$ and $k' = (3.5 \pm 0.3) \times 10^{11}$ $M^{-2}\ s^{-1}$.[27]

$$k_{obsd} = k_0 + k'[H^+] \tag{8}$$

In analogy to the corresponding oxidation by ClO_2^-,[7c] the net conversion to halide (eq 3) in the presence of excess reductant may be taken to occur also with excess oxidant. However, the straightforward exponential decay curves obtained, in combination with the absence of an initial sharp drop in absorbance, indicate that the overall rate is being determined by the first step in the sequence, the initial attack on BrO_2^-, and that bromite is reduced more slowly than any state intervening between 3+ and 1−, a conclusion in agreement with the very high rate ($k = 6 \times 10^6$ $M^{-1}\ s^{-1}$) reported for the reaction of B_{12r} with Br_2.[7b]

If the k' term in (8) is assumed to represent the oxidation of B_{12r} by $HBrO_2$, the bimolecular specific rate for this path, obtained by multiplying k' by the reported K_A (1.3×10^{-5} M)[28] for bromous acid, is 4×10^6 $M^{-1}\ s^{-1}$, a value comparable to the corresponding figure (1.2×10^6)[7c] for $HClO_2$–B_{12r}.

We cannot say as yet why the marked kinetic advantage that positive bromine enjoys over chlorine in the oxidations of B_{12r} by the analogous halic acids ($k_{HBrO_3} = 1 \times 10^6$; $k_{HClO_3} = 4 \times 10^3$ $M^{-1}\ s^{-1}$; 25 °C, $\mu = 0.52$ M)[7c,29] does not extend to the tripositive halogen acids. In effect, our experiments monitor the initial slow step, the reduction of Br(III) to a derivative of Br(II), and neither thermodynamic data nor self-exchange rates appear to have been reported for this conversion in aqueous media. The question is further complicated by evidence[7c] that reactions of B_{12r} with oxyhalogen acids may proceed predominantly via an inner-sphere path, in which case the ease of formation of the respective precursor complexes may enter the picture. Comparisons of the reactivities of these halogen(III) species toward additional metal ion reductants may be instructive.

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(19) (a) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(20) Silverman, J.; Dodson, R. W. *J. Phys. Chem.* **1952**, *56*, 846.

(21) Objections to applying (6) and similar relationships to reactions of Fe^{3+}(aq) with reductants having strongly conjugated ligand systems appear to apply minimally to Fe–Co reactions. See: Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(22) Lexa, D.; Saveant, J.-M. *Acc. Chem. Res.* **1983**, *16*, 235.

(23) Macartney, D. H. *Inorg. Chem.* **1986**, *25*, 2222. This author presents arguments for utilizing the indicated value, calculated from measurements of a series of unequivocal outer-sphere reactions, in preference to a much larger specific rate, measured directly by ^{51}V NMR spectroscopy[24] and presumed to apply to a process that is predominantly inner sphere.

(24) Giuliano, C. R.; McConnell, H. M. *J. Inorg. Nucl. Chem.* **1959**, *9*, 1971.

(25) Although several kinetic studies pertaining to the reactions of bromite have been described,[26] we find no previous report of investigations dealing with reductions by metal ion centers.

(26) See, for example: (a) Engel, P.; Oplatka, A.; Perlmutter-Hayman, B. *J. Am. Chem. Soc.* **1954**, *76*, 2010. (b) Ferranti, F.; Indelli, A. *Can. J. Chem.* **1979**, *57*, 1524. (c) Otero, C.; Rodenas, E.; Cachaza, J. *An. Quim., Ser. A.* **1984**, *80*, 78; *Chem. Abstr.* **1984**, *101*, 90051y.

(27) In addition, we perceive a hint of general-acid catalysis. If $H_2PO_4^-$ is increased from 2 to 10 mM while the pH is kept at 6.47, the rate of the B_{12r}–BrO_2^- reaction increases by 30%. This effect is similar to (but less marked than) those observed[4b] for the B_{12s}–ClO_2^- and B_{12s}–BrO_3^- reactions.

(28) Noyes, R. M. *J. Phys. Chem.* **1986**, *90*, 5407.

(29) As expected, the much more powerful reductant B_{12s} reacts with bromite too rapidly for measurement by our methods. The assigned lower limit for this reaction (25 °C, $\mu = 0.2$ M) is 1.3×10^7 $M^{-1}\ s^{-1}$, at both pH 10 and pH 13 (G.C.P., unpublished experiments, 1987).