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Electron Transfer. 72. Reductions of Oxyhalogens by Vitamin B_{12s} (Cob(I)alamin)[1]

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Vitamin B_{12s} (cob(I)alamin), the Co(I) derivative of vitamin B_{12}, reduces BrO_3^-, IO_3^-, and ClO_2^- to the corresponding halide ions in aqueous media. Specific rates for these reductions increase with acidity (in the pH range 5.2–10.2), and each reaction is subject to general-acid catalysis. Overall rates are determined by the first step in the reduction sequence. The $[H^+]$-proportional kinetic terms are attributed to reaction of the ring-protonated form of B_{12s} with the anionic reductants. Relative reactivities of the protonated and nonprotonated forms of B_{12s} are very nearly the same for the three oxidants. General-acid catalysis (by $H_2PO_4^-$, H_3BO_3, and HCO_3^-) is taken to reflect reaction through complexes in which the catalyzing acid is hydrogen bonded to the imidazole function; in each case, the strongest acid in the trio, $H_2PO_4^-$, is the most effective catalyst. Vitamin B_{12s} reduces ClO_2^- 10^2 times as rapidly as does B_{12r}, its Co(II) analogue, whereas the Marcus model for outer-sphere electron transfer, in conjunction with the 0.78-V difference in the formal potentials of the two reductants, predicts a ratio of at least $10^{6.5}$. This discrepancy suggests that the B_{12r}–ClO_2^- reaction proceeds mainly by an inner-sphere route. Among the points left unresolved are the role of protonation in facilitating the oxidation of B_{12s} and whether the initial attack by Co(I) entails the transfer of one or two electrons.

An earlier study[2] dealt principally with the reduction of oxyhalogen species using cob(II)alamin (B_{12r}), the Co(II) analogue of vitamin B_{12}. It was observed that the reactions of B_{12s}, the corresponding Co(I) analogue, with oxyhalogens (except for ClO_3^-) were too rapid to be followed with ordinary mixing techniques, a finding that was not astonishing in view of the much more negative formal potential of B_{12s}.[3] In the present extension, we have examined the reactions of B_{12s} with the bromate, iodate, and chlorite ions. Measurable rates were obtained by using stopped-flow spectrophotometry and by raising the pH of the media to the range 5–10.5. Our use of buffer systems has led to the inference that these reactions are subject to general-acid catalysis, a conclusion that could not be drawn for the reductions by B_{12r}, which were studied at much higher acidities.

Experimental Section

Materials. Sodium iodate (Baker and Adamson), sodium bromate (Sargent Chemicals), hydroxocobalamin hydrochloride (Sigma), glycine (Aldrich), sodium borohydride (Fisher), and sodium chlorite (Alfa)[4,5] were used as received, as were buffer components (Fisher Chemicals). Lithium perchlorate, for use in kinetic experiments, was prepared as described.[6] All reactions were carried out under N_2 in distilled water that had been previously boiled and purged with N_2 for at least 4 h.

Cob(I)alamin (B_{12s}) was generated in solution from the cobalt(III) complex, hydroxocobalamin hydrochloride, by two methods. The reduction in acidic solutions was carried out with zinc amalgam,[7] whereas reductions in basic solution employed sodium borohydride[8] in the presence of catalytic quantities of $PdCl_4^{2-}$. For stoichiometric experiments, B_{12s} solutions were prepared directly in spectrophotometric cells,[7] whereas, for kinetic runs, solutions of B_{12s} were generated externally and then transferred under N_2 to the reservoir syringe of the stopped-flow instrument.

Table I. Stoichiometries of the Reactions of Vitamin B_{12s} (Cob(I)alamin) with Oxyhalogen Species[a]

oxidant	pH	$10^5 \times [B_{12s}]$, M	$10^5 \times$ [Ox], M	$10^5 \times \Delta[B_{12s}]$, M	$\Delta[B_{12s}]/\Delta$[Ox]
IO_3^-	10.0	6.16	0.54	3.25	6.1
		6.16	0.43	2.43	5.7
		6.16	0.64	3.73	5.8
		4.76	0.43	2.38	5.6
		8.10	0.85	4.82	5.7
	1.4[b]	4.60	0.20	1.25	6.2
		6.00	0.47	2.98	6.3
BrO_3^-	10.0	6.16	0.61	3.85	6.3
		6.16	0.36	2.20	6.0
		6.16	0.54	3.42	6.3
		6.16	0.63	3.37	5.4
	1.4[b]	4.20	0.166	1.02	6.2
		5.94	0.33	1.98	6.0
ClO_2^-	10.0	6.16	0.44	1.81	4.1
		6.16	0.74	3.19	4.3
		6.16	1.34	5.20	3.9
		4.76	0.59	2.53	4.3
	3.0	8.30	0.96	4.20	4.4
		6.20	0.96	4.13	4.3
		6.20	1.11	4.07	3.7
		6.20	0.51	1.83	3.6
		6.20	1.41	4.38	4.0
		4.64	0.48	1.86	3.9

[a] Reactions were monitored at 387 nm. [b] Reference 2.

Stoichiometric Studies. Stoichiometries of the reactions, with the Co^I complex in excess, were determined by adding a measured deficiency of oxidant to the reduced B_{12} solution, waiting 2–5 min, and then measuring the decrease in absorbance at 387 nm. These changes were compared to those observed when B_{12s} was treated with excess oxidant.[9] Representative results appear in Table I.

Kinetic Studies. Rates were estimated from measurements of decreases in absorbance at 387 nm made by using a Durrum-Gibson stopped-flow spectrophotometer. Acidities were regulated by addition of known concentrations of phosphate buffers (Na_2HPO_4 + NaH_2PO_4), bicarbonate buffers (Na_2CO_3 + $NaHCO_3$), or borate buffers (H_3BO_3 + NaOH) to the oxidant solutions before mixing; pH values of the resulting solutions were checked experimentally. Total ionic strength was maintained near 0.50 M by addition of $LiClO_4$. Reactions were first order

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(2) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 3689.

(3) Lexa, D.; Saveant, J.-M. *Acc. Chem. Res.* **1983**, *16*, 235. Formal potentials (vs. NHE) of +0.30 V for B_{12r} and –0.48 V for B_{12s} (pH 1) are listed. Both values are strongly acid dependent.

(4) The purity of this sample of $NaClO_2$, as estimated by the method of Kolthoff,[5] was 78.0%, in agreement with the value of 80% given on the label. Attempted recrystallization did not improve its quality. Since the impurities were taken to be NaCl (which does not react with B_{12s}) and $NaClO_3$ (which reacts much more slowly than $NaClO_2$), this oxidant was used as received and a correction made for the estimated purity.

(5) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. "Quantitative Chemical Analysis", 4th ed.; Collier-Macmillan: Toronto, 1969; p 852.

(6) Dockal, E. R.; Everhart, E. T.; Gould, E. S. *J. Am. Chem. Soc.* **1971**, *92*, 5661.

(7) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 2635.

(8) Kaufmann, E. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 7051. In a typical reaction, the following concentrations were used: $[Co(III)] = 5 \times 10^{-5}$ M; $[BH_4^-] = 1.2 \times 10^{-3}$ M; $[PdCl_4^{2-}] = 6 \times 10^{-6}$ M.

(9) When stoichiometric experiments were performed with cob(I)alamin generated with $NaBH_4$, the initial quick drop in absorbance due to the primary reaction was sometimes followed by a slow rise, probably resulting from partial regeneration of Co(I) by the slight excess of BH_4^- present. This rise, which was more pronounced for experiments with iodate and chlorite than with bromate, did not seriously complicate interpretation of the results.

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each in oxidant B_{12s} but were generally carried out under pseudo-first-order conditions with the oxidant in greater than fivefold excess.[10] Changing the concentration of borohydride (from 4×10^{-4} to 3×10^{-3} M) did not significantly affect the rate of the primary redox reaction.

Conversions were generally followed to at least 5 half-lives. Replicate reactions, with the same pair of master solutions, were carried out until decay curves for three successive runs superimposed. Rate constants, obtained from logarithmic plots of absorbance differences against reaction time, agreed to better than 6% for runs with different master solutions. Kinetic profiles gave no indication of intermediates formed or destroyed on a time scale comparable to that for the measured disappearance of B_{12s}. Moreover, no sharp drop in absorbance occurred immediately after mixing, thus ruling out the rapid formation of a partially reduced halogen species. In all cases, the oxidation of the initial Co(II) product (B_{12r}) to Co(III) was slow enough so that no difficulty was encountered in monitoring the primary reaction.

Results and Discussion

Reactions of IO_3^- and BrO_3^- with excess B_{12s} are seen (Table I) to consume very nearly 6 mol of Co(I), whereas that with ClO_2^- exhibits a 4/1 stoichiometry. All oxidants may then be considered to be reduced cleanly to the 1− state. The straightforward exponential decay curves observed with the oxidant in excess, in conjunction with the absence of an initial sharp drop in absorbance, indicate that the overall rate is being determined by the first step in the reaction sequence, the initial attack on oxyhalogen. It then follows that the oxidants taken are reduced more slowly than any of the halogen oxidation states intervening between 5+ (or 3+) and 1−.

Representative kinetic data, pertaining to the reductions of bromate and iodate, are assembled in Tables II and III. Second-order specific rates (k_{obsd} values) are found to depend not only on pH but also on the concentrations of the buffer acids taken—$H_2PO_4^-$, H_3BO_3, and (in the case of the iodate reduction) HCO_3^-. The reductions are thus subject to general-acid catalysis, and the rate law may then be expressed as shown in eq 1, where

$$\text{rate} = [B_{12s}][Ox](k_0 + k_H[H^+] + k_P[H_2PO_4^-] + k_B[H_3BO_3] + k_C[HCO_3^-]) \quad (1)$$

k_0 denotes the specific rate for the [acid]-independent kinetic component, k_H denotes that for the H^+-catalyzed path, and k_P, k_B, and k_C pertain to the paths catalyzed by $H_2PO_4^-$, H_3BO_3, and HCO_3^-.[11]

A nonlinear least-squares refinement,[12] minimizing the function $(k_{obsd} - k_{calcd})^2$ (where the k's represent second-order specific rates), yields the individual parameters listed in Table IV for oxidations by BrO_3^- and IO_3^-, and the corresponding treatment of chlorite data (which are perceptibly less precise than those for the halates) yields parameters for the B_{12s}–ClO_2^- reaction.

Table II. Representative Kinetic Data for the Oxidation of Vitamin B_{12s} (Cob(I)alamin) with Bromate[a]

pH	[HA], M	[A$^-$], M	k_{obsd}[b]	k_{calcd}[c]
A. Phosphate Buffers: HA = $H_2PO_4^-$; A$^-$ = HPO_4^{2-}				
6.85	0.025	0.050	7.8	8.3
6.85	0.0125	0.025	5.0	4.9
6.85	0.0050	0.010	3.1	2.9
6.85	0.0075	0.0015	1.55	1.73
6.34	0.0050	0.0035	5.0	3.9
5.72	0.0100	0.0020	10.6	9.6
5.23	0.020	0.0015	23	24
B. Borate Buffers: HA = H_3BO_3; A$^-$ = $H_2BO_3^-$				
9.00	0.0025	0.00123	1.09	1.20
9.00	0.010	0.005	1.40	1.44
9.00	0.040	0.020	2.4	2.4
9.0	0.080	0.040	3.7	3.7
10.00	0.0050	0.025	1.14	1.26
8.96	0.0211	0.0089	1.85	1.79
8.30	0.0276	0.0028	2.08	2.01
C. Carbonate Buffers: HA = HCO_3^-; A$^-$ = CO_3^{2-}				
10.25	0.030	0.030	0.95	1.10
10.25	0.0020	0.0020	1.14	1.10

[a] Temperature 22 °C; $\mu = 0.50$ M ($LiClO_4$); $[B_{12s}]_0 = 5 \times 10^{-5}$ M; $[BrO_3^-] = 0.0135$ M. [b] Second-order rate constants (in $M^{-1}\ s^{-1} \times 10^{-3}$) $= -d[B_{12s}]/dt[B_{12s}]^{-1}[BrO_3^-]^{-1}$. [c] Rate constants (in $M^{-1}\ s^{-1} \times 10^{-3}$) calculated from eq 1 with use of the parameters in Table IV.

Table III. Representative Kinetic Data for the Oxidation of Vitamin B_{12s} (Cob(I)alamin) with Iodate[a]

pH	[HA], M	[A$^-$], M	k_{obsd}[b]	k_{calcd}[b]
A. Phosphate Buffers: HA = $H_2PO_4^-$; A$^-$ = HPO_4^{2-}				
6.85	0.025	0.050	4.4	4.5
6.85	0.0050	0.10	1.27	1.34
6.85	0.00075	0.0015	0.56	0.67
6.34	0.0050	0.0035	1.53	1.58
5.72	0.010	0.0020	3.5	3.5
B. Borate Buffers: HA = H_3BO_3; A$^-$ = $H_2BO_3^-$				
9.00	0.0025	0.00123	0.58	0.48
9.00	0.010	0.0050	0.63	0.60
9.00	0.040	0.020	1.14	1.09
9.00	0.080	0.040	1.60	1.74
8.60	0.025	0.0049	0.87	0.85
9.11	0.0155	0.0145	0.70	0.69
10.00	0.0050	0.025	0.42	0.52
C. Carbonate Buffers: HA = HCO_3^-; A$^-$ = CO_3^{2-}				
10.25	0.060	0.060	1.18	1.17
10.25	0.030	0.030	0.81	0.81
10.25	0.0075	0.0075	0.50	0.53

[a] Temperature 22 °C; $\mu = 0.50$ M ($LiClO_4$); $[B_{12s}]_0 = 5 \times 10^{-5}$ M; $[IO_3^-] = 1.1 \times 10^{-4}$ to 2.3×10^{-4} M. [b] Second-order rate constants (in $M^{-1}\ s^{-1} \times 10^{-6}$) (see Table II). [c] Specific rates (in $M^{-1}\ s^{-1} \times 10^{-6}$) calculated from eq 1 with use of parameters in Table IV.

The principal species present in the solutions at hand are the deprotonated (uninegative) form of B_{12s} (the conjugate acid of which exhibits a pK_A value of 4.7)[3] and the anionic forms of the oxidant.[13,14] The k_0 terms in Table IV may then be taken to apply simply to the bimolecular reaction between the two deprotonated anions.

The k_H term in the rate law pertains to a path proceeding through a transition state consisting of the principal oxidant and reductant species plus an additional proton. Analogous kinetic terms observed for reductions of oxyhalogens by cob(II)alamin at lower pH's have been attributed[2] to reactions of the protonated oxidants ($HBrO_3$, HIO_3, and $HClO_2$), but this cannot be the predominant path here, for such an assignment would require

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(10) Possible experimental ambiguity in these systems resulted from the reaction of traces of O_2 upon mixing of the reactant with the coreagent solution. For example, in the absence of oxyhalogen species, relatively shallow decay curves having half-life periods near 50 ms were observed at pH 6.1 and curves with $t_{1/2}$ near 2 s were noted at pH 8.0. Concentrations of the oxidant were therefore adjusted so that the primary reactions were much more rapid than these, and the order in oxidant was checked. The procedures described were not applicable to the study of B_{12s} with the more slowly reacting chlorate; severe distortion of the kinetic curves resulting from release of hydrogen bubbles (formed from the reaction of BH_4^- with $H_2PO_4^-$) was encountered.

(11) It is assumed that catalysis by HPO_4^{2-} is negligible in comparison to that by $H_2PO_4^-$, which is a much stronger acid.

(12) Plots of k_{obsd} vs. the concentration of the buffering acid, HA, at constant values of the ratio [HA]/[A$^-$] gave, as slopes, trial values of k_P, k_B, and k_C used in these refinements. Values of the intercepts, when plotted against [H$^+$], gave trial values of k_0 and k_H. Individual data points were weighted in inverse proportion to k_{obsd}. The refinements converged after three cycles. Tables II and III compare observed rates with those calculated by the rate law (1).

(13) Reported pK_A values for HIO_3, $HBrO_3$, and $HClO_2$ are, respectively, 0.5,[14a] −2.3,[14b] and 1.66.[14c]

(14) (a) Naiditch, S.; Ricci, J. F. *J. Am. Chem. Soc.* **1939**, *61*, 3268. The value recorded by these workers (0.79 at $\mu = 0$ M) has been adjusted to $\mu = 0.5$ *M*. (b) Choppin, G. R.; Ensor, D. D. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1226. (c) Smith, R. M.; Martell, A. E. "Critical Stability Constants"; Plenum Press: New York, 1976; Vol. 4, p 134.

Table IV. Kinetic Parameters for the Oxidations of Vitamin B_{12s} (Cob(I)alamin) with Oxyhalogen Species[a]

oxidant	k_0[b]	k_H[c]	k_P[d]	k_B[d]	k_C[d]
IO_3^-	$(4.4 \pm 0.4) \times 10^5$	$(7.5 \pm 1.4) \times 10^{11}$	$(1.58 \pm 0.11) \times 10^8$	$(1.63 \pm 0.18) \times 10^7$	$(1.22 \pm 0.21) \times 10^7$
BrO_3^-	$(1.11 \pm 0.12) \times 10^3$	$(3.0 \pm 0.2) \times 10^9$	$(2.7 \pm 0.2) \times 10^5$	$(3.2 \pm 0.5) \times 10^4$	not obsd
ClO_2^-	$(5.1 \pm 0.6) \times 10^4$	$(1.05 \pm 0.06) \times 10^{11}$	$(3.8 \pm 0.7) \times 10^6$	$(2.4 \pm 1.8) \times 10^5$	not obsd
ClO_3^-[e]	81	7.3×10^4			

[a] Reactions at 22 °C; $\mu = 0.5$ M ($LiClO_4$). [b] Specific rate for the acid-independent path ($M^{-1}\ s^{-1}$). [c] Specific rate for the H^+-catalyzed path ($M^{2-}\ s^{-1}$). [d] Termolecular specific rates for paths catalyzed by $H_2PO_4^-$, H_3PO_3, and HCO_3^- ($M^{2-}\ s^{-1}$). [e] Reactions at 25 °C (see ref 2).

Table V. Comparison of Specific Rates for Oxidation of the Protonated and Deprotonated Forms of Vitamin B_{12s} (Cob(I)alamin)[a]

oxidant	k_{BH}[b]	k_{BH}/k_0[c]
IO_3^-	1.5×10^7	37
BrO_3^-	6.0×10^4	60
ClO_2^-	2.1×10^6	42

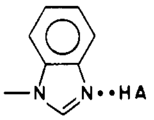
[a] Reactions at 22 °C; $\mu = 0.5$ M ($LiClO_4$). [b] Bimolecular specific rates ($M^{-1}\ s^{-1}$) for oxidation of the acidic (N-protonated) form of B_{12s}, Co^IH, calculated by dividing k_H (Table IV) by K_A (2.0×10^{-5}) for B_{12s}. [c] Ratio of k_{BH} to the specific rate for the acid-independent path (k_0 in Table IV).

bimolecular specific rates approaching and, in the case of $HBrO_3$ and HIO_3, greatly exceeding the diffusion-controlled limit in aqueous media.[15] It appears instead that it is the reductant that is undergoing protonation (at the benzimidazole nitrogen):

$$Co(I)^- \underset{pK_A\ 4.7}{\overset{H^+}{\rightleftharpoons}} Co^IH \xrightarrow[k_{BH}]{Ox^-} \text{products} \qquad (2)$$

Calculated bimolecular rate constants (k_{BH} values) for oxidations of the ring-protonated form of the reductant (Co^IH) are compared to those for oxidation of the deprotonated form (k_0) in Table V. The near constancy of the ratio k_{BH}/k_0 tends to confirm our suggestion that the protonation equilibrium applies to the reductant. Moreover, it is consistent, according to the model of Marcus,[16] with the predominance of the outer-sphere mechanism throughout the series, although it does not demand this.[17]

Additional catalysis by the weak acids $H_2PO_4^-$ (pK_A 7.1), H_3BO_3 (pK_A 9.2), and (for the iodate reaction) HCO_3^- (pK_A 10.4) points to the operation of reaction paths through complexes in which the catalyzing acid is hydrogen bonded to the imidazole function in B_{12s} (I) with only partial proton transfer. As expected,



I

the strongest acid in this group is, for each oxidation, the most effective catalyst.[18,19]

The rate constant for oxidation of the protonated B_{12s} by ClO_2^- may be compared with that for the corresponding oxidation of the protonated cobalt(II) species B_{12r} ($2.1 \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C).[2,20] The ratio of the two specific rates is 1×10^2, whereas the difference in formal potentials of the two reductants, 0.78 V,[3] corresponds, by the Marcus–Hush treatment,[16,21] to a $10^{6.5}$-fold difference. The departure from the outer-sphere model[22] is thus in the direction suggesting a predominant inner-sphere component[17] for reduction by B_{12r}, a conclusion similar to that already drawn for reduction of ClO_3^-.[2]

The present study leaves several points unresolved. For example, we cannot account, even in a qualitative fashion, for the reversal in relative reactivities of Br(V) and I(V) when the reductant is changed from B_{12r} (which reduces BrO_3^- much more rapidly)[2] to B_{12s} (which reduces IO_3^- much more rapidly). In experiments with B_{12r}, measured rates pertained to the initial slow step, the reduction of pentapositive to tetrapositive halogen. Hence, any analysis of trends should take into account the properties of the latter state and their possible variation with acidity. Although there is evidence that Br(IV) and I(IV) intervene in other halate reductions,[23] thermodynamic data concerning these states are lacking. The problem is further complicated by inclusion of B_{12s} reactions, for there is no certainty (see below) that the latter reductant is acting as a single electron donor in our systems.

A second, more puzzling, question pertains to the role of protonation in facilitating the oxidation of B_{12s} in the reactions at hand, for in the vast majority of more familiar cases, protonation of a reductant lowers its reducing potential. It may be that we are seeing the results of an alteration in conformation of B_{12s}. Although cobalt(I) is predominantly 4-coordinate,[24] some dipole–dipole attraction may hold the benzimidazole nitrogen near, but not bonded to, the coordination center in the basic form. Protonation of the nitrogen of the heterocyclic ring should eliminate or reverse this attraction and increase the accessibility of the reducing site.

Finally, we cannot say, on the basis of the present observations, whether B_{12s} is reacting as a 1- or 2e donor, an important mechanistic ambiguity associated also with earlier studies of reductions by cob(I)alamin.[2,7,25] Although a single electron transaction analogous to that occurring with B_{12r} is conceivable[26] and is consistent with the observed formation of the cobalt(II) product, there is also the possibility that these reactions are in-

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(15) Bimolecular specific rates for proposed paths involving the protonated oxidants may be calculated by multiplying the recorded k_H values by the acidity constants for the halic acids. The resulting products are $6 \times 10^{11}\ M^{-1}\ s^{-1}$ for $HBrO_3$, $2.3 \times 10^{11}\ M^{-1}\ s^{-1}$ for HIO_3, and $2 \times 10^9\ M^{-1}\ s^{-1}$ for $HClO_2$. The diffusion-controlled limit for reactions of this type in solution may be estimated as $6 \times 10^9\ M^{-1}\ s^{-1}$. (See, for example: Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, 1981; p 169.)

(16) (a) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 653. (b) *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(17) Gould, E. S. *Inorg. Chem.* **1979**, *18*, 900.

(18) A log–log plot (three points) of the *k* values for general-acid catalysis of the B_{12s}–IO_3^- reaction (Table IV) vs. the acidity constants for the catalyzing acids (suitably corrected for statistical factors)[19] is close to linear with a slope (Brønsted coefficient) of 0.33.

(19) See, for example: Bell, R. P. "The Proton in Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 197.

(20) The present B_{12s}–ClO_2^- experiments deal with solutions of pH 6.2–10.2, whereas the earlier B_{12r} study[2] embraced the pH range 2.4–3.7. Reflecting the differences in predominant B_{12} species in the two acidity ranges, the reaction of protonated B_{12s} generates a $[H^+]$-proportional kinetic term, whereas that of protonated B_{12r} generated an $[H^+]$-independent term. Similar comparisons cannot be made with the B_{12r}–BrO_3^- and B_{12r}–IO_3^- reactions, neither of which exhibited an [acid]-independent kinetic term.

(21) It is assumed here that an increase in ΔG^* resulting from an increase in the standard potential of the reductant is half the increase in $\Delta G°$. (See, for example: Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.)

(22) Note also that Lexa[3] has presented data showing that electron self-exchange in the Co(I)–Co(II) corrin system is more rapid than that in the Co(II)–Co(III) system, a difference that should further favor reduction by B_{12s}.

(23) See, for example: (a) Birk, J. P.; Kozub, S. G. *Inorg. Chem.* **1973**, *12*, 2460. (b) Bakac, A.; Thornton, A. T.; Sykes, A. G. *Ibid.* **1976**, *15*, 274. (c) Furrow, S. D.; Noyes, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 42. (d) DeKepper, P.; Epstein, I. R. *Ibid.* **1982**, *104*, 49. (e) Cooke, D. O. *J. Chem. Soc., Chem. Commun.* **1984**, *589*.

(24) Kaufmann and Espenson[8] have presented arguments that benzimidazole-bound (5-coordinate) B_{12s} can constitute only a minor fraction of total cob(I)alamin in aqueous solution.

(25) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 824.

(26) If these reactions are outer sphere (as the nearly constant k_{BH}/k_0 ratios in Table V hint, but do not prove), they would necessarily be single-electron transactions. No convincing report of outer-sphere transfers of more than one electron has yet appeared.

itiated by a change of two electrons, forming B_{12a} (the cobalt(III) analogue of B_{12s}), which has been shown[27] to undergo rapid comproportionation (eq 4). Previous examinations of B_{12s} re-

$$Co^{I}-H + IO_3^- \rightarrow [H-Co^{I}-O-IO_2] \rightarrow Co^{III}-OH + IO_2^- \quad (3)$$

$$Co^{III}-OH + Co^{I}-H \rightarrow 2Co^{II}-OH_2 \text{ (rapid)} \quad (4)$$

actions[7,28] appear to favor 2e initiation, whereas studies of halate reductions by metal center reductants that can partake in either 1- or 2e changes demonstrate the feasibility of a series of single-electron transfers.[23b,29] Resolution of this matter awaits further study.

Registry No. BrO_3^-, 15541-45-4; IO_3^-, 15454-31-6; ClO_2^-, 14998-27-7; $H_2PO_4^-$, 14066-20-7; H_3BO_3, 10043-35-3; HCO_3^-, 71-52-3; B_{12s}, 18534-66-2.

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A High-Valent Ruthenium(VI) Dioxo Cation of 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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A high-valent *trans*-$[Ru(TMC)O_2]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) cation has been produced from *trans*-$[Ru(TMC)Cl_2]^+$ through H_2O_2 oxidation. This novel diamagnetic ruthenium(VI) dioxo species has been subjected to detailed spectroscopic and electrochemical characterization. The UV–vis absorption spectra of *trans*-$[Ru(TMC)O_2]^{2+}$ and the previously reported *trans*-$[Ru(NH_3)_4O_2]^{2+}$ exhibit a weak vibronic structured absorption band at ~390 nm. Cyclic voltammetric and controlled-potential coulometric experiments showed that the reduction of *trans*-$[Ru(TMC)O_2]^{2+}$ to *trans*-$[Ru(TMC)O(H_2O)]^{2+}$ proceeded by a single-step two-electron-transfer process.

Introduction

The chemistry of high-valent ruthenium(IV) oxo amine complexes has received much attention in recent years.[1] However, there have been relatively few reports on high-valent ruthenium(VI) oxo species[2] despite the fact that *trans*-dioxoosmium(VI) species have been known for more than 1 decade. We have recently found that H_2O_2 oxidation of an aqueous solution of *trans*-$[Ru(TMC)Cl_2]Cl$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) led to the formation of a yellow solid that we previously formulated as $[Ru(TMC)O(H_2O)](ClO_4)_2$.[3] Here, we would like to report the preparation, together with the spectroscopic and electrochemical characterization, of this high-valent ruthenyl ion. Our work clearly indicates that the previously reported $[Ru(TMC)O(H_2O)]^{2+}$ is best formulated *trans*-$[Ru^{VI}(TMC)O_2]^{2+}$.

Experimental Section

$K_2[RuCl_5H_2O]$ (Johnson and Matthey) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) (Strem) were used as supplied. All chemicals and solvents used were of analytical grade.

***trans*-$[Ru(TMC)O_2](Y)_2$ (Y = ClO_4, PF_6).** *trans*-$[Ru(TMC)Cl_2]Cl$[4] (0.3 g) and silver toluene-*p*-sulfonate (0.54 g) in deionized water (25 mL) were heated on a steam bath for 1/2 h. The resulting yellow solution (sometimes appeared as brownish yellow) was filtered off to remove the insoluble silver(I) chloride. H_2O_2 (3 mL; 30%) was slowly added to the filtrate that was then heated on a steam bath for about 5 min. The course of the reaction was followed by monitoring the UV–vis spectral changes of the solution. When the vibronic structured absorption band at ~390 nm had fully developed in 5–10 min, a saturated aqueous solution of $NaPF_6$ (5 mL) was added. Upon cooling, a yellow microcrystalline solid of *trans*-$[Ru(TMC)O_2]PF_6$ slowly deposited. This was then filtered off, washed with a diethyl ether/acetone mixture (10:1) and dried under vacuum at room temperature. Analytically pure samples of *trans*-$[Ru(TMC)O_2](PF_6)_2$ could be obtained by dissolving the crude yellow solid in acetone, filtering if necessary, followed by the subsequent addition of diethyl ether. The perchlorate salt was similarly prepared with $NaClO_4$ instead of $NaPF_6$. Yields were usually greater than 60%. Anal. Calcd for *trans*-$[Ru(TMC)O_2](ClO_4)_2$: C, 28.57; H, 5.44; N, 9.52; Cl, 12.0. Found: C, 28.60; H, 5.40; N, 9.60; Cl, 12.10. IR (Nujol mull): $\nu(Ru{=}O)$ 855 cm^{-1}. μ_{eff} ~0 μ_B at 25 °C. Λ_M for *trans*-$[Ru(TMC)O_2](PF_6)_2$ in H_2O 256 $\Omega^{-1}\ cm^2\ mol^{-1}$ at 20 °C. UV–vis spectral data [λ_{max}, nm (ϵ)] in H_2O: ~445 (sh) (50), 388 (560), ~305 (sh) (960), 256 (1.03×10^4), 225 (1.28×10^4).

***trans*-$[Ru(NH_3)_4O_2]Cl_2$.** This complex was prepared by the method of Griffith and his co-workers.[2] Hydrated ruthenium hydroxide was prepared by the hydrolysis of $RuCl_3{\cdot}xH_2O$ in 0.1 M NaOH. The complex has been found to be unstable upon exposure to moisture. IR (Nujol mull): $\nu(Ru{=}O)$ 845 cm^{-1}. UV–vis spectral data [λ_{max}, nm (ϵ_{max})] in 1 M $HClO_4$: ~450 sh (~40), 390 (~800), 300 (~800), 255 (br) (~10^4), 210 (~5×10^3).

Physical Measurements. Elemental analyses of the newly prepared complexes were performed by the Australian National Laboratory. IR spectra were measured in Nujol mulls on a Perkin-Elmer 577 spectrophotometer (4000–200 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. Magnetic susceptibilities of solid samples were measured by the Guoy method using mercury tetrakis(thiocyanato)cobaltate(II) as the calibrant. ^1H NMR spectra were measured in D_2O or acetonitrile with a JEOL FX90Q Fourier transform NMR spectrometer. Tetramethylsilane was used as the internal standard.

Cyclic voltammograms were obtained with Princeton Applied Research (PAR) instruments: Model 175 (Universal Programmer); Model 173 (potentiostat-galvanostat). Pyrolytic graphite and glassy-carbon electrodes were used as appropriate as the working electrode. The reaction cell was a standard PAR Model K64 three-electrode jacketed polarographic cell that was maintained at ±0.1 °C by thermostated water. Cyclic voltammograms were recorded with a Houston Model 2000 X-Y recorder at slow scan rates (<1 V s^{-1}) and with a Tektronix Model 5103N storage oscilloscope at high scan rates (1 V s^{-1}). Controlled-potential coulometric electrolysis was carried out with a PAR Model 9610 coulometric cell system that was supplied with a PAR Model 377 synchronous stirring motor. A platinum-wire-gauze electrode was

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