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Registry No. **1**, 68307-35-7; **2**, 68307-37-9; **3**, 68307-39-1; $[Ni(P\text{-}SEt)_2](BF_4)_2$, 68307-40-4; $Ni(P\text{-}SEt)_2$, 68307-41-5; $[Ni(CN)(P\text{-}SEt)_2]BF_4$, 68307-42-6; 1-pentene, 109-67-1.

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(17) P. Rigo, unpublished results.

Contribution from the Chemistry Division,
Argonne National Laboratory, Argonne, Illinois 60439,
and the Ames Laboratory and Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Pulse Radiolytic Study of the Oxidation of Vitamin B_{12r} by Dibromide Ions[1a]

Dan Meyerstein,[1b,c] James H. Espenson,*[1d] Debra Ann Ryan,[1d] and William A. Mulac[1b]

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Bromine oxidizes one-equivalent reducing agents such as divalent metal complexes in general[2,3] and Co(II) complexes including vitamin B_{12r}[2] in particular to the trivalent state in a noncomplementary fashion, the net process consuming 2 mol of M(II)/mol of bromine. The rate equation for a large number of complexes shows a first-order dependence on both reducing agent and bromine, consistent with an initial one-equivalent process.

Detailed mechanisms for the first and rate-limiting step have been considered;[2,3] it is likely[4] that the dibromide ion $Br_2^-\cdot$ is formed in this step (or immediately thereafter).

$$M^{II} + Br_2 \rightarrow Br_2^-\cdot + M^{III} \quad (\text{or } Br\cdot + Br\text{–}M^{III}) \qquad (1)$$

We have undertaken for the system M^{II} = Co^{II}(corrin) or vitamin B_{12r} a study of the requisite second major reaction, that by which $Br_2^-\cdot$ is consumed, a process necessarily very rapid compared to the first. Margerum[3] points out two plausible sequences which can be invoked to complete the overall reaction, both consistent with the data at hand.

These alternatives consist of direct oxidation, whether by an inner-sphere or outer-sphere mechanism (eq 2), and of

$$Br_2^-\cdot + M^{II} \rightarrow Br^- + Br\text{–}M^{III} \quad (\text{or } Br^- + M^{III}) \qquad (2)$$

$$Br_2^-\cdot + Br_2^-\cdot \rightarrow Br_2 + 2Br^- \qquad (3)$$

dibromide disproportionation (eq 3). The present work seeks to resolve these possibilities for the oxidation of vitamin B_{12r}.

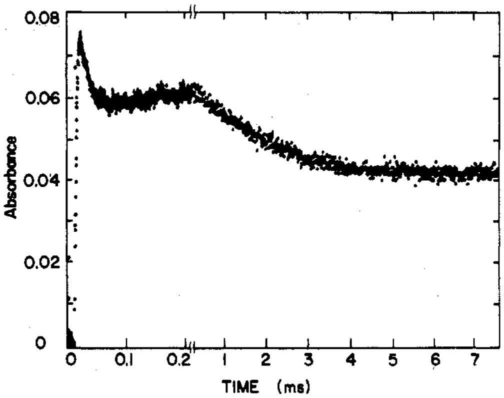


Figure 1. Kinetic data from a pulse radiolysis experiment showing the change in absorbance (optical path 2 cm) at 365 nm with time in a run with $[B_{12r}]_0$ = 15 μM and $[Br^-]$ = 11 mM. The initial rapid decrease corresponds to the reaction of dibromide ion (eq 4), the small increase to eq 7, and the final, slower decrease to aquation of bromocobalamin, eq 5.

Table I. Kinetic Data Reactions of $Br_2^-\cdot$ with Vitamin B_{12r}[a]

conditions			$Br_2^-\cdot$ + [Co(II)] $10^{-9}k_4$/ dm^3 mol^{-1} s^{-1}		Br–[Co(III)] aquation $10^{-2}k_d$/ s^{-1} [b]
10^5 × $[B_{12r}]_0$/M	$[Br^-]$/M	λ/nm		second k/s^{-1}	
1.5	0.011	365	2.8		6.2
		380	3.7		5.4
3.0	0.010	350	4.5	~5 × 10^3	
		365	3.8		7.2
		365	3.7		7.9
3.0	0.011	365		1.9 × 10^4	6.0
		380	3.0		5.4
3.0	0.11	365		2.4 × 10^4	6.6
		380	2.4		6.9

[a] At T = 22 ± 1 °C, μ = $[Br^-]$ in solutions saturated with N_2O at pH ~4.5. [b] From eq 6 with K_5 = 1.8 M^{-1}.

Results and Discussion

Pulse radiolysis of solutions of sodium bromide saturated with N_2O produces[6] the dibromide ion $Br_2^-\cdot$, which in the absence of oxidizable substrate disappears by disproportionation[6] ($2k_3 = 3.3 \times 10^9$ dm^3 mol^{-1} s^{-1}). We find that with B_{12r} present at pH 4.5, the rate of disappearance of the absorption due to $Br_2^-\cdot$ (ϵ_{365} 7800 ± 200 dm^3 mol^{-1} cm^{-1})[6] is accelerated while a new absorption at λ 365 nm of an unstable intermediate appears. After two further steps a permanent absorption spectrum due to stable products (vitamin B_{12a}, aquocobalamin) is observed.

The timed sequence of three successive changes at 365 nm is shown in Figure 1. The first reaction occurring is

$$Br_2^-\cdot + [Co(II)] \rightarrow Br^- + Br\text{–}[Co(III)] \qquad (4)$$

The kinetics of this first step were evaluated from runs in which B_{12r} was varied in the range (1.5–3.0) × 10^{-5} M; the best data were obtained at 380 nm with other runs at 350 and 365 nm. The data correspond to half-times between 3.4 and 14 μs; the results are summarized in Table I and give k_4 = (3.4 ± 0.6) × 10^9 dm^3 mol^{-1} s^{-1}.

The final reaction stage with $t_{1/2}$ ~ 1 ms corresponds to the much slower aquation of bromocobalamin, reaction 5,

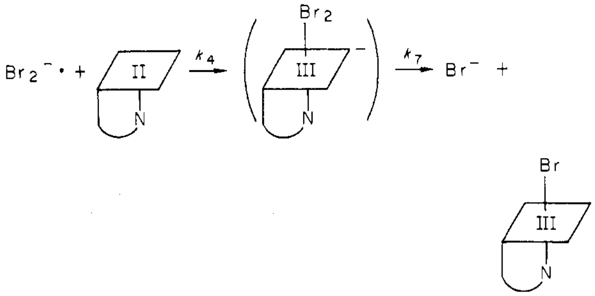
$$(H_2O)\text{–}[Co(III)]^+ + Br^- \underset{d}{\overset{f}{\rightleftarrows}} Br[Co(III)] + H_2O \qquad (5)$$

for which Thusius[7] has reported kinetic and thermodynamic data. Since the formation constant for bromocobalamin is relatively small, $K_5 = 1.8$ M^{-1}, its aquation is nearly complete at the bromide ion concentrations used in this work, 0.01–0.11 M Br$^-$. Correcting for the residual amount of Br–[Co(III)], only 20% at the highest [Br$^-$], permits k_d to be calculated from the observed rate constant.

$$k_d = k_{obsd}/(1 + K_5[Br^-]) \tag{6}$$

The mean value is $k_d = (6.4 \pm 0.7) \times 10^2$ s^{-1} (22 ± 2 °C, μ = [Br$^-$] = 0.01–0.11 M). Thusius reports $k_d = 5.9 \times 10^2$ s^{-1} (26 ± 1 °C, μ = 1.0 M). The absorbance decrease accompanying this reaction is consistent with that expected for reaction 5.

Between reactions 4 and 5 there can be seen a barely discernible spectral change, a slight rise in absorbance at 365 nm with $k \sim (1 \pm 1) \times 10^4$ s^{-1}. The effect appears reproducible but it is sufficiently small in magnitude, only some 10% of the change for reaction 5 at 365 nm, that it remains of uncertain origin. One possibility is that it might arise from dissociation of Br$^-$ from the dibromide adduct[8] of [Co(III)], which one might envisage to be the primary product of reaction 4.



(7)

The conclusions from this study are the following: (a) the reaction of Br$_2^-$· with B$_{12r}$ proceeds by an inner-sphere mechanism, as has been established also by direct observation for some M(II) complexes including Fe$^{2+}_{aq}$,[10] Cr$^{2+}_{aq}$,[10] Co^{II}NTA,[11] Mn^{II}NTA,[11] Ni^{II}([14]4,11-dieneN$_4$)$^{2+}$,[9] and Co^{II}([14]4,11-dieneN$_4$)$^{2+}$ [12] and inferred for others;[2,3,13] (b) the rate constants and concentrations are such that the reaction of B$_{12r}$ with Br$_2$ has as its second step reaction 4 rather than reaction 3 (at typical concentrations, ~99.7% of the Br$_2^-$· produced reacts by eq 4, 0.3% by eq 3); and (c) the aquation rate of bromocob(III)alamin can be verified by a completely independent method.

Experimental Section

Solutions of vitamin B$_{12r}$ were prepared by hydrogen reduction of B$_{12a}$ over Adams' catalyst.[14] Solutions for pulse radiolysis contained the desired concentration of B$_{12r}$ (15–60 μmol dm^{-3}) and sodium bromide (0.01–0.11 M) in water and were saturated with nitrous oxide. The pulse duration was 4 ns. Data were collected and analyzed using equipment at Argonne National Laboratory, which has been described.[15]

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Registry No. Vitamin B$_{12r}$, 14463-33-3; Br$_2^-$·, 12595-70-9.

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Contribution from the Department of Chemistry and the
Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19104

Synthesis of Two New Cobaltaborane Complexes: 1-(η-C_5H_5)CoB_5H_9 and 2-(η-C_5H_5)CoB_9H_{13}

Robert Wilczynski and Larry G. Sneddon*

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Recent advances in metalloborane chemistry continue to demonstrate the close electronic and structural relationships between traditional organometallic complexes and boron cage compounds. In this paper, we report that the direct reaction of pentaborane(9) and (η-C$_5$H$_5$)Co(CO)$_2$ using hot/cold reaction techniques results in the formation of two new cobaltaborane complexes, 1-(η-C$_5$H$_5$)CoB$_5$H$_9$ and 2-(η-C$_5$H$_5$)CoB$_9$H$_{13}$. The new sandwich complex 1-(η-C$_5$H$_5$)CoB$_5$H$_9$ provides an additional bridge between the two areas of chemistry indicated above, since it is isoelectronic with ferrocene and is shown to exhibit a dynamic behavior which suggests that it is a close structural analogue of hexaborane(10).

Experimental Section

Materials. Cyclopentadienylcobalt dicarbonyl, (η-C$_5$H$_5$)Co(CO)$_2$, was obtained from Strem Chemicals and vacuum distilled before use. Pentaborane(9) was obtained from laboratory stock. All solvents were reagent grade and used without further purification. Preparative thin layer chromatography was conducted on 0.5 mm (20 × 20 cm) silica gel F-254 plates (Merck). Column chromatography was performed on silica gel (Merck, 70–270 mesh).

Physical Measurements. Boron-11 NMR spectra at 32.1 MHz and proton NMR spectra at 100 MHz were obtained on a JEOL PS-100 pulse Fourier transform spectrometer equipped with the appropriate decoupling accessories. High- and low-resolution mass spectra were recorded on either an AEI MS-902 spectrometer located at the University of Virginia or a Perkin-Elmer Hitachi RMH-2 spectrometer. Infrared spectra were obtained on a Perkin-Elmer 521 spectrophotometer.

General Procedure. All reactions were run in a hot/cold reactor which consisted of an evacuated, cylindrical, quartz tube (30 mm diameter × 30 cm) equipped with a greaseless Teflon stopcock. During a reaction the tube was maintained in a vertical position and its central portion heated by a Variac-controlled heating tape, while the lower section was cooled with an appropriate bath.

In a typical reaction, 3 mmol of (η-C$_5$H$_5$)Co(CO)$_2$ and 5 mmol of B$_5$H$_9$ were vacuum distilled into the reactor which was then maintained at 225 °C/75 °C for 1 day with frequent interruptions for removal of the generated carbon monoxide. The reactor was then