chemistry of dimetal species that contain metal-metal multiple bonds. The reactions of other complexes of this type, viz., $Re_2Br_4(dppm)_2$, $Mo_2Cl_4(dppm)_2$, and $W_2Cl_4(dppm)_2$, with CO and RNC ligands are currently under investigation.

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Supplementary Material Available: Tables of bond distances and bond angles; anisotropic thermal parameters; hydrogen atom positional parameters; and observed and calculated structure factors for $Re_2Cl_4(dppm)_2(CO)_2$ (20 pages). Ordering information is given on any current masthead page.

Homolysis and Electron-Transfer Reactions of Benzylcobalamin

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Abstract: The rate constants have been evaluated for decomposition of the benzylcobalamin species present in acetate buffers ($PhCH_2[Co]$) and in dilute perchloric acid ($PhCH_2[Co]\cdot H^+$) in the presence of oxygen, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (4-HTMPO), and iron(III). Many of these reactions are governed by the initial and rate-limiting homolytic cleavage of the cobalt-carbon bond. In the case of 4-HTMPO, the kinetic inhibition by vitamin B_{12r}($[Co^{II}]$), together with the equilibrium constant for benzyl transfer between benzylcobalamin and pentaaquobenzylchromium(2+), permits the evaluation (±20%) of these rate constants: $[Co^{II}]\cdot H^+ + PhCH_2\cdot$ ($k = 3.5 \times 10^8\ M^{-1}\ s^{-1}$) and 4-HTMPO + $PhCH_2\cdot$ ($k = 5.4 \times 10^7\ M^{-1}\ s^{-1}$). In addition to homolysis, $PhCH_2[Co]\cdot H^+$ reacts with Fe^{3+} by a direct oxidative pathway. The rate varies with $[Fe^{3+}]$ and $[H^+]$ consistent with rate-limiting internal electron transfer within a binuclear complex. A three-component mixture of $PhCH_2[Co]\cdot H^+$, O_2, and ascorbic acid activates O_2 for oxidation of ascorbic acid via binding of O_2 to the base-off form of benzylcobalamin.

Considerable interest has been focused on the reactions of Co-C bonds in organocobalt compounds, especially derivatives of vitamin B_{12} and model complexes. This includes questions of the Co-C bond strength, evaluated from thermodynamic cycles and from kinetic measurements.[1-6] The latter assignments depend strongly on the differentiation between authentic unimolecular homolysis reactions and various types of bimolecular attack processes. This distinction can be ambiguous, particularly if only oxygen is used as the reagent intended to draw homolysis to completion, since certain chain mechanisms for many O_2 reactions can show a zeroth-order dependence on $[O_2]$ and yet involve a mechanism with steps other than homolytic cobalt-carbon bond cleavage.[7] That is one of the issues addressed in this study.

Until recently, certain unknown organocobalamins were thought incapable of isolation owing to steric constraints imposed by the corrin ring. Even benzylcobalamin, where electronic effects should dominate, was unknown. Several compounds, including benzylcobalamin, have recently been prepared.[8] This requires carefully chosen experimental conditions, especially a sufficiently high $[H_3O^+]$ to ensure formation of the base-off complex, a more stable form. They owe their existence to the flexibility of the corrin ring, which adopts a "downward" distorted configuration in response to the steric and electronic demands of the cobalt-alkyl interaction.[8] This in turn promotes the rupture of the bond between cobalt and the axial base, 5,6-dimethylbenzimidazole. Thus, the secondary alkylcobalamins exist primarily in the "base-off" form, and the less sterically strained benzylcobalamin exists as a pH-dependent mixture of the two.[9]

In part, this work concerns the reaction of benzylcobalamin with oxygen and its relation to unimolecular homolysis. The original report of the oxygen reaction[9] concluded that it proceeded by unimolecular homolysis but was based upon evidence we consider to be indicative but not definitive. As it so happens, that assignment has been substantiated by the more detailed results reported here. We have in addition found that benzylcobalamin undergoes oxidative cleavage by reaction with iron(III) ions, that it equilibrates the benzyl group between itself and chromium(II) ions, and that it activates O_2 for oxidation of ascorbic acid.

Results and Interpretation

Homolysis. The decomposition of benzylcobalamin in the presence of oxygen follows first-order kinetics. When conditions chosen were the same as employed previously,[9] the values agreed well (Table I). The rate constants are independent of $[O_2]$ (0.3-1.2 mM, air-saturated and oxygen-saturated solution). This was true for both species of benzylcobalamin—$PhCH_2[Co]$, the more reactive base-on form existing in buffer solutions (e.g., 0.1 M acetate buffer at pH 5.5 and 1 M phosphate buffer) as well as $PhCH_2[Co]\cdot H^+$, the longer-lived base-off form present at lower pH (e.g., in 1 M H_3PO_4 and in $HClO_4/LiClO_4$ solutions).

Three kinetic tests must be satisfied for the observed rate of aerobic decomposition really to correspond to the rate of homolysis. The first-order rate constant must be independent of the concentration of radical scavenger, it must be the same when different scavengers are used, and it must decrease with addition of one homolysis fragment (in this case, $[Co^{II}]$), as the radical-cobalt

[†] Henry Gilman Fellow, Iowa State University, 1983-1984.

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(7) See, for example, Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 704.
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Table I. Rate Constants for the Unimolecular Homolysis of Base-On and Base-Off Forms of Benzylcobalamin

conditions	temp, °C	scavenger	k, s^{-1}	ref
		1. Base-On $PhCH_2B_{12}$		
1 M phosphate buffer, pH ?	24	air and O_2	$(2.30 \pm 0.18) \times 10^{-3}$	*a*
			2.3×10^{-3}	*b*
0.1 M acetate buffer, pH 5.5	25.0	air and O_2	$(2.7 \pm 0.12) \times 10^{-3}$	*a*
	25.0	O_2/4-HTMPO mix	2.66×10^{-3}	*a, c*
	25.0	4-HTMPO alone	2.77×10^{-3}	*a, c*
	23.3	4-HTMPO/B_{12r}	1.8×10^{-3}	*a, d*
		2. Base-Off $PhCH_2B_{12}{\cdot}H^+$		
1 M phosphoric acid	25.0	air and O_2	3.0×10^{-5}	*a*
			2.8×10^{-5}	*b*
$HClO_4$ (0.015–0.44 M), μ = 0.1–1.0 M	35.0	air and O_2	$(7.9 \pm 1.3) \times 10^{-5}$	*a*
		Fe^{3+}	$\sim 8 \times 10^{-5}$	*a, e*

[a] This work. [b] Reference 1. [c] [4-HTMPO] = 0.46–5.5 × 10^{-n} M. [d] With added B_{12r}, kinetic inhibition is noted (see text). [e] Value extrapolated to $[Fe^{3+}] = 0$.

recombination becomes competitive with the radical–scavenger reaction.

The second criterion was met with 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (abbreviated 4-HTMPO), which alone among the reagents tried cleanly[10] scavenged free benzyl radicals. As in the case of reaction under oxygen, benzylcobalamin decomposes fairly rapidly when 4-HTMPO is present, with $k = (2.70 \pm 0.11) \times 10^{-3}$ s^{-1} at 25.0 °C in 0.1 M acetate buffer at pH 5.5. (To avoid interference between this reaction and a slower secondary reaction between 4-HTMPO and [Co^{II}], absorbance measurements were made at 336.2 nm, an isosbestic point in the $H_2O[Co^{III}]^+$–[Co^{II}] spectra.) The constancy of k over a range of 4-HTMPO concentrations (0.46–5.5 mM) and agreement between it and the rate constant when O_2 was used support the assignment of this as homolytic cleavage. In the case of the base-off complex present in acidic solution, extrapolation to $[Fe^{3+}] = 0$ of data from the reaction of $PhCH_2[Co]{\cdot}H^+$ with Fe^{3+} (presented in a later section of this article) leads to $k = 8 \times 10^{-5}$ s^{-1}, again the same as the O_2-induced homolysis rate constant (see Table I).

Kinetic retardation is observed when vitamin B_{12r} (=[Co^{II}]) was added simultaneously with 4-HTMPO. The sequence of reactions is

$$PhCH_2[Co] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co^{II}] + PhCH_2\cdot \qquad (1)$$

$$PhCH_2\cdot + \text{4-HTMPO} \xrightarrow{k_2} \text{RNO (adduct)} \qquad (2)$$

With the steady-state approximation for the concentration of benzyl radicals, the rate of reaction is given by

$$\frac{-d[PhCH_2B_{12}]}{dt} = \frac{k_1k_2[PhCH_2B_{12}][\text{4-HTMPO}]}{k_{-1}[B_{12r}] + k_2[\text{4-HTMPO}]} \qquad (3)$$

To avoid interference from a slower reaction of [Co^{II}] with 4-HTMPO, measurements were made by using the method of initial rates at 336.4 or 283.8 nm, wavelengths which are H_2O-[Co^{III}]$^+$–[Co^{II}] isosbestic points. The initial rates of absorbance change were converted to a concentration basis by using known molar absorptivities. They refer to an average concentration of benzylcobalamin during the initial reaction period. The initial rates (R_i) were determined at several concentrations and are shown in Figure 1 as a plot suggested by the linearized equation

$$\frac{[PhCH_2B_{12}]_{av}}{R_i} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\frac{[B_{12r}]}{[\text{4-HTMPO}]} \qquad (4)$$

The data analysis was carried out in two ways. When the parameters were freely floated, a nonlinear least-squares fit to eq 3 and 4 yields $k_1 = (1.9 \pm 0.1) \times 10^{-3}$ s^{-1} and $k_{-1}/k_2 = 5.2 \pm 0.4$ (at 23.4 °C). If, on the other hand, the value of k_1 is fixed at the value extrapolated to this temperature,[11] 2.16×10^{-3} s^{-1}, the fit is nearly as good with $k_{-1}/k_2 = 6.5 \pm 0.3$. The two methods are in satisfactory agreement, and we have adopted the latter value in the balance of the analysis.

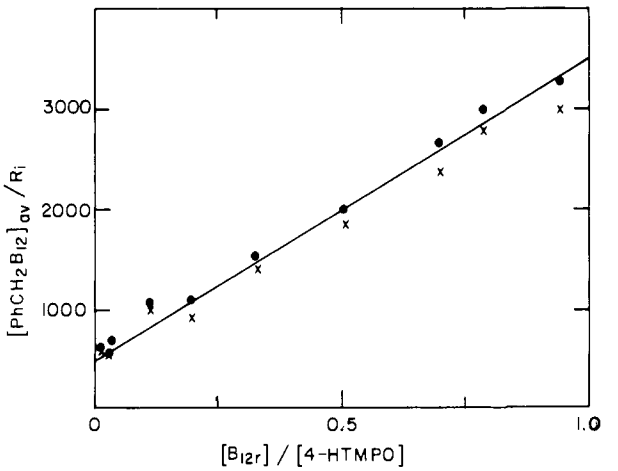


Figure 1. Retarding effect of added B_{12r} on the homolysis of benzylcobalamin in solutions containing various concentrations of B_{12r} and 4-HTMPO illustrated by the fit of the initial rate variations to the concentration ratio in accord with eq 4. Initial rates were evaluated spectrophotometrically at the B_{12a}–B_{12r} isosbestic wavelengths of 336.4 and 283.0 nm, symbolized respectively as ● and X.

This set of experiments, by virtue of the [Co^{II}] retardation, provides the most convincing support for homolysis. These data do not afford individual values for the rate constants k_{-1} and k_2 but only for their ratio. Other experimental data can be used to provide a full resolution, however, as presented later in this article.

Only benzaldehyde has been reported as a product of homolysis of benzylcobalamin in the presence of oxygen.[9] In acetate buffer, benzaldehyde is indeed the principal product (90:10 PhCHO/$PhCH_2OH$), but in 0.1 M $HClO_4$ almost a 1:1 ratio of the two (actually 54:46) was found. This is the expected result, since the principal path for radical oxidation is[12]

$$PhCH_2 + O_2 \rightarrow PhCH_2OO\cdot \qquad (5)$$

$$2PhCH_2OO\cdot \rightarrow PhCHO + PhCH_2OH + O_2 \qquad (6)$$

Oxidative Cleavage with Fe^{3+}. In a search for other reagents which would promote homolysis of benzylcobalamin, enhanced rates of decomposition were noted when Fe^{3+} was added. This reaction yields Fe^{2+} (detected spectrophotometrically as its 1,10-phenanthroline complex), $PhCH_2OH$ (99% yield by GC), and the cobalt(III) corrin, aquocobalamin or B_{12a} (detected spectrophotometrically). The stoichiometry corresponded to a

(10) These attempts included the use of $Co(NH_3)_5X^{2+}$, which reacts too slowly, if at all, with both B_{12r} and $\cdot CH_2Ph$ to draw homolysis to competition. Other unsuccessful attempts included H_2O_2 and Fe^{3+}, which react directly with benzylcobalamin more rapidly than homolysis, and Cu^{2+} which entered into interfering redox reactions.

(11) With k_1 corrected from $\Delta H^{\ddagger}$ reported in ref 9.

(12) Maillard, B.; Ingold, K. U.; Sciano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095 and references therein.

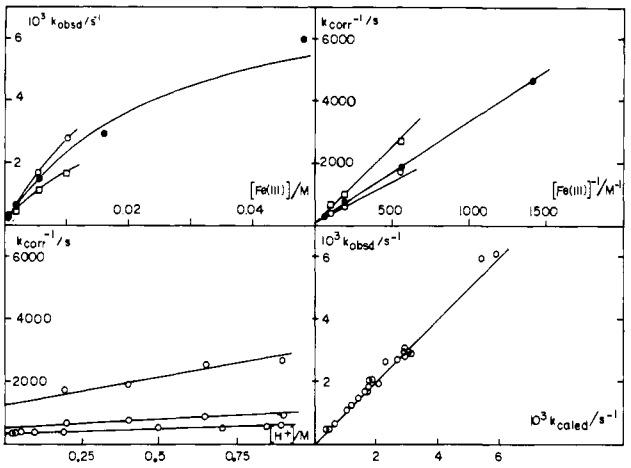


Figure 2. Concentration dependences shown by the pseudo-first-order rate constant (35 °C, μ = 1.00 M) for reaction of benzylcobalamin with iron(III). (a) k_{absd} vs. [Fe^{3+}] at different [H^+], 0.200 (open circles), 0.400 (filled circles), and 0.900 M (squares); (b) linear variation of $1/(k_{obsd} - k_1)$ (or $1/k_{corr}$) with $1/[Fe^{3+}]$ at the same three [H^+]; (c) linear variation of $1/k_{corr}$ with [H^+] at three [Fe^{3+}], 1.77 (top), 5.32, and 9.93 mM (bottom); (d) composite of all variations, comparing experimental and calculated (eq 8) values of k. The solid curves in every panel are those from the overall nonlinear least-squares fit.

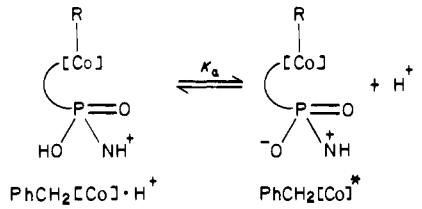
consumption ratio of 1.92:1 (based on benzylcobalamin consumption) or 1.87:1 (based on the Fe^{2+} found), establishing occurrence of the following overall reaction:

$$PhCH_2[Co]\cdot H^+ + 2Fe^{3+} + 2H_2O = H_2O[Co^{III}]^+ + 2Fe^{2+} + PhCH_2OH + 2H^+ \quad (7)$$

This reaction is considerably faster than homolysis, and its rate varied with [Fe^{3+}] and [H^+]. The variations are complex in form, although it will be shown that they do arise from reasonable phenomena. The kinetic data can be summarized as follows: (1) With a large stoichiometric excess of Fe^{3+}, pseudo-first-order kinetics are observed, yielding rate constants k_{obsd}; (2) the first-order dependence of k_{obsd} on [Fe(III)] observed at lower concentrations tends toward zeroth-order at higher [Fe(III)] (Figure 2a); (3) the rate is the same with Fe(III) alone as with Fe(III)–O_2 mixtures. Indeed, k_{obsd} extrapolates not to zero at [Fe(III)] = 0 (even when O_2 is absent) but to the independently determined value of k_1 for the homolysis reaction (eq 1); (4) the dependence of k_{corr}, the rate enhancement above homolysis ($k_{corr} = k_{obsd} - k_1$) is such that $1/k_{corr}$ varies linearly with $1/$[Fe(III)] at a given [H^+] (Figure 2b) and $1/k_{corr}$ varies linearly with [H^+] at a given [Fe(III)] (Figure 2c). These variations lead to the following rate law

$$\frac{-d[PhCH_2B_{12}]}{dt} = \left\{k_1 + \frac{kK_{Fe}[Fe(III)]}{1 + K_{Fe}[Fe(III)] + [H^+]/K_a}\right\}[PhCH_2B_{12}] \quad (8)$$

The parameters are k_1, the previously determined rate constant for homolysis, together with three other constants defined in terms of the steps in the mechanism shown in eq 9–12, which are invoked



(9)

to explain the observed kinetics. These steps are as follows: (1) the known[13] acid ionization of the phospho diester group of the nucleotide loop (eq 9) to form a species symbolized as $PhCH_2$-[Co]*; (2) rapid and reversible association of $PhCH_2$[Co]* with Fe^{3+} (eq 10); (3) rate-limiting electron transfer (eq 11) forming

$$PhCH_2[Co]^* + Fe^{3+} \overset{K_{Fe}}{\rightleftharpoons} \text{adduct} \quad (10)$$

$$\text{adduct} + H_2O \xrightarrow{k_{11}} PhCH_2OH + Fe^{2+} + H^+ + [Co^{II}] \quad (11)$$

$$[Co^{II}] + Fe^{3+} + H_2O \xrightarrow{\text{fast}} H_2O[Co^{III}]^+ + Fe^{2+} \quad (12)$$

(in possibly more than a single step) benzyl alcohol, Fe^{2+}, and [Co^{II}]; and (4) oxidation of [Co^{II}] by a second Fe^{3+} (eq 12), which we found occurs rapidly.

The data were fit to eq 8 by using a nonlinear least-squares program. With k_1 and K_a fixed at their known values,[14] 7.9 × 10^{-5} s^{-1} and 0.60 M, respectively, $k_{11} = (8.4 \pm 0.3) \times 10^{-3}$ s^{-1} and $K_{Fe} = 60.6 \pm 7.0$ M^{-1} (35 °C, μ = 1.0 M).[15] Since reactions 7, 9, and 12 are known independently, the new results are in eq 10 and 11. The conclusion is that oxidative cleavage is preceded by association; indeed, the deprotonated phosphoryl oxygen may provide the binding site for iron, although no confirmation for that is known.

In the formulation shown in eq 11, the adduct is regarded as an intermediate in the reaction, rather than as a nonproductive "dead-end", although both formulations would give identical kinetics. Nonetheless, the adduct seems to be a reasonable precursor complex, since it appears that eq 11 forms a benzyl–cobalt(IV) intermediate (eq 13), the cleavage of which leads to the indicated products (eq 14). That is suggested by the formation

$$PhCH_2[Co^{III}]\cdots Fe^{3+} \xrightarrow{k} PhCH_2[Co^{IV}]^+\cdots Fe^{2+} \quad (13)$$

$$PhCH_2[Co^{IV}]^+\cdots Fe^{2+} \xrightarrow{H_2O} PhCH_2OH + [Co^{II}] + Fe^{2+} + H^+ \quad (14a)$$

$$PhCH_2[Co^{IV}]^+\cdots Fe^{2+} \xrightarrow{Cl^-} PhCH_2Cl + [Co^{II}] + Fe^{2+} \quad (14b)$$

of increasing quantities of benzyl chloride as Cl^- is added to the medium. At 0.1 M HCl, benzyl chloride is the major product. Earlier work[16–20] has attested to organocobalt(IV) formation as a pathway to oxidative cleavage and to the ease of nucleophilic displacements from it (eq 14).

Benzaldehyde vs. Benzyl Alcohol Formation. These two major products arise from decomposition of benzylcobalamin and also from benzylpentaaquochromium(2+).[21] The relative yields under the same reaction conditions (0.1 M $HClO_4$), expressed as the ratio PhCHO/$PhCH_2OH$ with an accuracy ± 2%, are as follows:

conditions	from $PhCH_2[Co]\cdot H^+$	from $(H_2O)_5CrCH_2Ph^{2+}$
O_2	54:46	88:12
O_2 + Fe^{3+} (0.02 M)	14:86	92:8
Fe^{3+} (0.02 M)	1:99	0:97[21]

The formation of essentially equal yields of the two from homolysis of benzylcobalamin in the presence of O_2 has already

(13) Brown, K. L.; Hakimi, J. M. *Inorg. Chim. Acta* **1982**, *67*, L29.

(14) The value of K_a cited is that for methylcobalamin;[13] the site of protonation is remote from the alkyl group, and the change in R is likely to have minimal effect. Just as with methylcobalamin, and consistent with this assumption, the occurrence of this equilibrium for benzylcobalamin is not manifest in spectrophotometric determinations of absorbance as a function of [H^+].

(15) When k_1 and K_a were also allowed to refine freely, the optimum least-squares values are $k_1 = (10.2 \pm 1.2) \times 10^{-5}$ s^{-1}, $K_a = 0.74 \pm 0.09$ M, $k = (9.8 \pm 0.4) \times 10^{-3}$ s^{-1}, and $K_{Fe} = 44.8 \pm 7.5$ M^{-1}.

(16) Halpern, J.; Topich, J.; Zamaraev, K. I. *Inorg. Chim. Acta* **1976**, *20*, L21.

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(19) Levitin, I. Ya.; Sigan, A. L.; Vol'pin, M. F. *J. Organomet. Chem.* **1976**, *114*, C53.

(20) Daub, G. W. *Prog. Inorg. Chem.* **1978**, *19*, 409.

(21) Plus 2.8% as bibenzyl.

been rationalized by eq 5 and 6. Oxidation exclusively to benzyl alcohol is caused by Fe^{3+}, both directly as in eq 13 and 14a or after $PhCH_2\cdot$ is formed (as in the case of the decomposition $CrCH_2Ph^{2+}$ in the presence of Fe^{3+}, where only unassisted homolysis occurs and direct reaction with Fe^{3+} is not observed). It is not surprising then that the two occur competitively when both O_2 and Fe^{3+} are present.

What is unexpected, however, is that the results for a given oxidant are not identical for the two benzylmetal complexes. Indeed, this result appears inconsistent with the claim that homolysis provides the principal path for both, since the product ratios should then be the same. The anomalous system is clearly $CrCH_2Ph^{2+}$ with O_2, where an enhanced and constant quantity of benzaldehyde is noted, even when Fe^{3+}–O_2 mixtures are employed. Despite that, there is an overwhelming body of evidence that the reactions of $CrCH_2Ph^{2+}$ occur by homolysis and involve a free $PhCH_2\cdot$ intermediate. We suggest that the problem be resolved as follows: The large yield of benzaldehyde arises from subsequent oxidation of much of the benzyl alcohol by CrO_2^{2+}, the chromium complex formed when Cr^{2+}, the other product of homolysis, reacts with O_2 ($k = 1.6 \times 10^8$ M^{-1} s^{-1}).[22] This and other reactions of CrO_2^{2+} are currently under investigation.[23]

Benzyl Transfer to Chromium. When Cr^{2+} is added to benzylcobalamin at $[H^+] = 0.1$ M, two reactions are observed. First, any $H_2O[Co^{III}]^+$ present is rapidly reduced by Cr^{2+} to $[Co^{II}]\cdot H^+$.[24,25] The benzylcobalamin also reacts with Cr^{2+} to form $[Co^{II}]\cdot H^+$ (detected spectrophotometrically) and $(H_2O)_5CrCH_2Ph^{2+}$ (presumably, although the absorption spectrum of the latter is so weak in comparison with the B_{12} species that the organochromium ion is not detected). Conversion of $PhCH_2[Co]\cdot H^+$ to $B_{12r}\cdot H^+$ is incomplete, however, and the extent of conversion depends upon $[Cr^{2+}]$. These results suggest a reversible benzyl-transfer equilibrium,

$$PhCH_2[Co]\cdot H^+ + Cr^{2+} \rightleftharpoons [Co^{II}]\cdot H^+ + CrCH_2Ph^{2+} \qquad (15)$$

This formulation is confirmed by the reverse reaction: Addition of $CrCH_2Ph^{2+}$ to acidic solutions of $[Co^{II}]\cdot H^+$[26,27] results in formation of easily measurable concentrations of benzylcobalamin. On the basis of the absorbance changes measured at λ 428 and 469 nm, and when only data from experiments made up to have concentrations such that the equilibrium position was appropriately balanced were used, so that reliable concentrations could be calculated from the absorbance readings at equilibrium, the equilibrium constant for the reaction is $K_{15} = (2.1 \pm 0.1) \times 10^{-3}$ at 25 °C.

Rate Constants for Reactions of Benzyl Radicals. From the data obtained, it becomes possible to calculate directly certain individual rate constants to a precision of some 10–20%. The equilibrium constant K_{15} is a composite of four rate constants, $K_{15} = k_1k_f/k_{-1}k_d$, where k_1 and k_{-1} refer to the reversible homolysis of $PhCH_2[Co]\cdot H^+$ (eq 1), and k_d and k_f are the analogous rate constants for homolytic dissociation and formation of $(H_2O)_5CrCH_2Ph^{2+}$.

With the values $k_1 = 2.0 \times 10^{-5}$ s^{-1} and $k_d = 2.3 \times 10^{-3}$ s^{-1} at 25 °C, the ratio k_f/k_{-1} becomes 0.24. This compares with ratio of 0.42 and 0.63 for the respective reactions of Cr^{2+} and $[Co^{II}]\cdot H^+$ with $\cdot CH_2(CH_3)_2OH$ and $\cdot CHOHCH_2OH$.[28] Since k_f has recently been evaluated[29] as $(8.5 \pm 0.6) \times 10^7$ M^{-1} s^{-1}, $k_{-1} = 3.5 \times 10^8$ M^{-1} s^{-1} for $[Co^{II}] + PhCH_2\cdot$, a value which lies near rate constants for the reactions of other aliphatic radicals with $[Co^{II}]$ (cf. $k = 1.5 \times 10^9$ and 2.4×10^8 M^{-1} s^{-1} for $\cdot CH_3$ and $\cdot CH_2C(CH_3)_2OH$, respectively).[28,30]

Provided the value of k_{-1} is also applicable to the reaction between $PhCH_2\cdot$ and $[Co^{II}]$ in acetate buffer, given the ratio k_{-1}/k_2 determined in this work, $k_2 = 5.4 \times 10^7$ M^{-1} s^{-1} for the reaction between 4-HTMPO and $PhCH_2\cdot$ (eq 2).

Accelerated Autoxidation of $PhCH_2[Co]$ by Mild Reducing Agents. Mild reducing agents greatly increase the rate of the reaction between benzylcobalamin and oxygen in perchloric acid solutions over the homolysis-limited rate. For instance, it increases 27-fold over homolysis with 4.66×10^{-3} M ascorbic acid (H_2A), and 2.7-fold with the same concentration of hydroquinone. (In the absence of O_2, however, these reducing agents do not react with benzylcobalamin in acidic solutions.) A related observation has been noted qualitatively before[31] in the case of $[Co^{II}] + O_2 + H_2A$ but not for an organocobalamin. The rate for the latter ternary combination is first-order in $[PhCH_2[Co]\cdot H^+]$ and $[O_2]$, but less than first-order in $[H_2A]$. The reaction yields $H_2O[Co^{III}]^+$, not $[Co^{II}]$. These data, which can be interpreted to suggest the intervention of a reactive steady-state adduct between benzylcobalamin and O_2, do not define the mechanism completely. We present them here simply to cite what we believe is an unprecedented instance of O_2 activation by an organocobalamin. This bears some resemblence to the $[Co^{II}]$–O_2–H_2A case.[32]

Experimental Section

Benzylcobalamin was prepared as described,[9] except that the final extraction was made from 1 M perchloric acid, rather than hydrochloric acid, since traces of chloride ions alter the reactions and products (e.g., eq 14b). The hydroxocobalamin used in this procedure, and also used to prepare B_{12r},[33] was purchased from Sigma Chemical Co. Solutions of pentaaquabenzylchromium(2+) ions were prepared from Cr^{2+} and $PhCH_2Br$ in aqueous acetone and purified by ion-exchange chromatography.[34,35] Other compounds were purchased or were prepared by using standard procedures.

Kinetic data were obtained by using a Cary Model 219 recording spectrophotometer equipped with thermostated cell holders. In acetate buffers, the disappearance of $PhCH_2[Co]$ was followed at 350 or 336.2 nm (ϵ 1.95×10^4 and 1.83×10^4 M^{-1} cm^{-1}, respectively) and in perchloric acid solutions by monitoring $PhCH_2[Co]\cdot H^+$ at 428 nm (ϵ 1.23×10^4 M^{-1} cm^{-1}). The kinetics experiments employed benzylcobalamin in the range 1×10^{-5} to 2×10^{-4} M, and product analyses were done by using concentrations of the order of 10^{-3} M.

Gas chromatographic analyses were conducted by using a Varian 3740 instrument on a 12-ft OV-1 column. Known compounds were used for calibrations and, on occasion, as internal standards.

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(23) Reactions of CrO_2^{2+} currently under investigation provide tentative support for this conclusion; Bakac, A.; Brynildson, M. E.; Bruhn, S. L.; Espenson, J. H., unpublished observations.

(24) The B_{12a} is often present in small concentration from prior decomposition and oxidation of benzylcobalamin; it is reduced to $B_{12r}\cdot H^+$ by Cr^{2+} at a specific rate of 14.3 M^{-1} s^{-1} (ref 25).

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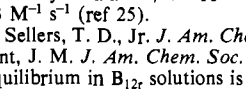
(27) The principal equilibrium in B_{12r} solutions is



for which $pK_a = 2.9$. The protonated species represented in the text and in eq 15 as $B_{12r}\cdot H^+$ is the predominant form at pH 1.

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