Alkali-Induced Decompositions of Alkylcorrins, Alkylcobaloximes, and Related Compounds[1]

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Alkylcobalt derivatives of a variety of cobalt complexes including cobalamins, cobinamides, cobaloximes, and other model compounds of vitamin B_{12} decompose with Co–C bond cleavage on reaction with warm alkali. Under anaerobic conditions, alkylcobalamins and -cobinamides carrying a hydrogen in the β-position decompose by way of β-elimination to form alkenes. Alkylcobaloximes produce mixtures of alkenes and alkanes, whose ratio is dependent on the concentration of base. Predominant formation of alkenes is typical of reactions in strong base (6–9 M NaOH). At lower base concentrations, the relative yields of alkanes increase. Among secondary alkylcobaloximes, alkane yields never exceed 25%. Ethane yields from ethylcobaloxime exceed 50% only over a relatively narrow range of base concentrations (0.3–2 M NaOH). The ethyl derivatives of other vitamin B_{12} model compounds also decompose by competitive formation of ethylene and ethane. In the decomposition of 5-hexenylaquocobaloxime in weak base substantial amounts of methylcyclopentane are generated, a fact consistent with the intermediate formation of the 5-hexenyl radical and a homolytic mechanism of Co–C bond cleavage in the alkane-forming reaction.

Introduction

The lability of the Co–C bond of alkylcobalt complexes of vitamin B_{12} model compounds to alkali was first noted in 1966, when Schrauzer and Windgassen reported that methylaquocobaloxime decomposes on heating in concentrated KOH to yield methane.[3] In 1970, Schrauzer, Weber, and Beckham briefly mentioned that higher alkylcobaloximes decompose in alkali primarily to yield olefins and the Co(I) nucleophile.[4] Recently, there has been renewed interest in reactions of this type. Specifically, Brown has carried out kinetic investigations of the reactions of methyl- and ethylaquocobaloximes with aqueous base at 50 °C.[5-9] With ethylaquocobaloxime, the formation of both ethane and ethylene was observed, with ethane being the main product.[7] The seeming discrepancy between these results and those in ref 4 can be resolved when it is noted that Brown used base concentrations between 0 and 1 M, whereas the previous work was carried out in hot 6 M NaOH.

In this paper, data on the base-induced decomposition of ethylaquocobaloxime and of a variety of other alkylcobaloximes, -cobalamins, and -cobinamides and related compounds (see Figures 1 and 2) are reported at base concentrations from 0.3 to 9 M NaOH. It was our main intent to establish the conditions favoring β-elimination by examining a wide range of complexes and base concentrations. However, a number of experiments were also carried out to determine the mechanism of Co–C bond cleavage in the reactions yielding alkanes. For the specific case of ethylaquocobaloxime, Brown concluded that ethane is produced by way of a reaction involving Co–C bond homolysis as the first step.[9] We will show that this step is indeed plausible.

Results

Alkylcobalamins and -cobinamides. The base-induced decompositions of simple alkylcorrins have not previously been examined in detail, although spectral changes in basic solutions of methyl-, ethyl-, and vinylcobinamides have been reported.[10,11] In the present study, we have investigated the decompositions of many alkylcorrins in basic solutions ranging from 0.3 to 8.75 M in NaOH. These reactions were carried out under argon at 50 °C. The compounds examined were ethyl-, *n*-propyl-, isopropyl, *n*-butyl-, isobutyl, and *sec*-butylcobalamins and all the corresponding cobinamides. The alkyl groups of these compounds all contain at least one β-hydrogen, and the sole hydrocarbon products observed were alkenes.

Table I. Relative Yields of Alkenes from the Base-Induced Decompositions of Alkylcorrins under Aerobic and Anaerobic Conditions

	rel aerobic yield,[a,b] %	
alkylcorrin	0.9 M NaOH	2.5 M NaOH
ethylcobinamide	205	89
n-propylcobinamide	240	75
isobutylcobinamide	80	54
ethylcobalamin	310	91
n-propylcobalamin	270	106

[a] After 18 h at 50 °C. [b] Relative to anaerobic yields of 100%.

The reactions in base were compared with decompositions in neutral solution at 50 °C, which also generate only alkenes. *n*-Alkylcobalamins and primary alkylcobinamides require incubation overnight to produce substantial alkene yields (>50%) when decomposed in 2.5 M NaOH. By comparison, after 18 h in neutral solution *n*-alkylcobalamins produce only ca. 15% yields, and primary alkylcobinamides produce yields of less than 5%. The reactions of secondary alkylcobinamides are somewhat faster, producing quantitive yields of alkenes in both basic and neutral solutions within 18 hours. Secondary alkylcobalamins are still faster; the yields from these compounds are quantitive within 1 h.

The influence of oxygen on base-induced decomposition reactions was examined by comparing the 18-h yields of alkenes under argon and air. Only primary alkylcobinamides and *n*-alkylcobalamins were used in these studies. In 0.9 M NaOH, oxygen generally caused the alkene yields

(1) Paper No. 55 of a series "Studies on Vitamin B_{12} and Related Compounds".
(2) National Science Predoctoral Fellow, 1978–1981.
(3) Schrauzer, G. N.; Windgassen, R. J. *J. Am. Chem. Soc.* **1966**, *88*, 3738.
(4) Schrauzer, G. N.; Weber, J. H.; Beckham, T. M. *J. Am. Chem. Soc.* **1970**, *92*, 7078.
(5) Brown, K. L. *Inorg. Chim. Acta* **1978**, *31*, L401.
(6) Brown, K. L. *J. Am. Chem. Soc.* **1979**, *101*, 6600.
(7) Brown, K. L.; Hessley, R. K. *Inorg. Chem.* **1980**, *19*, 2410.
(8) Brown, K. L.; Hessley, R. K. *Inorg. Chim. Acta* **1981**, *53*, L115.
(9) Brown, K. L. *J. Chem. Soc., Chem. Commun.* **1981**, 598.
(10) Firth, R. A.; Hill, H. A. O.; Pratt, J. M.; Thorp, R. G.; Williams, R. J. P. *J. Chem. Soc. A* **1968**, 2428.
(11) Pailes, W. H.; Hogenkamp, H. P. C. *Biochemistry* **1968**, *7*, 4160.

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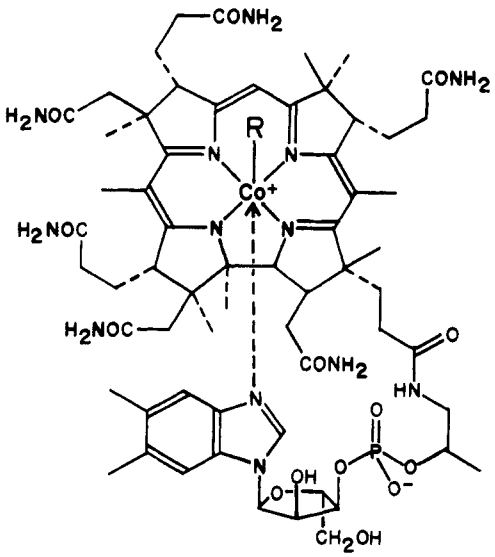


Figure 1. The structure of alkylcobalamins. Alkylcobinamides lack the axial base and phosphoribosyl moeities.

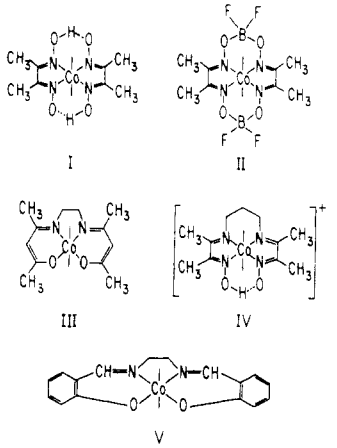


Figure 2. Structures of the vitamin B_{12} model compounds studied. Chelate I is called a cobaloxime, while chelates II–V will be referred to by number.

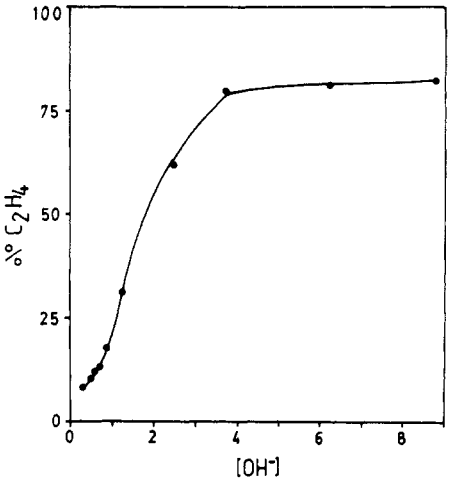


Figure 3. The base dependence for the formation of ethylene from ethylcobaloxime, plotted as a percentage of the total hydrocarbons produced.

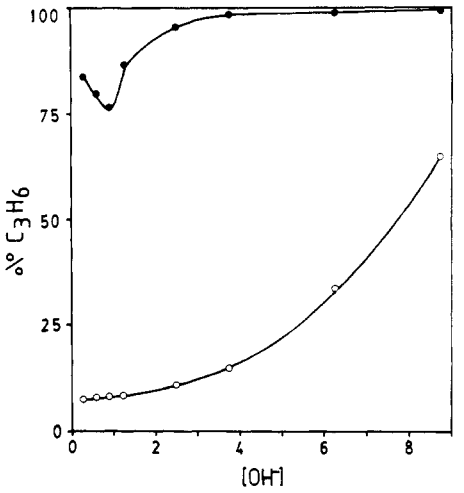


Figure 4. The base dependences for the formation of propylene from *n*-propylcobaloxime (○) and isopropylcobaloxime (●), plotted as percentages of the total hydrocarbons produced.

to increase, whereas in 2.5 M NaOH most yields were decreased. These results are shown in Table I.

Decomposition of primary alkylcobinamides and *n*-alkylcobalamins in basic solutions containing 25% 2-propanol and 25% methanol produced small yields of alkanes in addition to the usual alkenes. These yields were only about 1%, except in the case of *n*-propylcobinamide, which produced 5% propane in 0.9 M NaOH.

Alkylcobaloximes. When **ethylaquocobaloxime** is decomposed in anaerobic aqueous base[12] at 50 °C, ethylene and ethane are formed. Their proportions are dependent on the concentration of base. For any given base concentration, the ratio of ethane to ethylene is independent of cobaloxime concentration and time, in accord with previous investigations.[7] The base dependence of ethylene formation, plotted as a percentage of the total hydrocarbons produced, is shown in Figure 3. Ethylene is the principle product at all base concentrations above 2 M. Ethane, which accounts for the balance of the hydrocarbons formed, is the main product only at low base concentrations.[13] Traces of *n*-butane (≪1%) are also formed in weak base.

The proportions of ethane and ethylene shown in Figure 3 are not changed when sodium chloride is used to maintain constant ionic strength in the 0.3–1.0 M NaOH range. Likewise, these proportions are not altered by the presence of 10% methanol. However, oxygen causes substantial changes. In base concentrations below 1 M, ethane yields were decreased by 65–85% in the presence of oxygen, while the ethylene yields were approximately doubled. In terms of moles, this increase in ethylene was less than the decrease in ethane. Photolysis of anaerobic, alkaline solutions of ethylaquocobaloxime produces primarily ethylene. Lesser amounts of ethane and *n*-butane are formed.

***n*-Propyl-** and **isopropylaquocobaloximes** produce propane and propylene in anaerobic, basic solutions at 50 °C. In addition, traces of *n*-hexane are detected in the reactions of the *n*-propyl isomer. The base dependences for the formation of propylene from these cobaloximes is

(12) When alkylaquocobaloximes are dissolved in base, an equilibrium is established between the alkylaquocobaloxime and the alkylhydroxocobaloxime. In the basic solutions used in these studies, the hydroxo complex is the predominant species present. For ethylhydroxocobaloxime = ethylaquocobaloxime + hydroxide, K = 0.13 M at 50 °C in 1 M aqueous KCl.[7] Base can also remove protons from the oxygen atoms of the equatorial ligands, although they are strongly held by hydrogen bonds. Yoshida, N.; Fujimoto, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3526.

(13) On the basis of his data in 0–1 M [OH^-], Brown proposed a kinetic scheme which predicts that ethane should be the main product at all hydroxide concentrations above 0.01 M and that the ratio of ethane to ethylene should level out to ca. 5.6–1 above 1 M [OH^-].[7] The experimental results in this paper show that this scheme cannot be applied to any solutions where [OH^-] > 1 M.

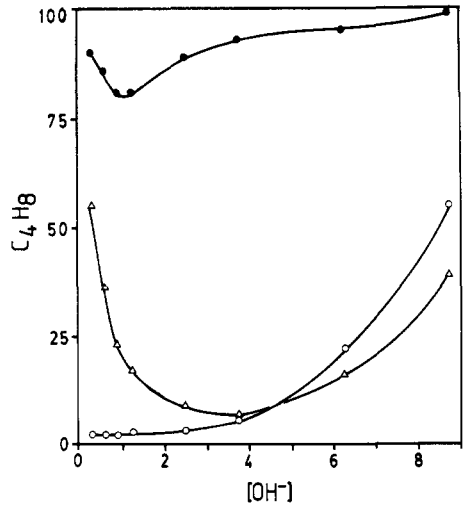


Figure 5. the base-dependences for the formation of butenes from *n*-butylcobaloxime (○), isobutylcobaloxime (△), and *sec*-butylcobaloxime (●), plotted as percentages of the total hydrocarbons produced.

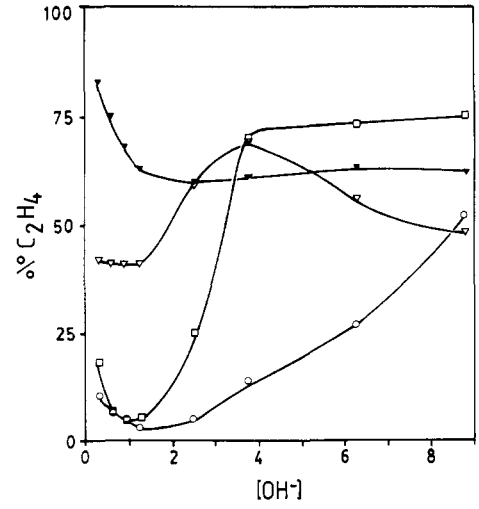


Figure 6. The base dependences for the formation of ethylene from chelate II (△), chelate III (○), chelate IV (▼), and chelate V (□), plotted as percentages of the total hydrocarbons produced.

shown in Figure 4. *n*-Propylcobaloxime yields primarily propane at low and intermediate base concentrations. In contrast, isopropylcobaloxime forms mainly propylene regardless of the concentration of base. Propane production from this complex is less than 25% even under optimal conditions, which occur around 1 M NaOH.

When *n*-propylcobaloxime is reacted with base in the presence of oxygen, the yields of propane are reduced and propylene yields increase, as was observed with ethylcobaloxime. Nitrous oxide, a scavenger for Co(I),[14,15] does not affect the hydrocarbon yields from *n*-propylcobaloxime. However, isopropylcobaloxime generates only half as much propane under nitrous oxide as it does under argon, while the propylene yields are unaffected.

Significantly, ethane is formed when isopropylcobaloxime is decomposed in anaerobic 0.9 M NaOH in the presence of ethyl bromide. Ethylene was also produced, as well as the expected yields of propane and propylene. The ethylene results principally from the dehydrohalogenation of ethyl bromide and is also seen in a control reaction containing no cobaloximes. No ethane was formed in the control reaction. These results demonstrate the formation of the Co(I) nucleophile (see Discussion).

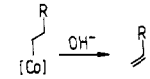
Figure 5 shows the percentages of butene formed from ***n*-butyl-, isobutyl-,** and ***sec*-butylaquocobaloximes** at 50 °C in various concentrations of base. *n*-Butylcobaloxime produces *n*-butane and 1-butene with a base profile which is similar to that of *n*-propylcobaloxime. Isobutylcobaloxime produces isobutane and isobutylene. In this case, olefin production is maximal at both the lowest and highest base concentrations examined. In most solutions, the alkane is the major product. *sec*-Butylcobaloxime forms 1-butene, cis- and *trans*-2-butenes, and *n*-butane in alkali. The curve plotted in Figure 5 represents the sum of the butenes formed. This total consists primarily of 1-butene, which accounts for 76% of the hydrocarbons formed at 0.6 M NaOH, 91% at 3.75 M NaOH, and 99% at 8.75 M NaOH. The 2-butenes are formed in the greatest percentage at low base concentrations and constitute less than 1% of the product total at high base concentrations. *trans*-2-Butene is formed in slight preference to *cis*-2-butene. The alkane formed, *n*-butane, represents only 20% of the product distribution at its maximum (1 M NaOH) and only 1% in strong base.

Ethyl Derivatives of Chelates II–V. Ethyl derivatives of chelates II–V were prepared to see if these compounds yielded the same products in base as ethylcobaloxime. This proved to be the case, since both ethane and ethylene were formed. However, the base dependences for ethylene formation vary from complex to complex and are shown in Figure 6.

5-Hexenylcobaloxime. 5-Hexenyaquocobaloxime was prepared as a probe for the formation of radicals in the alkane forming reaction (see Discussion). Accordingly, a sample of this cobaloxime was decomposed in 0.9 M NaOH at 50 °C under anaerobic conditions. Over the course of 2 days, three samples were removed from the gas phase and analyzed for C6 hydrocarbons. The only products detected were methylcyclopentane and 1,5-hexadiene, in a ratio of 7:1.

Discussion

Trends among Alkylcobalt Complexes. Among the alkylcobalt complexes examined, the alkylcobalamins and -cobinamides appear to react with base in the most straightforward fashion, producing only alkenes. These reactions are comparatively slow when the alkenes are formed only by a base-induced reaction, as shown in eq 1. Primary alkylcobinamides, for example, have half-lives on the order of 12–18 h in 2.5 M NaOH at 50 °C.



(1)

Reaction according to eq 1 must be distinguished from spontaneous decomposition, which also generates alkenes but is *not* base induced (eq 2). This reaction occurs in

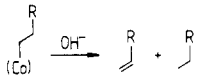
(2)

both neutral and basic solutions, and the rate varies with the structure of the alkyl group and the corrin.[16,17] Isopropylcobalamin, for example, decomposes with a half-life of only 3 min in neutral solution at 25 °C. *n*-Propylcobinamide, on the other hand, has a half-life on the order of months in neutral solution. Accordingly, the generation

(14) Banks, R. G. S.; Henderson, R. J.; Pratt, J. M. *J. Chem. Soc., Chem. Commun.* **1967**, 387.
(15) Banks, R. G. S.; Henderson, R. J.; Pratt, J. M. *J. Chem. Soc. A* **1968**, 2886.
(16) Grate, J. H.; Schrauzer, G. N. *J. Am. Chem. Soc.* **1979**, *101*, 4601.
(17) Schrauzer, G. N.; Grate, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 541.

of alkenes in basic solutions is entirely base induced in the case of primary alkylcobinamides and entirely spontaneous with secondary alkylcobalamins. Alkylcorrins whose neutral solution stabilities are intermediate between those of primary alkylcobinamides and secondary alkylcobalamins must produce alkenes in basic solutions according to both eq 1 and 2, since the rates of both both processes are of comparable magnitude.

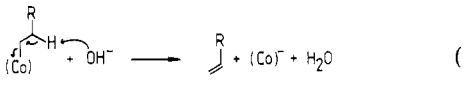
Alkylcobaloximes are far less prone to spontaneous decomposition than are alkylcorrins[16] but are also base sensitive. Thus, alkylcobaloximes containing hydrogen in the β-position decompose in base to form alkenes and alkanes (eq 3). The proportions of these products are dependent


(3)

on both the concentration of base and the structure of the alkyl group. Ethylcobaloxime exemplifies the importance of basicity in determining the products. In most concentrations of base, ethylene is the major product. In weak base, ethane predominates. The importance of structure can be seen by comparing the base profiles of *n*-propyl- and isopropylcobaloximes. *n*-Propylcobaloxime is a typical primary alkylcobaloxime, producing mainly alkanes in weak base and alkenes in concentrated base. Isopropylcobaloxime is representative of secondary alkylcobaloximes, generating primarily alkenes in all concentrations of base. The butylcobaloximes also demonstrate large changes in the product ratio as the structure of the alkyl group is changed.

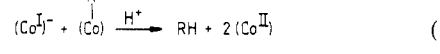
The ethyl derivatives of chelates II–V show that reaction according to eq 3 is typical of vitamin B_{12} model compounds. In addition, these chelates provide examples of coordination by oxygen as well as nitrogen, and the degree of charge donation to cobalt is varied. This influences the ease with which these complexes can be reduced and has consequences that will be discussed below.

Co–C Bond Cleavage by β-Elimination. Of the two hydrocarbon-forming reactions which are induced by base, the pathway leading directly to alkenes is most readily understood and is shown in eq 4. Hydroxide ion causes


(4)

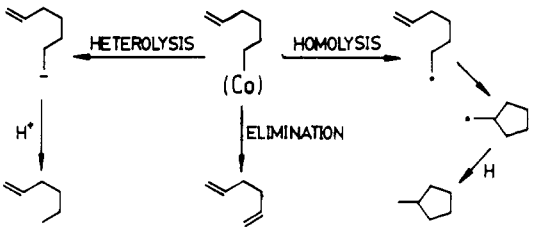
a β-elimination by attacking a β-hydrogen, and two electrons are transferred to cobalt, forming Co(I) and alkene. The formation of Co(I) was confirmed by decomposing isopropylcobaloxime in the presence of ethyl bromide. Co(I) reacts with ethyl bromide to form ethylcobaloxime, which decomposes under the weakly basic conditions employed to form ethane and ethylene. Since ethylene is also formed by the direct dehydrohalogenation ethyl bromide, only ethane formation is diagnostic of the intermediate presence of ethylcobaloxime. Experimentally, a substantial yield of ethane was observed.

The formation of Co(I) in the β-elimination reaction suggested that reductive cleavage of Co–C bonds might also occur in the same solutions. This would produce alkanes[3] according to eq 5. To obtain evidence for this


(5)

reaction, *n*-propyl- and isopropylcobaloximes were decomposed in weak base under an atmosphere of nitrous oxide. This gas rapidly oxidizes Co(I),[14,15] thereby preventing it from inducing reductive cleavage. Hydrocarbon yields from *n*-propylcobaloxime in the presence of nitrous

Scheme I



oxide were identical with those under argon. These results were anticipated since this cobaloxime generates primarily alkanes and only a relatively small percentage of Co(I) under these conditions. However, propane yields from isopropylcobaloxime under nitrous oxide were only half as great as those under argon. These results indicate that Co(I)-induced reductive cleavage can be an important contributing pathway for alkane formation under conditions where alkene formation is predominant.

The ethyl derivatives of chelates II–V vary in the percentages of ethylene formed in weak base. The tendency to generate more ethylene parallels the ease with which these chelates can be reduced to the Co(I) state. Both chemical observations[18] and electrochemical measurements[19] have shown that II and IV are easier to reduce than III and V. Consequently, II and IV provide a better leaving group for the β-elimination reaction, which accounts for the greater percentages of ethylene observed.

Co–C Bond Cleavage by Homolysis. Although it has been shown that alkanes can be generated by a reductive cleavage reaction which accompanies β-elimination, another pathway must also exist to account for the large alkane yields observed under certain conditions. In principle, this pathway could involve the initial formation of either carbanions or radicals. Previous investigators have attempted to differentiate between these possibilities by studying the incorporation of ligand or solvent protons into the ethane produced by ethylcobaloxime.[9] This approach, however, is subject to certain drawbacks, since the ligand protons can exchange with solvent under basic conditions,[20] and both carbanions and radicals could incorporate hydrogen from the ligand methyl groups.[21] Nevertheless, evidence for the formation of radicals was obtained when it was observed that in $CH_3OD/D_2O/OD^-$ solution, ethylcobaloxime-containing deuterated equatorial methyl groups produced 46% C_2H_6 and 54% C_2H_5D.[9]

As an alternative approach to differentiating between radical and carbanion forming mechanisms, we prepared 5-hexenylaquocobaloxime. If radicals are formed initially in the base-induced alkane-forming reaction, this cobaloxime will produce 5-hexenyl radicals. Such radicals are known to cyclize to methylcyclopentyl radicals at a rate of 10^5 s^{-1},[22] as shown in eq 6. The corresponding carbanion


(6)

does not cyclize.[23] Accordingly, base-induced Co–C bond

(18) Schrauzer, G. N.; Sibert, J. W.; Windgassen, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 6681.

(19) Bigotto, A.; Costa, G.; Mestroni, G.; Pellizer, G.; Puxeddu, A.; Reisenhofer, E.; Stefani, L.; Tauzher, G. *Inorg. Chim. Acta, Rev.* **1970**, *4*, 41.

(20) Cartano, A. V.; Ingraham, L. L. *Bioinorg. Chem.* **1977**, *7*, 351.

(21) Since the ligand protons can be removed by hydroxide,[20] it follows that they can also be removed by carbanions. Photolytic studies have shown that radicals can abstract hydrogen from the equatorial methyl groups of cobaloximes.[18]

(22) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.

cleavage of 5-hexenylcobaloxime should produce methylcyclopentane if the reaction is homolytic and 1-hexene if it is heterolytic. In either case, 1,5-hexadiene should also be formed by the β-elimination reaction. This is shown in Scheme I.

When 5-hexenylcobaloxime was, in fact, decomposed in 0.9 M NaOH, the only products detected were methylcyclopentane and 1,5-hexadiene. Thus the Co–C bond cleaves homolytically, to form radicals, in the alkane-forming reaction. Other observations that support this conclusion are the decreases in alkane yields in the presence of oxygen (to be discussed below) and the observation of radical coupling products from ethyl- and *n*-propylcobaloximes (*n*-butane and *n*-hexane, respectively).

Photolysis of alkylcobaloximes is also known to produce radicals and coupling products,[18] as well as alkenes. It is interesting that photolysis of ethylcobaloxime produces predominantly ethylene in neutral and weakly basic solutions, whereas the thermal reaction in weak base produces mainly ethane. Apparently, the photoexcited state, which relaxes to form primarily ethylene and hydridocobaloxime, must be significantly different from the transition state in the thermal reaction leading to ethane and Co(II).

The Effects of Oxygen on Hydrocarbon Yields. Since alkenes were the sole products in the base-induced decompositions of alkylcorrins, it appeared that these compounds reacted only by β-elimination. In this regard the corrins seemed to differ from the model compounds, which underwent both homolysis and β-elimination. However, the possibility remained that the alkylcorrins might also undergo homolysis but that the resulting radicals do not terminate by hydrogen abstraction to yield alkanes. This possibility seemed likely, since vitamin B_{12} has been shown to more resistant to hydrogen abstraction than the model complexes.[18] Oxygen was chosen as a convenient probe for the occurrence of homolysis, since it scavenges radicals efficiently but does not affect the β-elimination reaction.[24]

In accord with the homolytic mechanism discussed in the preceding section, the alkane yields from ethyl- and *n*-propylcobaloximes were substantially reduced in the presence of oxygen. The radicals combine with oxygen to yield alkylperoxy radicals[25] (eq 7) at a rate which is faster

$$RCH_2\dot{C}H_2 + O_2 \longrightarrow RCH_2CH_2OO^{\cdot} \qquad (7)$$

than the rate of hydrogen abstraction from the equatorial ligands. The alkylperoxy radicals must then terminate to yield primarily oxygenated products.[26]

The presence of oxygen also affected the alkene yields, which were increased. This result can be plausibly explained by the rearrangement of a fraction of the alkylperoxy radicals to hydroperoxyalkyl radicals, which then undergo β-scission to yield alkenes[26] as shown in eq 8.

$$RCH_2CH_2OO^{\cdot} \longrightarrow R\dot{C}HCH_2OOH \longrightarrow RCH{=}CH_2 + {}^{\cdot}O_2H \qquad (8)$$

Significant increases in alkene yields via eq 7 and 8 can only be expected when homolysis is favored over β-elimination. Under such conditions, the yield of alkenes by direct elimination is small to begin with, and the number of radicals generated by homolysis is large enough by comparison that only a small fraction of them must terminate by eq 7 and 8 to produce measurable increases in alkene yields. The base profiles of the alkylcobaloximes indicate that these requirements are met when the alkyl group is primary and unbranched and solutions are weakly basic.

Reactions of primary alkylcorrins in weak base in the presence of oxygen produced results similar to those of the cobaloximes. The yields of alkenes after 18 h were increased relative to reactions under argon. This suggests that homolysis does occur and that it is a significant pathway under these conditions.

Under more strongly basic conditions, alkene yields from some of the alkylcorrins were decreased in the presence of oxygen. Yields measured under these conditions represent over 50% of the reaction, and mass balance considerations explain the observed decreases. Under oxygen, some of the Co–C bonds are destroyed by homolysis, combination of the resulting radicals with oxygen, and termination to give oxygenated products. This leaves fewer Co–C bonds to decompose via alkene formation. Under argon, homolysis does not influence the final yields of alkenes, since radicals can rapidly recombine with vitamin $B_{12}r$[27] (eq 9), restoring the Co–C bond for further reaction.

$$R^{\cdot} + [Co^{II}] \longrightarrow \overset{R}{\underset{|}{[Co]}} \qquad (9)$$

The occurrence of homolysis was confirmed when *n*-propylcobinamide produced propane in the presence of 2-propanol, which readily donates hydrogen to radicals.[28] Other alkylcorrins also generated alkanes in the presence of isopropanol but in smaller yields. The greater tendency of *n*-propylcobinamide to form alkanes under these conditions is consistent with the observation that *n*-propylcobaloxime generates more alkanes than most other alkylcobaloximes.

Since oxygen effects indicate that a substantial degree of homolysis occurs when alkylcorrins are decomposed in weak base and only small yields of alkanes were obtained in the presence of 2-propanol, it must be concluded that vitamin $B_{12}r$ scavenges radicals (eq 9) more rapidly than they can abstract hydrogen. The model compounds, on the other hand, undergo homolysis and do produce alkanes. The rate at which these complexes scavenge radicals must be slower than that of vitamin $B_{12}r$, and the radicals can terminate by the abstraction of hydrogen from the equatorial ligands. These conclusions parallel the results of flash photolytic studies, which indicate that vitamin $B_{12}r$ combines with methyl radicals at a near diffusion-controlled rate.[27] The same reaction with Co(II) in vitamin B_{12} model compounds is 1–2 orders of magnitude slower.[27]

Summary

The base-induced decompositions of alkylcobalt complexes containing a β-hydrogen occur by two principal pathways. The first, β-elimination, leads directly to the formation of alkenes. The second, homolysis of the Co–C bond, leads to the formation of alkanes from vitamin B_{12} model compounds but not from alkylcorrins themselves. Nevertheless, the occurrence of homolysis in the base-induced decomposition of alkylcorrins is evident from the effects of oxygen on alkene yields. In a reaction which is secondary to β-elimination, alkanes can be formed by Co(I)-induced reductive cleavage of the Co–C bond.

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Experimental Section

Materials. Hydroxocobalamin was obtained from Merck, Sharp and Dohme Research Laboratories, Rahway, NJ. Dicyanocobinamide was obtained from Calbiochem Behring Corp. Argon was purified by passage through two chromous scrubbers in series, followed by a tube of anhydrous calcium sulfate and a tube of solid KOH. All other reagents and chemicals were commercial products and were used as received or dried and distilled, as necessary.

Methods and Instrumentation. All alkylcobalt compounds were handled in dim light or in aluminum foil wrapped glassware. Lower hydrocarbons (C_2–C_4) were determined on a Varian Aerograph Model 2000 GLC employing a 6 ft × $^1/_8$ in. column packed with phenyl isocyanate on Porasil C (80–100 mesh) with helium as the carrier gas and flame ionization detection. The column temperature was between 25 and 45 °C, depending on the gases being measured. C_6 hydrocarbons were determined with a Hewlett-Packard Model 700 gas chromatograph equipped with an 8 ft × $^1/_8$ in. column of *n*-octane on Porasil C (100–120 mesh) maintained at 115 °C, with helium as the carrier gas and flame ionization detection. Identities of hydrocarbons were verified by cochromatography with authentic commercial samples. No effort was made to detect C_8 or C_{12} hydrocarbons. NMR spectra were determined on either a Varian EM-360 60-MHz NMR spectrometer or on a 360-MHz instrument which has been described in ref 29. Optical absorption spectra were recorded on a Beckman DK-2A recording spctrophotometer.

Base-Induced Co–C Bond Cleavage Reactions of Alkylcobaloximes. All alkylcobaloximes were aquo derivatives and were prepared by standard procedures.[30] They were characterized by 60-MHz NMR spectra. 5-Hexenylaquocobaloxime was characterized by its 360-MHz NMR spectrum. Co–C bond cleavage reactions were carried out in 38-mL serum bottles. In typical experiments, 9 mL of base, prepared by dilution of 50% w/v NaOH or 1.00 M NaOH, was added to each bottle. The bottles were then sealed with silicone septa and flushed with Ar for 1 h via inlet and exit needles. After preheating the bottles to 50 °C, 1 ml of a 1 mg/mL stock solution of the alkylcobaloxime (also dearated for 1 h) was added to each bottle with an Ar-flushed syringe. The resulting solutions were 0.3–8.75 M in NaOH. The bottles were stored for 18 h in a thermostated oven maintained at 50 °C and then allowed to cool prior to analyzing samples from the gas phase by GLC. Some cobalt complexes have limited solubility in strongly basic solutions, which resulted in lowered yields of hydrocarbons in the gas phase. Relative yields of alkenes and alkanes were readily determined, however.

The effects of oxygen on ethyl- and *n*-propylcobaloximes were determined in experiments in which the Ar flushing step was eliminated. Thus, these experiments were done under an atmosphere of air. Decompositions of propylcobaloximes in the presence of nitrous oxide were done by flushing bottles with nitrous oxide for 15 min after the Ar-flushing step. Ethylcobaloxime was photolyzed in anaerobic bottles at 0 °C 15 cm from a 150-W tungsten floodlamp. Photolysis and experiments under oxidizing gases were done by using base concentrations in the 0.3–1.0 M NaOH range.

Decomposition Reactions of Alkylcorrins. Alkylcobalamins were prepared from hydroxocobalamin by the reaction of vitamin B_{12s} with the appropriate alkyl halide. Dicyanocobinamide was converted to cyanoaquocobinamide by phenol extraction from 1 N HCl. This complex was reduced to the Co(I) state and reacted with the appropriate alkyl halide, forming the alkylcobinamide. The latter was dissolved in 1 N HCl and recovered by phenol extraction. Precipitation with ether yielded the alkylaquocobinamide in solid form. The purity of all alkylcorrins were checked by examining their visible spectra. Anaerobic base decompositions were carried out by using the procedures outlined above. Stock solutions of alkylcorrins were 1–10 mM in water (determined spectroscopically). The sole hydrocarbons produced were alkenes. Alkanes were not detected or were present in only trace amounts (<0.1%). After determining the 18-h yields, reaction mixtures were photolyzed. Samples were again removed from the gas phase and analyzed. By these methods, the extent of reaction after 18 h could be readily determined. If alkylcobinamides are not completely freed of cyanide, small amounts of alkanes are formed on decomposition in base. The effects of oxygen on alkene yields were determined in 2.5 and 0.9 M NaOH under an atmosphere of air. Reactions in neutral solutions were carried out in 0.1 N (pH 7) sodium phosphate buffer.

Decomposition Reactions of Ethyl Derivatives of Chelates II–V. Ethyl derivatives of chelates II–V were prepared by standard procedures.[31] Chelate IV was isolated as the tetrafluoroborate salt. Reactions in base were carried out by using the procedures outlined above. Stock solutions of chelates II, III, and V were prepared in methanol (1 mg/mL) due to the relatively low solubility of these complexes in water. The stock solution of chelate IV was 1 mg/mL in water.

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Registry No. II, 82495-42-9; III, 17712-73-1; IV, 53266-17-4; V, 15488-68-3; ethylcobinamide, 18194-92-8; *n*-propylcobinamide, 82495-43-0; isobutylcobinamide, 82510-90-5; ethylcobalamin, 13422-56-5; *n*-propylcobalamin, 13985-72-3; ethylaquocobaloxime, 26025-30-9; *n*-propylaquocobaloxime, 28182-23-2; isopropylaquocobaloxime, 30974-89-1; *n*-butylaquocobaloxime, 30974-86-8; isobutylaquocobaloxime, 29131-78-0; *sec*-butylaquocobaloxime, 57104-96-8; 5-hexenylcobaloxime, 77974-42-6; oxygen, 7782-44-7.

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