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Cobalt Corrin Catalyzed Photoreduction of CO_2

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Cobalt corrins (B_{12}) are found to act as homogeneous catalysts for photoreduction of CO_2 to CO and formic acid. Photoreduction is carried out in acetonitrile/methanol solutions containing *p*-terphenyl as a photosensitizer and triethylamine as a reductive quencher. Photolysis ($\lambda \geq 300$ nm) leads to production of CO and formic acid as well as H_2. The rate of production of all three products is considerably higher with the corrins (hydroxocobalamin, cyanocobalamin, and cobinamide) than with cobalt tetra-*m*-tolylporphyrin. The mechanism of CO_2 reduction in all cases is via a species formed by one-electron reduction of the Co(I) complex. Radiolytic studies of the Co(I) complex formed from hydroxocobalamin in aqueous solutions show that this compound reacts very rapidly with solvated electrons and more slowly [$k = (1.2 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1}] with $CO_2^{\bullet-}$ radicals to produce different products. The initial reduction product is suggested to be mainly the hydride formed by protonation of a Co(0) corrin, $(HCoB_{12})^-$. The product of reaction with $CO_2^{\bullet-}$ is suggested to be the adduct $(CO_2CoB_{12})^{2-}$ or its protonated form $(HO_2CCoB_{12})^-$, identical to the adduct formed by reaction of CO_2 with the photochemically reduced Co(I) corrin, which proceeds to produce CO. H_2 is formed by reaction of the hydride with a proton. Side reactions leading to hydrogenation of the macrocycle also take place and limit the catalytic activity.

Introduction

Interest in reduction of CO_2 as a means of energy storage led to numerous studies on catalyzed electrochemical and photochemical reduction of CO_2.[1] Several transition metal complexes have been shown to act as electron-transfer mediators to catalyze the photochemical reduction of CO_2 to CO and formic acid.[2,3] Recent studies have shown that iron and cobalt porphyrins act as effective homogeneous catalysts for the photochemical process.[4−6] The mechanism was shown to involve reduction of the metal center to its M^0 oxidation state, which then reduces the CO_2. In the present study we demonstrate that Co corrins (B_{12}) also catalyze the reduction of CO_2 and that they are much more efficient catalysts than Co porphyrins under similar conditions.

In comparison with porphyrins, corrins are more saturated compounds; they have 6 instead of 11 double bonds in their tetrapyrrole macrocycle. The reduction potential for the Co^{II}/Co^{I} step in corrins depends on the axial ligand and the benzimidazole binding[7] but is in the same range as for CoTPP. The Co(I) complexes of both porphyrins and corrins are strong reductants and have been shown to reduce various organic halides. However, B_{12} was found to be a more stable catalyst than Co porphyrins in the electrochemical reduction of butyl bromide.[8] This effect was explained by the lower probability of proton attack on the corrin ring as compared with the porphyrin ring. Currently, B_{12} compounds are explored as catalysts for the chemical reduction of halogenated compounds as a means of environmental remediation.[9] In the present study we find Co corrins to be more stable catalysts than Co porphyrins in the photoreduction of CO_2. These two types of catalytic reduction involve different reactive intermediates; while reduction of alkyl halides occurs with the Co(I) complexes, reduction of CO_2 occurs only after the Co(I) complexes are further reduced. Therefore, we also attempted to characterize these highly reduced reactive species by pulse radiolysis studies on the reactions of Co(I) corrins with solvated electrons and with $CO_2^{\bullet-}$ radicals. Such studies cannot be carried out in organic solvents, because of production of other organic radicals that react with the cobalt center, and were, therefore, performed with aqueous solutions.

Experimental Section

Photoreduction of CO_2 with cobalt porphyrins was carried out in acetonitrile solutions containing triethylamine (TEA, 5%, 0.36 mol L^{-1}) as a reductive quencher.[5] The process was further sensitized by the addition of 3 mmol L^{-1} *p*-terphenyl (TP).[6] To examine whether cobalt corrins can catalyze the photochemical reduction of CO_2 and to compare the efficiencies of the two types of macrocyclic complexes, we attempted to carry out experiments with cobalt corrins under the same conditions as those used with the cobalt porphyrins.[5,6] However, this was not possible because the B_{12} compounds used, cyanocobalamin, hydroxocobalamin, and cobinamide (from Sigma),[10] were not sufficiently soluble in acetonitrile. Therefore, we carried out these experiments in acetonitrile/methanol (9/1 v/v) solutions and we performed parallel experiments with CoTTP (cobalt tetra-*m*-tolylporphyrin) in this solvent mixture for comparison.

Solutions (35 mL) in a 43 mL Pyrex bulb were saturated with CO_2 and then photolyzed with a Xe lamp. After various intervals, the headspace was analyzed for CO and H_2 by gas chromatography. In other experiments, 4 mL samples of the CO_2-saturated solutions in 1 cm × 1 cm × 4 cm optical cells were photolyzed for various intervals and then analyzed for CO in the headspace and for formic acid in the solution. Concentrations of formic acid were determined by ion chromatography

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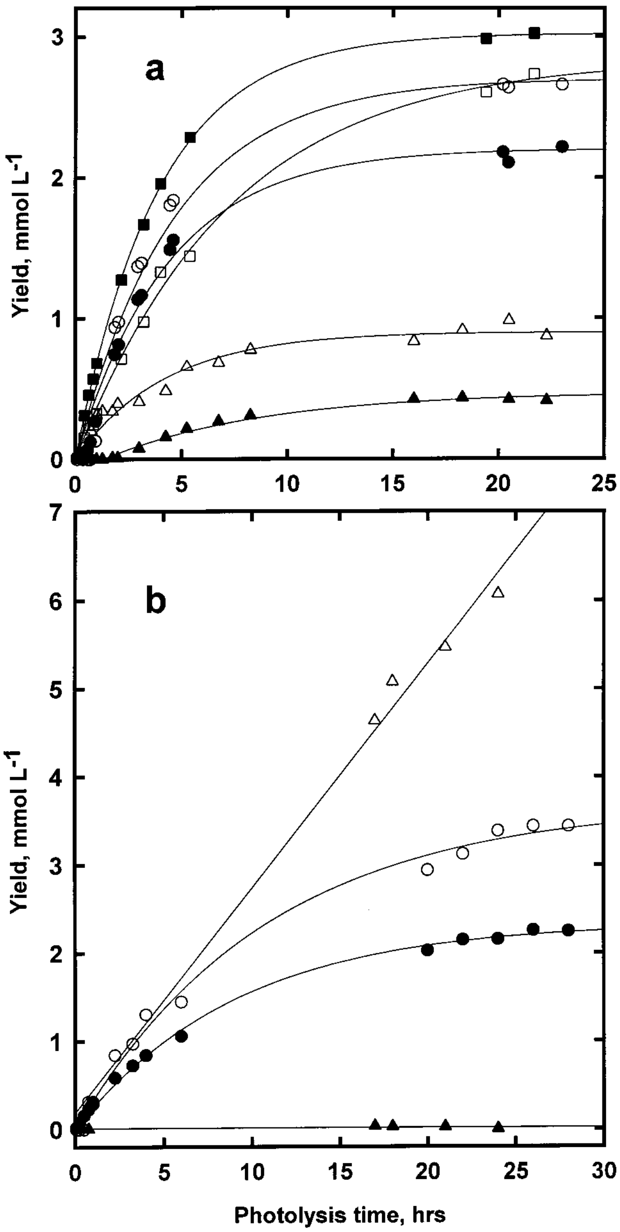

Figure 1. Photochemical production of CO (solid symbols) and H_2 (open symbols). (a) CO_2-saturated acetonitrile/methanol (9/1 v/v) solutions containing 5% TEA, 3 mmol L^{-1} TP, and 0.05 mmol L^{-1} cobalt complex: cyanocobalamin (circles), cobinamide (squares), and CoTTP (triangles). (b) Similar solutions containing hydroxocobalamin under CO_2 (circles) and under He (triangles). The solutions (35 mL) were photolyzed in a Pyrex bulb (headspace 8.4 mL) cooled by a water jacket, placed 10 cm away from an ILC Technology LX-300 UV Xe lamp.

after dilution with water. In both types of photolysis experiments, the irradiation vessel was cooled by water to maintain the solution at room temperature. Further experimental details of the analytical methods and the radiolysis techniques are similar to those given before.[6]

Results and Discussion

The amounts of CO and H_2 produced by photolysis of various solutions are presented in Figure 1. In all of these experiments both CO and H_2 were detected. This is clearly due to competition between CO_2 and protons for the reducing form of the catalyst. The two gases were produced in parallel from the early stages of the photolysis, except in the case of CoTTP, where production of CO appears to be slightly delayed (Figure 1a). Production of both gases stopped after extensive photolysis. The final CO/H_2 mixture contained 31% CO in the case of CoTTP, but a higher percentage of CO with the corrins: 40% with hydroxocobalamin, 45% with cyanocobalamin, and 53% with cobinamide. It is noted, however, that the sums of the yields of the two gases are similar for the three cobalt corrins used and are about 4 times greater than that obtained with CoTTP. The initial rate of production of CO (Table 1) is found to be between 7 and 13 times greater with the cobalt corrins than with CoTTP under identical conditions.[11]

TABLE 1: Photochemical Production of CO and H_2 in Acetonitrile/Methanol (9/1 v/v) Solutions Containing 5% TEA, 3 mmol L^{-1} TP, and 0.05 mmol L^{-1} Co Complex, Saturated with Either CO_2 or He[a]

		initial rate of formation, mmol L^{-1} h^{-1}		total yield, mmol L^{-1}	
complex	gas	CO	H_2	CO	H_2
CoTTP	CO_2	0.037	0.07	0.41	0.92
cyanocobalamin	CO_2	0.35	0.46	2.21	2.66
hydroxocobalamin	CO_2	0.25	0.43	2.25	3.44
hydroxocobalamin	He	0	0.26	0	6.07[b]
cobinamide	CO_2	0.48	0.30	3.02	2.73

[a] Other conditions as in Figure 1. The estimated standard uncertainties are ±10% for the values of CO and ±20% for the values of H_2. [b] Continues to increase; see Figure 1b.

To confirm that the source of CO is the CO_2, we conducted parallel experiments with identical solutions saturated with He instead of CO_2. We find that the yield of CO becomes undetectably low under He while the yield of H_2 rises linearly to values that exceed the total yield of both gases observed with CO_2-saturated solutions (Figure 1b). Blank experiments with CO_2-saturated solutions in the absence of B_{12} produced no detectable amounts of CO.

The yield of formate after various irradiation times could not be measured in the same experiment (except at the end of the photolysis). It was measured following irradiation of 4 mL samples in small optical cells. The yield of CO was also determined in these experiments, though less accurately than in the large bulb, but the yield of H_2 could not be determined with a reasonable accuracy except after very long irradiations. The yields of CO and formate are compared in Figure 2. The absolute yields of CO in Figure 2 are higher than those presented in Figure 1 due to the use of a different cell and different irradiation geometry. In the early stages of photolysis, both hydroxocobalamin and CoTTP produce less formate than CO, although the rates of production are about 5 times greater with the hydroxocobalamin than with the porphyrin (Figure 2). At longer irradiations, the yield of formate rises to higher levels than the yield of CO with hydroxocobalamin but not with the porphyrin. The total yield of formate is about 7 times higher with hydroxocobalamin than with CoTTP. Blank experiments in the absence of Co complexes gave no detectable CO and barely detectable amounts of formate (<0.1 mmol L^{-1}).

These results show that the cobalt corrins are much more efficient catalysts than cobalt porphyrins; they catalyze production of CO and formate from the early stages of photolysis at higher rates and they persist longer in solution to provide higher total yields under the present conditions (Figures 1 and 2). The total yields of products indicate turnover numbers >100 product molecules per B_{12} molecule consumed. Experiments with cobaloxime, often used as a model for B_{12}, gave very low yields of CO due to the lability of such a complex.

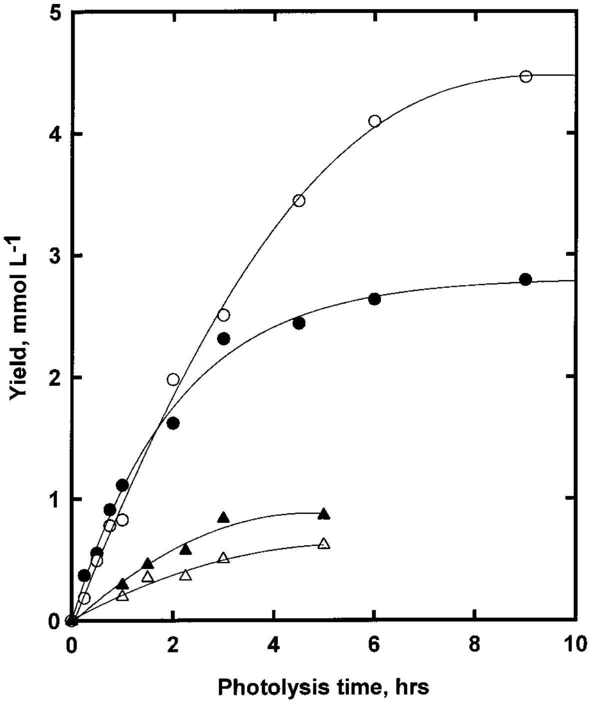

Figure 2. Photochemical production of CO (solid symbols) and HCOOH (open symbols) in CO_2-saturated acetonitrile/methanol (9/1 v/v) solutions containing 5% TEA, 3 mmol L^{-1} TP, and 0.05 mmol L^{-1} hydroxocobalamin (circles) or CoTTP (triangles). The solutions (4 mL) were photolyzed in a 1 × 1 × 4 cm optical cell cooled in a water bath, placed 10 cm away from the Xe lamp.

The mechanism for the catalyzed reduction of CO_2 by cobalt corrins must be similar to that for cobalt porphyrins. In both cases, the Co(I) complexes are stable in the presence of CO_2 and only their reduction products react with CO_2. This is demonstrated for hydroxocobalamin under our experimental conditions by the results shown in Figure 3. The figure shows the absorption spectrum of the Co(III) complex in ACN/MeOH/TEA solutions (λ_{max} 356, 533 nm) and the spectra of the Co(II) (λ_{max} 473 nm) and the Co(I) (λ_{max} 392 nm) complexes formed by photolysis. The latter species was stable for many hours in the presence of CO_2. From the spectral evolution as a function of photolysis time we estimate that the photochemical efficiency for reduction of the Co(II) corrin is lower than that for reduction of the Co(III) complex by a factor of 6.5. Furthermore, we find that in the presence of 3 mmol L^{-1} TP both photochemical yields are increased, by a factor of 2.3 for the first reduction and by a factor of 3 for the second reduction. These results parallel those found with the metalloporphyrins.[6]

Further photolysis of the Co(I) corrin under CO_2 leads to slow changes in absorption; the main peak at 392 nm decreases by a factor of 5 and shifts to 400 nm, and most of the absorption at longer wavelengths disappears to leave only a shoulder at 500 nm and a very weak shoulder at 600 nm (Figure 3). The product appears to have a yellowish color. The time of photolysis required to reach this stage is longer than the time required for the first two reduction steps, by a factor of 60 in the presence of TP and by a factor of 300 in the absence of TP. These spectral changes are ascribed to hydrogenation of the corrin macrocycle occurring as a side reaction in the reduction process. By comparing the time of evolution of these spectra and the time dependence of the production of CO and formate under identical conditions (Figure 2), we conclude that the yellowish products also catalyze the photoreduction of CO_2.

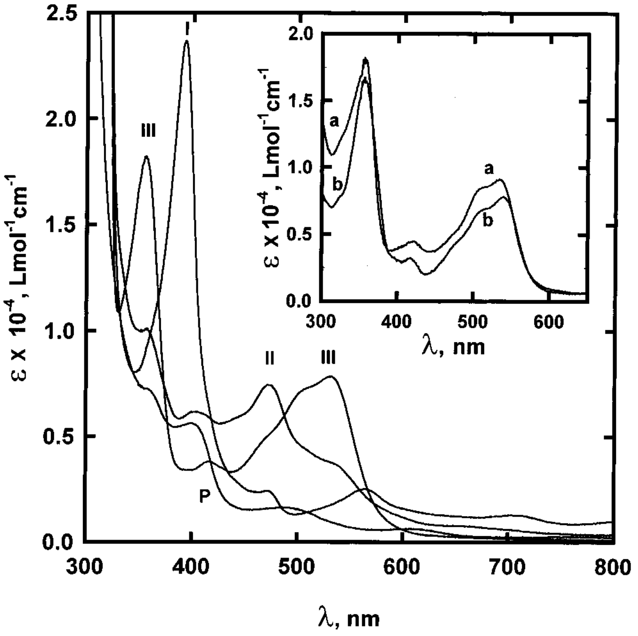

Figure 3. Photochemical reduction of hydroxocobalamin (0.05 mmol L^{-1}) in CO_2-saturated acetonitrile/methanol (9/1 v/v) solutions containing 5% TEA and 3 mmol L^{-1} TP. The solutions (4 mL) were photolyzed in a 1 × 1 × 4 cm optical cell cooled in a water bath, placed 10 cm away from the Xe lamp. The spectra of the Co(III), Co(II), and Co(I) complexes are labeled according to their oxidation state, II was formed within 20 s and I was formed within 2 min. The spectrum labeled P is that of the final product after 4 h of photolysis. The strong absorption seen below 330 in all the spectra is that of TP. The inset shows the spectrum of hydroxocobalamin in acetonitrile/methanol in the absence of TP, with (a) and without (b) 5% TEA.

From these results, and by comparison with earlier results on metalloporphyrins, we can summarize the photochemical processes taking place in the present system as follows. Photoreduction of the Co(III) corrins by TEA is an efficient process involving intramolecular electron transfer from an axially bound TEA to the metal center. That TEA binds to the Co(III) center was confirmed by the change in the spectrum of hydroxocobalamin in ACN/MeOH upon addition of TEA (the peak at 539 nm shifts to 533 nm and its molar absorption coefficient increases, Figure 3 insert).

$$(Et_3N{-}Co^{III}B_{12})^+ \xrightarrow{h\nu} Et_3N^{\bullet +} + Co^{II}B_{12} \qquad (1)$$

$$Et_3N^{\bullet +} + Et_3N \rightarrow Et_3NH^+ + Et_2NC^{\bullet}HCH_3 \qquad (2)$$

$$Et_2NC^{\bullet}HCH_3 + (Co^{III}B_{12})^+ \rightarrow Et_2N^+{=}CHCH_3 + Co^{II}B_{12} \qquad (3)$$

Photoreduction of the Co(II) and Co(I) corrins, however, probably involves a less efficient bimolecular processes, since TEA does not appear to bind to the lower oxidation states.

$$Co^{II}B_{12} + Et_3N \xrightarrow{h\nu} Co^{I}B_{12}^{\ -} + Et_3N^{\bullet +} \qquad (4)$$

$$Co^{I}B_{12}^{\ -} + Et_3N \xrightarrow{h\nu} Co^{0}B_{12}^{\ 2-} + Et_3N^{\bullet +} \qquad (5)$$

The photochemical yields are enhanced in the presence of TP because this compound is very effectively photoreduced by TEA[12] to produce the radical anion, $TP^{\bullet -}$, which in turn reduces all the Co corrins very rapidly.

$$\mathrm{TP} \xrightarrow{h\nu} \mathrm{TP}^* \tag{6}$$

$$\mathrm{TP}^* + \mathrm{Et_3N} \rightarrow \mathrm{TP}^{\bullet-} + \mathrm{Et_3N}^{\bullet+} \tag{7}$$

$$\mathrm{TP}^{\bullet-} + \mathrm{Co^{II}B_{12}} \rightarrow \mathrm{TP} + \mathrm{Co^{I}B_{12}}^{-} \tag{8}$$

$$\mathrm{TP}^{\bullet-} + \mathrm{Co^{I}B_{12}}^{-} \rightarrow \mathrm{TP} + \mathrm{Co^{0}B_{12}}^{2-} \tag{9}$$

Rate constants for these electron-transfer reactions were found to be near the diffusion-controlled limit for cobalt porphyrins[5] and phthalocyanines (to be published) and are expected to be very high for the corrins as well. The product of reduction of the Co(I) complex is written in reactions 5 and 9 as a Co(0) complex by analogy with the porphyrins.

Previous studies with iron and cobalt porphyrins[4−6,13] indicated that the metalloporphyrins are reduced to their $\mathrm{M^0P^{2-}}$ state which then react with CO_2. Similar steps may be assumed for the corrins.

$$\mathrm{Co^{0}B_{12}}^{2-} + \mathrm{CO_2} \rightarrow (\mathrm{CO_2CoB_{12}})^{2-} \tag{10}$$

$$(\mathrm{CO_2CoB_{12}})^{2-} + \mathrm{H^+} \rightarrow \mathrm{Co^{II}B_{12}} + \mathrm{CO} + \mathrm{OH^-} \tag{11}$$

In competition with this process, $\mathrm{Co^0B_{12}}^{2-}$ also reacts with protons to yield H_2.

$$\mathrm{Co^{0}B_{12}}^{2-} + \mathrm{H^+} \rightarrow (\mathrm{HCoB_{12}})^{-} \tag{12}$$

$$(\mathrm{HCoB_{12}})^{-} + \mathrm{H^+} \rightarrow \mathrm{Co^{II}B_{12}} + \mathrm{H_2} \tag{13}$$

Although Co(I) corrins also can react with protons to form the hydride and then molecular hydrogen,[14] in parallel with reactions 12 and 13, they do so only in acidic solutions and not under the conditions of the current photochemical experiments. Formate ions may be produced from the hydride by insertion of CO_2, as suggested for other metal complexes.[3c] In addition to these catalytic reactions, a side reaction leads to hydrogenation of the corrin double bonds, probably via protonation of the $\mathrm{Co^0B_{12}}^{2-}$ on a ring carbon. This leads to decoloration of the corrin as discussed above. The hydrogenated complexes also act as catalysts for reduction of CO_2 until they are deactivated or decomposed (see below).

In an attempt to characterize the product of reduction of Co(I) corrin and the CO_2 adduct, we carried out pulse radiolysis experiments. These experiments could not be carried out in the same solvent mixture or in other organic solvents because irradiation of these solvents produces organic radicals that react with the cobalt center to form additional products. Therefore, they were carried out in aqueous solutions containing formate ions, where irradiation produces only e_{aq}^- and $CO_2^{\bullet-}$ radicals. In earlier pulse radiolysis studies,[15] both of these species have been shown to react with Co(III) and Co(II) corrins rapidly. However, production of Co(I) corrin by γ-radiolysis under those conditions was not quantitative. In agreement with those results, we find that γ-radiolytic reduction of hydroxocobalamin (λ_{max} 358, 536 nm, ϵ_{358} 19 700 L mol^{-1} cm^{-1})[16] in deoxygenated aqueous solutions containing formate ions at pH 9 leads to quantitative formation of the Co(II) complex (λ_{max} 312, 475 nm) (Figure 4a).[17] Subsequent irradiation, however, leads to incomplete yield of the Co(I) complex (λ_{max} 388 nm) (87%), probably because of partial reaction at the benzimidazole ring. Therefore, to examine the reduction of the Co(I) complex by pulse radiolysis, we chose to produce it quantitatively by reduction with sodium borohydride[18] rather than by radiolytic reduction.

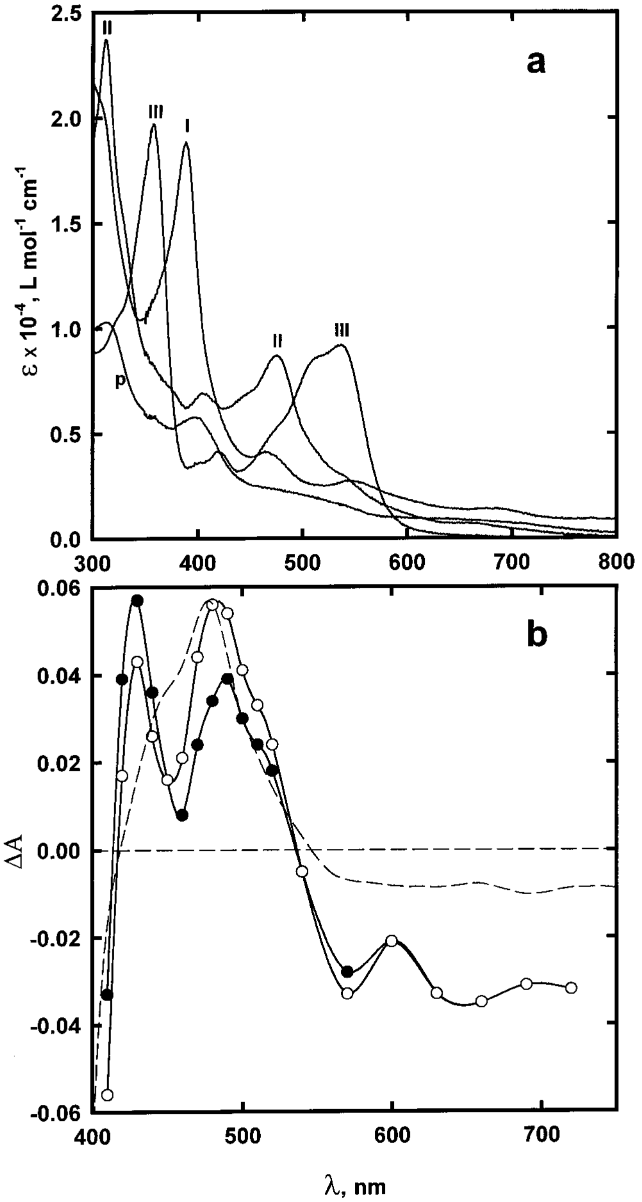

Figure 4. Radiolytic reduction of hydroxocobalamin in aqueous solutions containing 0.1 mol L^{-1} sodium formate and 0.01 mol L^{-1} sodium tetraborate at pH 9, deoxygenated by bubbling with ultrahigh purity Ar. (a) Spectra of the Co(III), Co(II), and Co(I) complexes, labeled accordingly, and of the bleached product (P) formed by γ-radiolysis. (b) Differential spectra observed by pulse radiolysis of the Co(I) complex, formed by reduction of the above starting solution with borohydride (see text), 3 μs (●) and 300 μs (○) after the pulse. The dashed line is the calculated ($\mathrm{Co^{II}B_{12}} - \mathrm{Co^{I}B_{12}}$) differential spectrum.

Aqueous solutions containing between 0.03 and 0.1 mmol L^{-1} hydroxocobalamin and generally 0.1 mol L^{-1} sodium formate and 0.01 mol L^{-1} sodium tetraborate as buffer were deoxygenated by bubbling with Ar, and then excess sodium borohydride was added. The solutions were left to stand in a syringe for 2−3 h until all the Co(III) was reduced to Co(I) and most of the excess borohydride decomposed. Then aliquots were transferred anaerobically to the irradiation cell, where they were irradiated with an electron pulse and their optical absorption was monitored as a function of time after the pulse. Two processes were observed: a rapid process showing the decay of the e_{aq}^- absorption and formation of another transient absorption, which was complete within a few microseconds, and a slower process, taking place over several hundred microseconds. Since the slower process was not observed in the absence of formate (using excess borohydride at high pH to scavenge the OH radicals) and since the rate of this slower process was linearly dependent on the concentration of the corrin complex, we ascribe it to reaction of the $CO_2^{\bullet-}$ radicals with the complex. From the linear dependence we calculate a rate constant of $(1.2 \pm 0.3) \times 10^8$ L mol^{-1} s^{-1} for the reaction of $Co^IB_{12}^-$ with $CO_2^{\bullet-}$ radicals. This value is about 1 order of magnitude lower than the rate constant for reaction of this radical with the Co(II) and the Co(III) oxidation states.[15] From the rate of the e_{aq}^- decay, we estimate a rate constant of $\approx 1 \times 10^{10}$ L mol^{-1} s^{-1} for the reaction of $Co^IB_{12}^-$ with e_{aq}^-.

The differential absorption spectrum recorded at the end of the fast process shows bleaching of the Co(I) corrin absorptions at the long wavelengths and formation of absorption with two peaks, at 430 and 490 nm (Figure 4b, solid circles). We assume that most of the hydrated electrons react with the cobalt center or the associated macrocycle to form a species that may be formulated as $Co^0B_{12}^{2-}$ but with some radical anion character.

$$Co^IB_{12}^- + e_{aq}^- \rightarrow Co^0B_{12}^{2-} \qquad (14)$$

This product is a strong nucleophile, which is likely to abstract a proton from water very rapidly and form the hydride.

$$Co^0B_{12}^{2-} + H_2O \rightarrow (HCoB_{12})^- + OH^- \qquad (15)$$

The hydride can react with water to yield molecular hydrogen.

$$(HCoB_{12})^- + H_2O \rightarrow Co^{II}B_{12} + H_2 + OH^- \qquad (16)$$

Since the differential spectrum observed several microseconds after the pulse (Figure 4b, solid circles) is not similar to the calculated $(Co^{II} - Co^I)$ difference spectrum (Figure 4b, dashed line), we ascribe this spectrum to the hydride formed by reaction 15. In addition to reduction of the central Co(I) corrin moiety, hydrated electrons are expected to react also at the benzimidazole moiety. This process is not likely to be followed by rapid electron transfer to the metal center, because the benzimidazole ring is not attached to the Co center at the Co(I) oxidation state.[7]

The differential spectrum recorded after the slower process (Figure 4b, open circles) is different from the early spectrum (solid circles) in the relative intensities of the two positive peaks. Therefore, we assume that the reaction of $Co^IB_{12}^-$ with $CO_2^{\bullet-}$ radicals does not involve electron transfer but rather addition of the radical to the cobalt center.

$$Co^IB_{12}^- + CO_2^{\bullet-} \rightarrow (CO_2CoB_{12})^{2-} \qquad (17)$$

The spectra of R−Co and H−Co complexes are generally similar, and thus the similarity in the peak positions of the early spectrum and the late spectrum is not surprising if we assume the above assignments. The adduct formed by reaction 17 may exist as formulated or may be protonated at the carboxyl moiety to form $(HO_2CCoB_{12})^-$. The adduct of $CO_2^{\bullet-}$ with $Co^IB_{12}^-$ is the same as that produced by reaction of $(Co^0B_{12})^{2-}$ with CO_2 (reaction 10) and will proceed to yield CO as in reaction 11.

The spectrum observed in Figure 4b (open circles) does not change over several milliseconds. The absorbance between 420 and 520 nm decays at longer times, with a first-order rate constant of (0.8 ± 0.4) s^{-1}, but the negative signals between 550 and 700 nm do not recover. This indicates that the decay does not lead to formation of the original $Co^IB_{12}^-$. The decay of the hydride could not be observed separately and thus it is not possible to conclude whether the hydride decomposed at the same time as the CO_2 adduct or during the formation of the CO_2 adduct. In any case, if the decay of the hydride and the CO_2 adduct is mainly via reactions 13 and 11, respectively, the only absorbing final product is expected to be $Co^{II}B_{12}$. However, the spectrum of the final product, monitored several seconds after the pulse, is not in agreement with that expected for formation of $Co^{II}B_{12}$ only (dashed line, Figure 4b). This suggests that other routes, leading to hydrogenation of the corrin macrocycle, also contribute to the observed decay and these are more important in the radiolytic experiments in aqueous solutions than in the photochemical experiments in organic solvents.

As mentioned above, photochemical production of CO and H_2 results also in the formation of hydrogenated complexes as side products. These complexes also catalyze the photoreduction process, but eventually the reaction stops. The limit is not due to depletion of TEA or TP but rather to decomposition of the corrin and accumulation of CO. Previous results with metalloporphyrins indicated that one of the main reasons for termination of the photoreduction process is the accumulation of CO in the solution. This effect was ascribed to binding of CO to the metal center to compete with the binding of CO_2. It was shown,[6] however, that CO does not bind to Co^0P^{2-} and, therefore, it was suggested that the hydrogenated complexes may react with CO_2 in their M^I oxidation state (as is the case with Co cyclam and similar complexes)[3] instead of the M^0 state and that CO binding to the M^I complexes inhibits CO_2 reduction. Such a mechanism may explain the termination of the catalytic process in the present system.

Recent results with iron porphyrins[6] and iron ions[19] indicated that continuous photoreduction of the iron porphyrin leads to demetalation but the released iron ions continue to catalyze the reduction of CO_2 until considerable amounts of CO are accumulated and terminate the process. Such a mechanism does not operate in the present case since free cobalt ions are not found to act as catalysts for photoreduction of CO_2 under the present conditions. Therefore, if the corrin macrocycle is highly hydrogenated and the metal ion is released, the catalytic process stops. Extension of the lifetime of the catalyst may be achieved by protecting the complex from hydrogenation, either by controlling the source of protons in the medium or by incorporating the complex into a protective matrix.

The present results indicate that the Co corrins are more effective catalysts than the Co porphyrin examined under the same conditions. The reason for this difference may lie in the fact that the main corrin macrocycle has only 6 double bonds, as compared with 11 double bonds in the porphyrin. When both macrocycles have a highly reduced Co center, the probability of protonation at the corrin macrocycle is lower than that at the porphyrin. This argument was advanced previously[8] to explain the advantage of B_{12} over Co porphyrin in the electrocatalytic reduction of halides, which takes place through a Co(I) complex, and should be valid as well for the photocatalytic reduction of CO_2, which takes place through a further reduced species. This comparison suggests that if the macrocycle is further saturated, to diminish the likelihood of protonation, the catalytic process may become even more efficient. However, by comparison with the earlier results obtained with Co cyclam and related complexes,[3c] it may be expected that the mechanism of catalysis will be different with the more saturated complexes; i.e., it will involve CO_2 binding to the Co(I) oxidation state followed by another reduction reaction. Nevertheless, if we compare the overall yields obtained in the present experiments with the Co corrins to the earlier results obtained with the various Co cyclam derivatives,[3c] we find that the corrins give comparable or better yields, depending on the particular complexes compared. Although these two groups of compounds are quite different in structure, this comparison suggests that it may be more advantageous to attempt to protect the catalysts against deactivation by preventing hydrogenation of the macrocycle rather than by starting with a more saturated macrocycle.

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(10) The mention of commercial equipment or material does not imply recognition or endorsement by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

(11) It should be noted that CoTTP is found to be a less efficient catalyst in the present experiments in acetonitrile/methanol solutions than in the earlier experiments in acetonitrile solutions without methanol.[6] Both the initial rate of production and the total yield are lower in the presence of MeOH, by a factor of 6 for CO and by a factor of 2 for H_2. The B_{12} compounds could not be studied in acetonitrile without methanol but were sufficiently soluble in *N*,*N*-dimethylformamide. The initial rate of photochemical CO production in DMF was 6.4 times higher with hydroxocobalamin than with CoTTP.

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