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Photolysis of methylcobalamin. Nature of the reactive excited state

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Abstract

Photolysis of methylcobalamin ($Co^{III}corrin(CH_3)L + H_2O + O_2 \rightarrow Co^{III}(H_2O)L + H_2CO + OH^-$) shows a pronounced wavelength dependence. It is suggested that the reactive excited state is of the ligand-to-ligand charge transfer (LLCT) type and involves the promotion of an electron from the Co–C σ-bond to a π^*(corrin) orbital. This LLCT transition mixes with the $\pi\pi^*$(corrin) transitions. Owing to this LLCT contribution, the $\pi\pi^*$-absorption bands are also photoactive but with reduced efficiency.

1. Introduction

Light sensitivity is one of the outstanding features of vitamin B_{12} and its derivatives such as the cobalamins [1–6]. Although the photochemistry of these compounds has been studied extensively, the reactive excited states have in most cases not been identified. Cyanocobalamin seems to be an exception. Evidence was obtained that the photoaquation of cyanocobalamin is initiated by excited ligand field states [7,8]. Generally, the identification of reactive excited states of cobalamins is hampered by the fact that their absorption spectra are dominated by the intense $\pi\pi^*$ intraligand bands of the corrin ligand. Any other absorptions are obscured by the corrin bands [1,5].

The photolysis of alkylcobalamins involves the homolysis of the Co^{III}–carbon σ-bond in the primary photochemical step [9]. By analogy with simple Co^{III} complexes [10], especially those with a Co–C bond [11,12], including cobaloximes [3,5], it may be assumed that the reactive excited states are of the ligand-to-metal charge transfer (LMCT) type. However, for alkylcobalamins, clear spectroscopic evidence for such an assignment has not yet been obtained. The present investigation was undertaken to explore the nature of the reactive excited state of methylcobalamin.

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2. Experimental details

2.1. Materials

Methylcobalamin was purchased from Aldrich and used as received. Its absorption spectrum ($\lambda_{max} = 267$ nm, $\epsilon = 16,300$; $\lambda_{max} = 282$ nm, $\epsilon = 15,400$; $\lambda_{max} = 290$ nm, $\epsilon = 14,000$; $\lambda_{max} = 317$ nm, $\epsilon = 11,000$; $\lambda_{max} = 342$ nm, $\epsilon = 11,700$; $\lambda_{max} = 376$ nm, $\epsilon = 9600$; $\lambda_{sh} = 432$ nm, $\epsilon = 3100$; $\lambda_{sh} = 495$ nm, $\epsilon = 6450$; $\lambda_{max} = 523$ nm, $\epsilon = 760$; $\lambda_{sh} = 556$ nm, $\epsilon = 5100$) agreed well with that reported previously [13]. The water used in the photochemical experiments was triply distilled.

2.2 Photolyses

The light source was an Osram HBO 100 W/2 lamp. The mercury lines at 254, 280, 313, 333, 366, 436, 546, and 577 nm were selected by use of Schott PIL/IL interference filters. Solutions of methylcobalamin were photolyzed in 1-cm spectrophotometer cells at room temperature. For quantum yield determinations the concentrations of methylcobalamin were such as to give essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer (which was calibrated) equipped with an RkP-345 detector.

Progress of the photolysis was monitored by UV-visible spectral measurements with a Shimadzu UV-2100 spectrophotometer. The photoproduct aquocobal-

amin was identified by its absorption spectrum (λ_{max} = 350 nm, ϵ = 25,600).

3. Results and discussion

The photolysis of aqueous methylcobalamin is well known to lead to the homolysis of the cobalt–carbon σ-bond in the primary photochemical step [9] (L = benzimidazole):

$$Co^{III}(corrin)(CH_3)L \longrightarrow Co^{II}(corrin)L + {}^{\cdot}CH_3$$

In the absence of oxygen an efficient regeneration of methylcobalamin takes place, while in the presence of oxygen an irreversible product formation occurs [1–6]:

$$Co^{III}(corrin)(CH_3)L + O_2 + H_2O \longrightarrow$$

$$Co^{III}(corrin)(H_2O)L + H_2CO + OH$$
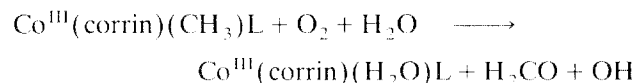
As indicated by the spectroscopic changes that accompany the photolysis (Fig. 1), the photoconversion of methylcobalamin to aquocobalamin is a very clean reaction that can be driven to completion. Interestingly, the quantum yield is not independent of the irradiating wavelength (Table 1). This quantum yield profile was observed qualitatively by Taylor et al. [13], but the variations observed in the present study are much larger, and should be useful for the identification and characterization of the reactive excited state. The quantum yield maximum coincides with the absorption maximum at λ = 317 nm (Fig. 1). Towards longer wavelength, the quantum yield drops. This decrease is not monotonous. Between 333 and 436 nm, a plateau is reached.
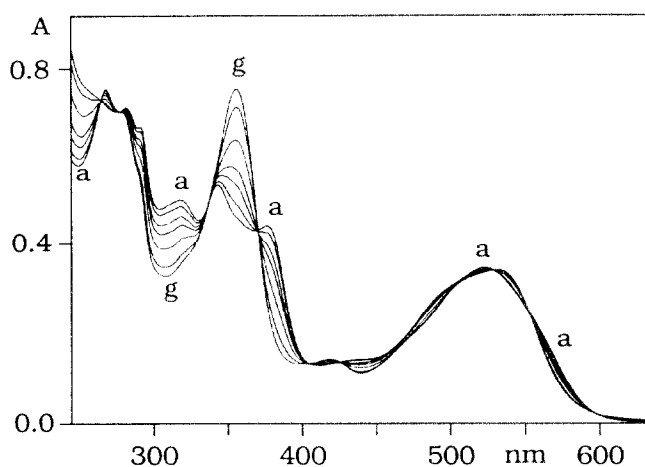

Fig. 1. Spectral changes during the photolysis of 4.76×10^{-5} M methylcobalamin in water at (a) 0, 1, 3, 5, 10, 30, and (g) 60 min irradiation times, with λ_{irr} = 546 nm (Osram HBO 100 W/2 lamp) and a 1-cm cell.

λ_{irr} (nm)							
254	280	313	333	366	436	546	577
Quantum yield 0.12	0.18	0.31	0.19	0.15	0.16	0.067	0.075

We suggest that the photolysis of methylcobalamin is initiated by a ligand-to-ligand charge transfer (LLCT) [14] excited state which involves the promotion of an electron of the cobalt–carbon σ-bond to a π^* orbital of the corrin ligand. This type of LLCT reactivity has been recently also observed for $Zn^{II}(R-DAB)R'_2$ with R–DAB = 1,4-diaza-1,3-butadiene and R' = alkyl or aryl anions [15]. LLCT (R' to R–DAB) excitation leads to the release of a radical R'.

In keeping with the maximum efficiency of the photolysis (Table 1), we assign the absorption band at λ_{max} = 317 nm to the LLCT (CH$_3$ to corrin) transition of methylcobalamin. We assume that the LLCT transition undergoes configuration interaction with the $\pi\pi^*$ corrin intraligand transitions that occur at lower energies. Corrin intraligand excitation at wavelengths above 313 nm is then also associated with the release of a methyl radical but with reduced efficiency. The assumption of LLCT/$\pi\pi^*$(corrin) mixing is supported by the following considerations, which are based on our knowledge of the electronic spectra of metalloporphyrins [16]. The metalloporphyrins are well suited for a comparison because for them the spectra and theory are much simpler [16] than those of metallocorrins [1,6]. Nevertheless, some basic features of the electronic structures and spectra are quite similar.

The electronic structures and spectra of metalloporphyrins have been studied, especially by Gouterman et al., who developed the four-orbital model [16]. In D_{4h} symmetry, the HOMOs of the porphyrin ligand are π orbitals of a_{1u} and a_{2u} symmetry. The LUMO is a degenerate π^* e_g orbital. The two lowest-energy transitions involve the promotion of an electron from the a_{1u}/a_{2u} orbitals to the e_g orbital. The corresponding absorptions appear as the Q($\alpha + \beta$) band at longer wavelengths and the B or Soret (γ) band at shorter wavelengths. Many metalloporphyrins display this "regular" absorption spectrum [16]. However, deviations ("irregular porphyrins") are well known [16]. In the context of the present study the "hyper porphyrins" are of particular interest. If an additional $a_{2u} \rightarrow e_g$ transition of different origin occurs in the same energy region as the $a_{2u} \rightarrow e_g$ $\pi\pi^*$ transition of the porphyrin, they mix by configuration interaction [16]. In such cases two absorptions appear in the Soret region. One is shifted to longer wavelength with respect to the

regular position. It appears with reduced intensity. The other band appears at shorter wavelength. Well-documented cases are p-type hyperporphyrins with metals such as Sn^{2+}, Pb^{2+} and Sb^{3+} which possess an extra electron pair in their p_z valence orbital [16,17]. It is of a_{2u} symmetry in D_{4h} metalloporphyrins and located at relatively high energies. The a_{2u} (p_z) to e_g π^* (porphyrin) metal-to-ligand charge transfer (MLCT) transition mixes with the a_{2u} π to e_g π^* intraligand porphyrin transition. Accordingly, a split Soret band is observed.

Six-coordinate metalloporphyrins M(porphyrin)LL' may be also of the hyper type if the axial ligands provide appropriate filled orbitals. Cytochrome P-450 displays a characteristic hyper spectrum with a split Soret band. It consists of a longer wavelength $\pi\pi^*$ absorption at 450 nm and a shorter wavelength LLCT band which is assigned to the transition from the axial mercaptide ligand to the π^* orbitals of the porphyrin [14,16–20].

Typical hyper spectra are apparently also displayed by organometallic d^6 metalloporphyrins of the form M(porphyrin)(R)L with R = alkyl [21]. For example, Co^{III}(TPP)R(pyridine) with TPP = tetraphenylporphyrin and R = CH_3, C_2H_5 or C_3H_7 show the split Soret band at 370 and 430 nm. We suggest that both bands originate from two $a_{2u} \rightarrow e_g$ transitions which are of the mixed LLCT (R to porphyrin)/intraligand $\pi\pi'$ (porphyrin) type. The axial ligands are characterized by a σ-orbital of a_{2u} symmetry, which is derived from the t_{1u} orbitals in O_h symmetry. In the case of the alkyl complexes, this a_{2u} orbital should occur at rather high energies owing to the presence of the cobalt–carbon σ-bond. Accordingly, both $a_{2u} \rightarrow e_g$ transitions are expected to occur at comparable energies and can mix efficiently. A similar hyper spectrum was also observed for $[Ir^{III}(OEP)(C_8H_{13})(CO)]$ with OEP = octaethylporphyrin [22]. The influence of σ-donation by axial ligands on the a_{2u} π porphyrin orbital seems to be of general significance [23,24]. However, if the a_{2u} σ-orbital of the axial ligands is quite stable and occurs at much lower energies than the a_{2u} π porphyrin orbital, LLCT/$\pi\pi^*$ (porphyrin) mixing will be rather small. The spectrum is then regular as it is observed for many other d^6 metalloporphyrins [16].

Let us now return to methylcobalamin. Although the corrin ligand is related to the porphyrin ring, detailed assignments of absorption bands are complicated by the lower symmetry of the corrin [1,5]. Fortunately, the basic pattern of the $\pi\pi^*$ spectra is similar to that for the porphyrins [1,5]. Cobalamins display a Q band that consists of α and β components and a B or Soret (γ) band. Some compounds such as cyanocobalamin show a regular (or "typical") [1] $\pi\pi^*$ corrin

spectrum (Soret band $\lambda_{max} = 361$ nm) while alkylcobalamins are "atypical" [1] or, in the terminology of porphyrins, are hyper-type [16]. On the basis of the quantum-yield profile of methylcobalamin and in analogy to alkylmetalloporphyrins (see above), we assign the band at $\lambda_{max} = 317$ nm to the LLCT transition from the cobalt–carbon σ-bond to the porphyrin π^* orbitals. The absorptions at $\lambda_{max} = 342$ and 376 nm are then assigned to the Soret transition which, however, has considerable LLCT character, as indicated by their photochemical activity. The wavelength-dependence of the quantum yield seems to reflect a decreasing LLCT contribution to the $\pi\pi^*$ corrin transitions with decreasing energies. Calculations on methylcobalamins [25] seem to support our conclusions. However, the interpretation of the electronic spectra [25–30] does not lead to unambiguous assignments [1,5]. The low symmetry of the corrin ligand introduces serious complications that can be avoided by using porphyrin complexes as suitable models.

Acknowledgment

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