PHOTOLYSIS OF ALKYLCOBALOXIMES, METHYL-SALEN, COBALAMINES AND COENZYME B_{12} IN PROTIC SOLVENTS: AN ESR AND SPIN-TRAPPING TECHNIQUE STUDY

Ph. MAILLARD and C. GIANNOTTI *

Institut de Chimie des Substances Naturelles, C.N.R.S., 91190 Gif sur Yvette (France)

Summary

The photolysis in protic solvents in the visible region >420 nm of several alkylcobaloximes, cobalamines, methyl salen, and coenzyme B_{12} has been studied by ESR spectroscopy including the use of spin-trapping techniques involving 5,5'-dimethylpyrroline-N-oxide (DMPO), phenyl-N-t-butylnitrone and α-4-pyridyl-1-oxide-N-t-butylnitrone. During the photolysis, hydrogen atoms are probably abstracted from the C(10) position of the corrin equatorial ligand in the case of coenzyme B_{12} and cobalamine derivatives. The ESR spectra of the anaerobic photolysis of alkylcobaloximes in aprotic solvents in the presence of DMPO, followed by the addition of air or pure oxygen, provide evidence for intraligand radical spin-trapping reactions.

Introduction

The use of spin-trapping techniques for quenching short-lived intermediates has led to an increased understanding of the mechanisms of photochemical reactions of transition metal complexes [1—5]. In order to determine the nature of the intermediates produced during the photolysis of cobalt(III) complexes and cobalamine derivatives in protic media, we have irradiated samples of alkylcobalt(III) complexes in the presence of spin-traps inside the ESR cavity [2].

In a previous paper we described [2] the photolysis of several cobalt(III) complexes in aprotic solvents and showed by ESR techniques and the use of several spin-traps that the light-induced excitation of these complexes is followed by the abstraction of a hydrogen atom and homolytic cleavage of the Co^{III}—C bond. In this paper we report the results of an ESR study of the

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* Author to whom inquiries should be directed.

photolysis in protic solvents of some alkylcobaloximes, a salen derivative, methyl- and cyano-cobalamines, and coenzyme B_{12} in protic solvents.

Experimental

The alkylcobaloximes (I—III) and the salen compound (IV) were prepared

I $R=CH_3$ $X = Py$

II $R=C_2H_5$ $X = Py$

III $R=CH_2 CH_2OH$ $X = Py$

IV $R=CH_3$ $X = Py$
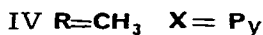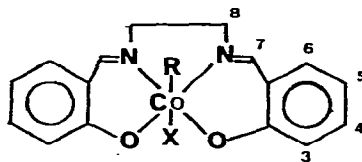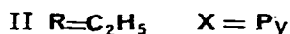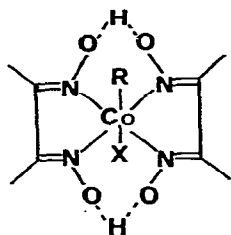
by published methods [6,7,8]; coenzyme B_{12}, cyanocobalamine, and methyl-cobalamine were obtained from Roussel—Uclaf and used without further purification. $^{17}O_2$ was provided by the Nuclear Research Centre (Saclay).

Solutions of compounds V—VII (5×10^{-3} M) in carefully purified methanol, water, or the corresponding deuteriated derivatives (CD_3OD, D_2O), were degassed at less than 10^{-3} torr on a mercury vacuum line by means by at least five freeze-pump thaw cycles. Solutions of compounds I—IV, which were less sensitive to molecular oxygen, were deoxygenated by bubbling through a slow stream of argon for 20 min. The deoxygenated solutions were immediately transferred into a quartz ESR flat cell and introduced into an ER-400X-RL cavity of a Bruker ER420 spectrometer equipped with a B-ST 100/700, B-MN 12, and B-A6 accessories for variable temperature, magnetic field calibration, and frequency measurements, respectively.

Irradiation was carried out with a Hanovia 977 B-0090 1000W Hg-Xe arc lamp in a model LH15 1H Schoeffel lamp housing. The light was focused through quartz lenses and filtered through 15 cm of flowing water and a Corning 3-73 filter. The spin-traps used were 5,5'-dimethylpyrroline-N-oxide (DMPO) [9], nitrosodurene (ND), phenyl-N-t-butylnitrone (PBN) [10—12] and α-4-pyridyl-1-oxide-N-t-butylnitrone (4-POBN) [13] (5×10^{-2} M concentration). All spin-adducts with PBN in methanol solution are very sensitive to light. In order to get ESR spectra corresponding to these spin-adducts with PBN we used a flash technique. ^1H NMR spectra were recorded on a ^1H 90 MHz Bruker spectrometer. The spin concentrations were measured by use of a BER 400 TE104 double cavity and a known concentration of DPPH (α,α'-diphenyl-β-picrylhydrazine).

R = CN   V

CH₃   VI

VII

O—O˙⁻ VIII

O—O—H IX

H   X
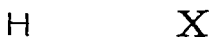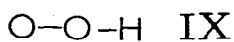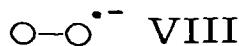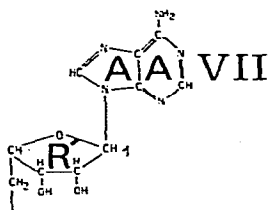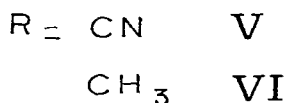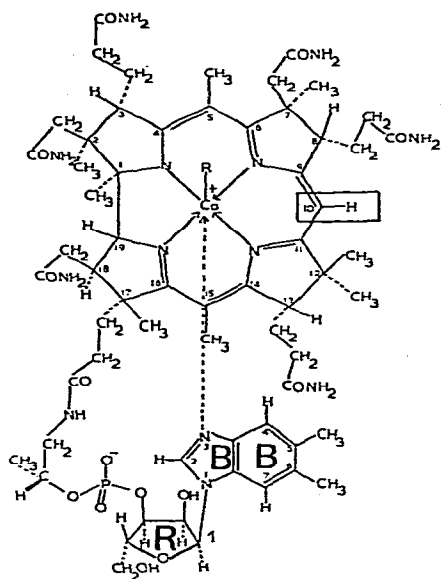
Results

We first showed that anaerobic photolysis of methanolic or aqueous solutions of alkylcobaloximes (I—III), salen derivative (IV), cobalamines (V, VI), and coenzyme B_{12} (VII) containing DMPO, PBN or 4-POBN, prepared in the dark, give no ESR signal. Furthermore, UV and ^{1}H NMR spectroscopy indicated that there was no reaction or association between the spin-traps and the cobalt(III) complexes.

On irradiation with visible light ($\nu > 420$ nm), anaerobic methanol or methanol-d_4 solutions of alkylcobaloximes (I—III) at 290 K containing DMPO as spin-trap immediately exhibit the characteristic ESR spectrum of hydrogen atom-trapped adduct (a_H 20.17 G, a_H 15.16 G [14—16]) however, if photolysis is carried out with PBN instead of DMPO as spin-trap, an ESR spectrum corresponding to the axial alkyl free-radical adduct is observed (Table 1).

The photolysis of anaerobic methanol or methanol-d_4 solutions of the salen

TABLE 1

HYPERFINE SPLITTING CONSTANTS FOR NITROXIDES PRODUCED BY RADICAL ADDITIONS TO PHENYL—N-t-BUTYLNITRONE (PBN) AT ROOM TEMPERATURE IN METHANOL

R	Radical source	g_{iso} ±0.0003	Splitting constants (G)	
			a(N)	a_β(H)
CH₃	VI, I	2.0054	15.50	3.83
CN	V	2.0054	14.42	2.83
CH(CH₃)₂	II	2.0055	15.33	2.99
CH₂CH₂OH	III	2.0059	13.83	1.83
5-Deoxyadenosyl	VII	2.0061	15.25	3.49

derivatives IV with DMPO as spin-trap results in a rather more complicated ESR spectrum which can be interpreted as the superimposition of the ESR spectra of the axial methyl radical (a_N 15.35 G, a_H 21.92 G) and the hydrogen atom spin-adduct [2,14—16], the spin density of the latter being twice that of the former.

Photolysis of a methanol solution of compound IV with PBN under the same conditions immediately shows an ESR spectrum characteristic of the methyl free-radical adduct; if the photolysis is stopped, the hydrogen adduct appears slowly.

ESR study of the anaerobic photolysis of cobalamines V and VI in methanol solution with DMPO and PBN reveals only the addition of the methyl [14] and cyano free-radicals to the spin-traps a_N 15.17 G, a_H 21.92 G on the DMPO and a_N 14.42 G, a_H 2.83 G on the PBN (Table 1) which come from the axial position.

Photolysis of coenzyme B_{12} (VII) along with DMPO in methanol immediately gives rise to an ESR spectrum which can be interpreted as the superimposition of two ESR signals; one coming from the addition of a hydrogen atom to DMPO and the other from the adenosyl free-radical spin-adduct (a_N 15.16 G, a_H 21.83 G). However, if the photolysis of these solutions is carried out with PBN as a spin-trap instead of DMPO, only the adenosyl-PBN free-radical adduct is observed (Table 1).

The photolysis of a methanolic solution of methylcobalamine (VI), with DMPO in the presence of nitrogen containing a small concentration of oxygen results in a complicated ESR spectrum corresponding to hydrogen atom and methyl free-radical spin-trapped adducts with DMPO.

The ESR study of the photolysis of an aqueous solution (pH 7) of alkyl-cobaloximes (I—III) with DMPO shows no ESR signal, but photolysis of these complexes in the presence of 4-POBN under the same conditions immediately gives an ESR spectrum corresponding only to the alkyl free-radical spin-adduct (Table 2). The difference in the reactivities of these two spin-traps is certainly due to the fact that 4-POBN is substantially more soluble in water than DMPO.

The ESR study of the photolysis of solutions of cobalamines (V—VII) in H_2O or D_2O at pH = 7 showed the presence of two free-radical spin-adducts, namely those from addition of hydrogen atoms and of alkyl free-radicals to

TABLE 2

HYPERFINE SPLITTING CONSTANTS FOR NITROXIDES PRODUCED BY RADICAL ADDITIONS TO α-4-PYRIDYL-1-OXIDE-N-t-BUTYLNITRONE (4POBN) AT ROOM TEMPERATURE IN AQUEOUS SOLUTION

R	Radical source	g_{iso} ±0.0003	Splitting constants		
			$a(N)$	$a_{\beta(H)}$	$a(C_{13})$
CH_3	VI	2.0059	15.91	2.75	7.49
CN	V	2.0072	15.99	2.99	
CH_2CH_2OH	III	2.0044	15.75	2.75	
$CH(CH_3)_2$	II	2.0059	15.83	2.16	
5'Deoxyadenosyl	VII	2.0058	15.66	2.66	

DMPO. Alkyl free-radicals can also be spin-trapped by 4-POBN (Table 2).

The photolysis of a solution of coenzyme B_{12} in D_2O at pH 7, also shows a hydrogen spin-adduct on DMPO, thus demonstrating that the abstractable hydrogen atom does not come from the solvent or from one of the readily exchangeable hydrogen atoms of coenzyme B_{12}.

In D_2O at pH 7, 19 protons of coenzyme B_{12} which are linked to nitrogen or oxygen atoms are exchangeable [17]. It has been shown by ^1H NMR studies
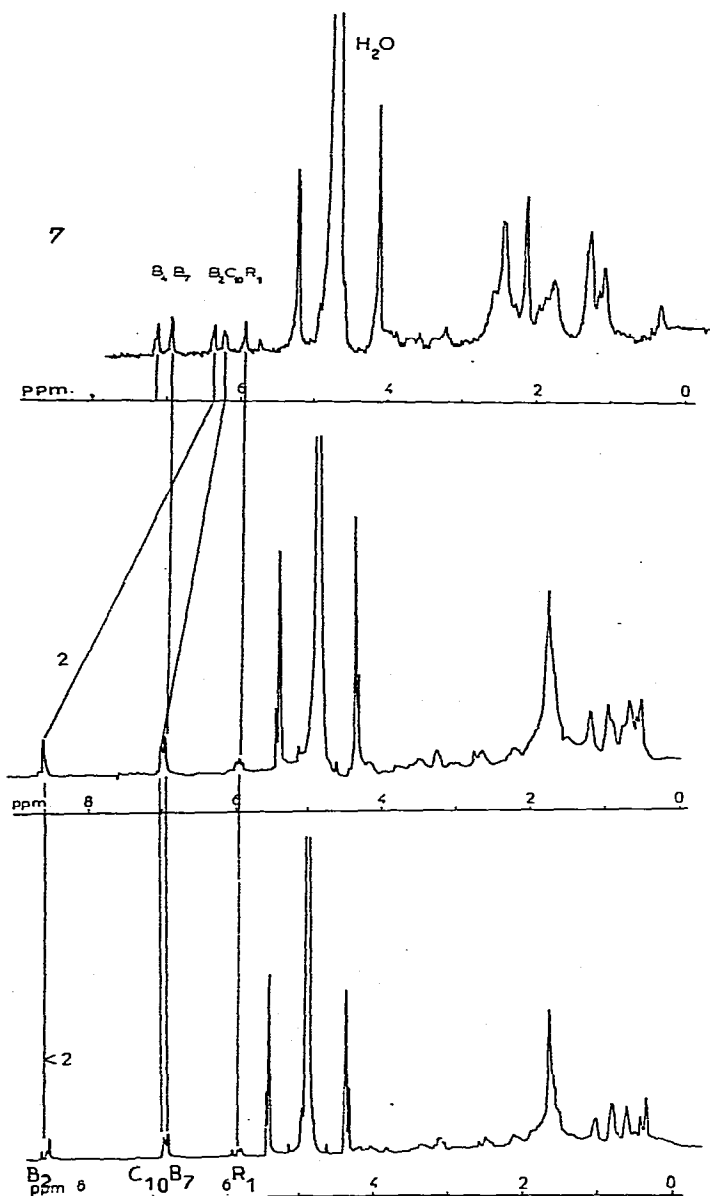

Fig. 1. 90 MHz ^1H NMR spectra of three solutions of cyanocobalamine (VI) in D_2O at room temperature. The pH of the solutions is indicated at upper left.

that the hydrogen at the C(10) position of the corrin ring of the cobalamines and coenzyme B_{12} is readily exchangeable in strongly acidic media [17—20].

The 90 MHz ^{1}H NMR study of cyanocobalamine (V) and coenzyme B_{12} (VII), in D_2O as a function of acidity (Fig. 1, 2) shows that at pH 7, several protons are exchanged by deuterium, but that the proton at the C(10) position is exchanged only in acidic media; the H/D exchange rates at the C(10) position
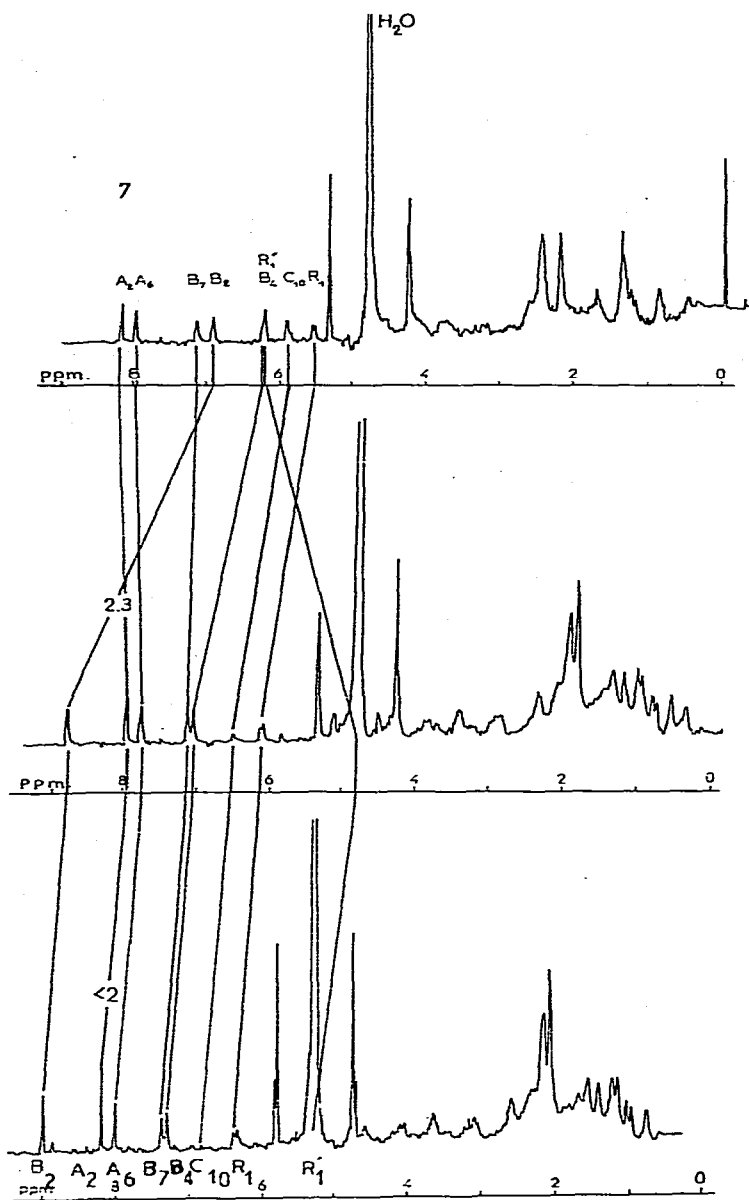

Fig. 2. 90 MHz ^{1}H NMR spectra of three solutions of CoB$_{12}$(VIII) in D_2O at room temperature. The pH of the solutions is indicated at upper left. These spectra show the disappearance of the signal of the C(10) proton following the pH.

are faster for coenzyme B_{12} than for cyanocobalamine, and the H/D exchange rates at the R(1) position are faster for cyanocobalamine than for coenzyme B_{12}. An ESR study of the photolysis of solutions of bisaquocobinamide and 10-chloromethylcobalamine in H_2O and methanol with all the previously mentioned spin-traps gave ambiguous results, because even after purification the products could not be obtained pure.

The continuous photolysis of toluene solutions of alkylcobaloximes (I—III) with DMPO at 230 K gives an ESR spectrum of the hydrogen atom but also an ESR signal coming from the Co^{II} complex in which the Co^{II}—C bond has not been cleaved [21]. After continuous photolysis of toluene or benzene solutions of alkylcobaloximes (I—III) with DMPO, if the sample tube is opened in the dark and cooled down to 150 K there is no evidence for a Co^{III} superoxide radical [22]. However, if after anaerobic irradiation at room temperature in toluene or benzene solution the tube is opened to the air, shaken and degassed again in the dark, without any further photolysis, an ESR spectrum is obtained consisting of a triplet of five lines (Fig. 3). This spectrum can be analysed in terms of a single nucleus of $I = 1$ with hyperfine splitting ($a_{N\alpha}$ 12.92 G) and two equivalent nuclei with $I = 1$ with hyperfine splitting ($a_{N\gamma} = 1.33$ G) and a g factor of 2.0060 ± 0.0002; the observed g factor is characteristic of organic nitroxide compounds [23].

Thus it is reasonable to assume that the nuclei with $I = 1$ are nitrogen nuclei. The observed parameters for this nitroxide radical are very similar to those of radicals of the type R—N$<^{O^{\cdot}}_{R}$ [23]. The shape of the signal observed is not affected if $^{17}O_2$ is added, after photolysis in the presence of DMPO, instead of air or $^{16}O_2$. Thus we may tentatively identify the radical as the product (C) (see Scheme 1) of attack of the dimethylglyoxime free-radical (B) formed after hydrogen atom abstraction by DMPO; C has two almost equivalent nitrogen nuclei, which accounts for the five lines of the triplet which arises from the nitroxide centre. We have also found that this radical species (Fig. 3) is not formed in protic solvents or with the other spin-traps (PBN, 4-POBN, and ND either singly or mixed); the shape of the signal is also not affected by the nature of any alkyl group (R) or Lewis base (X) in the axial position of the
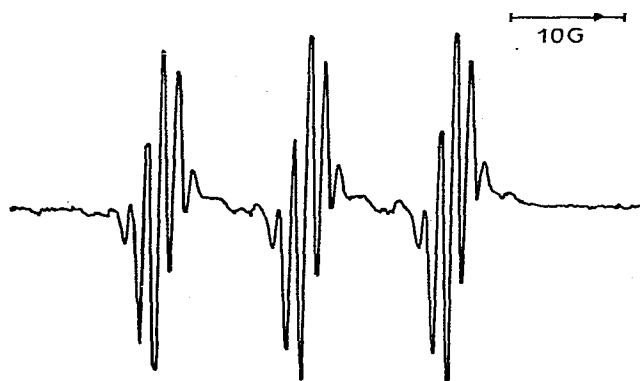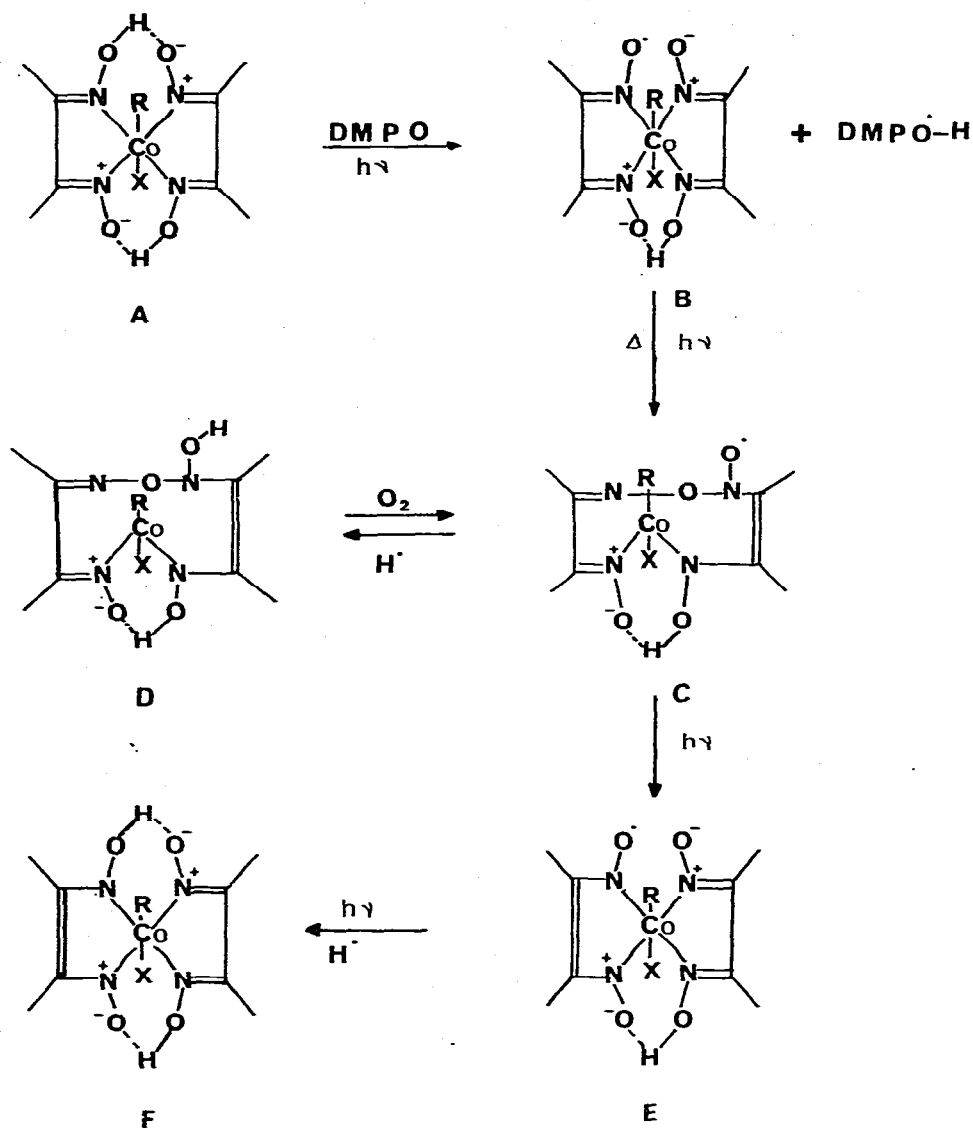

Fig. 3. ESR spectrum of the radical C obtained after continuous photolysis of toluene solutions of alkylcobaloximes with DMPO followed by addition of air at 20°C. Microwave frequency: 9.680 GHz; modulation intensity: 0.063 G; Microwave receiver gain: 3.2 × 10⁴; Microwave power: 25 mW.

SCHEME 1

complexes studied; however compounds such as alkylcyclohexylcobaloximes [2] give the same radical. The salen derivative IV, cobalamines V and VI, and coenzyme B_{12} (VII) do not give this spectrum, which confirms that the radical is probably influenced by the nature of the equatorial ligand. In support of this hypothesis, we found that the radical is stable at room temperature, as are nitroxides of this type; even after degassing several times, no hyperfine structure due to a ^{59}Co atom ($I = 7/2$) could be detected. Thus we must either assume that this radical has broken away entirely from the cobalt complex or that the Co nucleus is remote from the nitroxide centre; the proposed structure (C) correlates well with all these observations.

Radicals of this type are sensitive to light, and if the photolysis is resumed
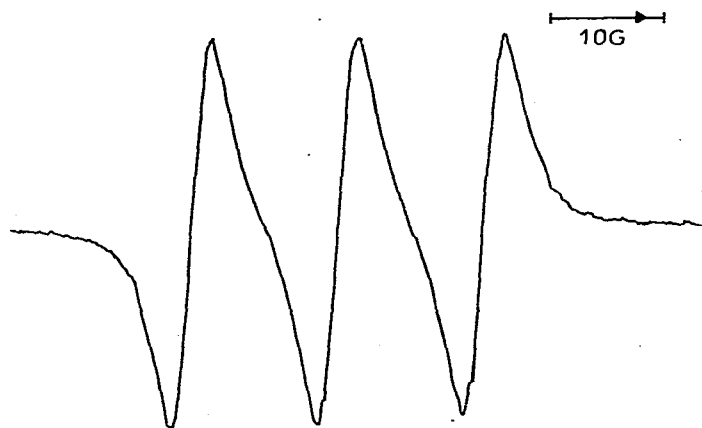
Fig. 4. ESR spectrum of the radical obtained by anaerobic photolysis of the radical C in toluene at 20°C. Microwave frequency: 9.305 GHz; Modulation intensity: 0.4 G; Microwave receiver gain: 3.2×10^5; Microwave power: 25 mW.
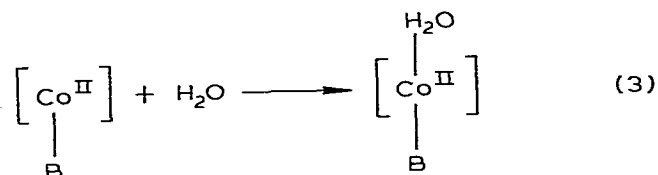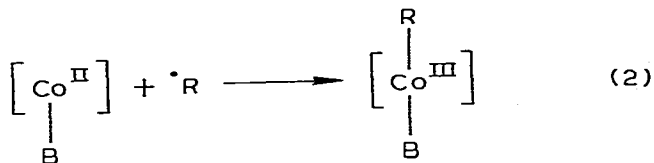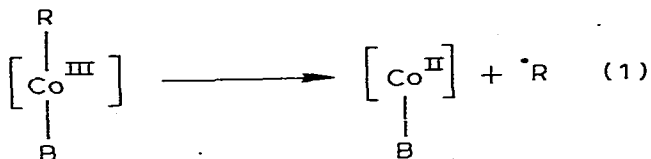
the spectrum (Fig. 3) of C disappears and is replaced by a broad triplet without any hyperfine coupling (Fig. 4) (a_N 13.70 G, g_{iso} 2.0056 ± 0.0002) [23]. This spectrum is also characteristic of a nitroxide radical and its structure could correspond to E. However all attempts to isolate this radical failed. Several determinations of the spin concentrations for radicals C and E (Fig. 3, 4) by comparison of the integrated signal with a known concentration of DPPH, indicate the presence of a paramagnetic species at concentrations between 1 and 0.1%.

A possible mechanism for the formation of C and E is presented in Scheme 1. Under visible light excitation, alkylcobaloxime A in the presence of DMPO gives the corresponding free-radical B by abstraction of a chelated hydrogen atom [2]. The radical B reacts rapidly with the second cobalt-coordinated dimethylglyoxime anion, which is a potential spin-trap [22]. The new radical C reacts with a hydrogen atom evolved during photolysis to give the stabilised complex D [24]; however D reacts with oxygen to reverts to C. Under visible lights irradiation in oxygenated solution, C regenerates E which can again abstract a hydrogen atom from another alkylcobaloxime molecule and form F.

Discussion

During photolysis of cobalt(III) coordination complexes (I—VII) in methanol or aqueous solutions two free-radical species are produced, namely a hydrogen atom and an alkyl free-radical. This is completely consistent with results obtained during the photolysis of these complexes in aprotic solvents [2]. Golding and coworkers demonstrated previously that during the photolysis of neutral aqueous solutions of alkylcobaloximes, the homolytic cleavage of the cobalt—carbon bond, and the production of an alkyl free-radical are very efficient processes [25]. One possible explanation is that the water molecule solvates the cobalt(II) complex (eq. 3) which is formed after homolytic cleavage of the Co^{III}—C bond (eq. 1); the latter reaction prevents the occurrence of the recombination process in reforming the original Co^{III}—C bond (eq. 2) and

promotes the photo-induced formation of the alkyl free-radical in preference to the departure of a hydrogen atom.

$$\begin{bmatrix} \overset{\displaystyle R}{\underset{\displaystyle B}{|} } \\ Co^{III} \end{bmatrix} \longrightarrow \begin{bmatrix} Co^{II} \\ \underset{\displaystyle B}{|} \end{bmatrix} + {}^{\bullet}R \quad (1)$$

$$\begin{bmatrix} Co^{II} \\ \underset{\displaystyle B}{|} \end{bmatrix} + {}^{\bullet}R \longrightarrow \begin{bmatrix} \overset{\displaystyle R}{\underset{\displaystyle B}{|} } \\ Co^{III} \end{bmatrix} \quad (2)$$

$$\begin{bmatrix} Co^{II} \\ \underset{\displaystyle B}{|} \end{bmatrix} + H_2O \longrightarrow \begin{bmatrix} \overset{\displaystyle H_2O}{\underset{\displaystyle B}{|} } \\ Co^{II} \end{bmatrix} \quad (3)$$

Methanol is less polar than water and does not easily solvate the cobalt(II) complex which is formed by homolytic cleavage of the Co^{III}—C bond, thus making the photo-induced abstraction of an hydrogen atom more efficient.

The results obtained during photolysis of compounds I—III in methanol solution are quite similar to those obtained in aprotic solvents, and allow the mechanisms which have been proposed [26] previously to be generalized.

The ESR study of the photolysis of methanol and aqueous solutions of cobalamines V and VI, coenzyme B_{12} (VII) alkylcobaloximes I—III and methyl-salen derivatives IV shows that the free-radical adducts which are formed are the same: the alkyl free-radical comes from the axial ligand and the hydrogen atom from the chelated hydrogen of the alkylcobaloximes [2] or from the 7 and 8 positions in the alkyl-salen IV. It has already been shown by ^{1}H NMR spectroscopy that protons in these positions are very labile [27].

The ESR study of the photolysis of coenzyme B_{12} (VII) in D_2O at pH 7 with DMPO shows that the hydrogen atom must come from the equatorial or axial ligand. Since we also get some hydrogen atom abstraction with the cyano-cobalamine, this hydrogen atom must come from the equatorial ligands or from the 5-6-dimethylbenzimidazole group. Bonnet et al. [28] and Hill et al. [29] showed, that the electrophilic reaction at the C(10) position is facilitated by an axial donating group on the cobalt atom whereas the electrophilic reaction at the R(1) position of the axial base is not facilitated by an axial donating group. Unfortunately, the ^{1}H NMR spectrum of such a compound cannot be recorded because VI and VII are only weakly soluble in methanol. We have shown previously that the hydrogen atoms which appear during photolysis of these compounds do not come from hydrogens which are linked to the nitrogen or oxygen atoms of the corrin cycle.

The lability of the H—C(10) bond could explain why this bond in the three compounds V—VII studied is cleaved upon anaerobic photolysis. The strength of the H—C(10) bond is very sensitive to the nature of the axial alkyl ligand, the nature of the base, and also to the solvent polarity. Water is a very polar solvent and its influence on the strength of the H—C(10) bond is more important than the *cis*-effect of the axial ligand. The ESR study of the photolysis of compounds V—VII and the formation of hydrogen atom spin-adducts on the trap are consistent with this observation. Methanol is less polar than water and its influence on the H—C(10) bond competes strongly with the *cis*-effect of the axial ligand; a cyano group also makes this bond harder to cleave than do methyl or 5'deoxyadenosyl groups.

The axial group in cyanocobalamine V and methylcobalamine VI does not facilitate the cleavage of the H—C(10) bond but the 5'deoxyadenosyl group weakens the H—C(10) bond sufficiently for cleavage of this bond does occur.

If photolysis of the methanolic solution of methylcobalamine VI is carried out in the presence of traces of pure oxygen or air, the departure of one hydrogen atom occurs rapidly. A possible explanation of this is that oxygen can be inserted into the Co^{III}—C bond [30], so that the energy of the H—C(10) bond is decreased significantly and the abstraction of this hydrogen is favoured. Thus the hydrogen atom which is spin-trapped by DMPO during photolysis of methylcobalamine VI will come from the hydrogen at the C(10) position of the corresponding methyldioxycobalamine which is formed because of the small percentage of oxygen remaining in solution. Direct evidence for the formation of stable alkyldioxycobalamines has not, however, been obtained [31]. Another possible explanation is the formation of a superoxide radical, (VIII) which could also abstract the hydrogen atom at the C(10) position to give the corresponding hydroperoxide derivative (IX), and this could be cleaved homolytically by visible light. However, the formation of superoxide radicals such as VIII is very difficult with V.

Finally, another possibility is the formation of a cobalt(I) derivative [32] which is a very strong nucleophile. By attacking the H—C(10) bond and abstracting a proton this cobalt(I) derivative could give the corresponding hydride (X) which could then be photolysed and cleaved homolytically, analogously to tin hydride derivatives [33]. The fact that, in the dark immediately after photolysis of salen derivative IV using visible light, we observe the hydrogen spin-adduct increasing in concentration is consistent with a multi-step mechanism at least for this compound, where the cleavage of a C—H bond is involved. A multi-step mechanism may also be invoked in the case of the cobalamines and coenzyme derivatives V—VII, because ESR studies of these derivatives at low temperatures reveal no evidence for organic radical species coming from the equatorial ligand and no clear evidence for the homolytic cleavage of the H—C(10) bond. Hence the way in which hydrogen abstraction occurs at the C(10) position in compounds V—VII cannot be stated precisely at present.

In the case of alkylcobaloximes, the formation of the radical species C (Fig. 3) provides evidence for homolytic cleavage of the chelated O—H bond and formation of a radical species which is stabilised in another hydroxy form (Scheme 1) and may be oxidized by a weak oxidant such as oxygen. In the case of benzylpyridinecobaloxime we have observed a similar intraligand spin-

trap adduct [22]. If after anaerobic photolysis of a benzene solution of benzyl-pyridinecobaloxime in the absence of DMPO, oxygen from the air is added in the dark, the axial ligand benzyl free-radical is spin-trapped by the equatorial dimethylglyoxime anion [22]. When the reaction is carried out without DMPO, a very fast back reaction between the hydrogen atom and B prevents the identification of the organic free-radical B which comes from the equatorial ligand.

Conclusion

In a series of papers [2,16,21,22,26] and in this work, we have shown that the photolysis of alkylcobaloximes is dependent upon the temperature at which the photolysis is carried out, upon the nature of the axial ligands, and upon the solvents used. In aprotic solvents there is a competition between abstraction of a hydrogen atom and homolytic cleavage of the Co^{III}—C bond with subsequent formation of the corresponding alkyl free-radical spin-adducts when spin-traps are present. In methanol and especially in water, the homolytic cleavage of the Co^{III}—C bond is strongly favoured over the departure of a hydrogen atom. The hydrogen atom comes from the hydrogen chelated into the dimethylglyoxime anion, and in some cases the two equatorial ligands work as an internal spin-trap.

The ESR and spin-trapping study of the visible light photolysis of aqueous or methanolic solution of salen derivative, cobalamines, and coenzyme B_{12} also reveals the immediate formation of the spin-trap adducts from the alkyl radical and the hydrogen atom.

The alkyl free-radical comes from the axial ligand whereas the hydrogen atom comes from the equatorial ligand. In the case of the salen derivative, the hydrogen atom probably comes from the C(7) or C(8) position, but for the cobalamines and coenzymes B_{12}, it probably comes from the C(10) position of the equatorial ligand after cleavage of the H—C(10) bond followed by further reactions.

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