Journal of Organometallic Chemistry, 99 (1975) 145—156

ELECTRON SPIN RESONANCE STUDIES OF THE ANAEROBIC AND AEROBIC PHOTOLYSIS OF ALKYLCOBALOXIMES

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(Received March 13th, 1975)

Summary

Aerobic and anaerobic photolysis of methyl(pyridine)cobaloxime, benzyl(pyridine)cobaloxime and analogous compounds in $CHCl_3$ results only in an electron transfer reaction from an equatorial ligand producing photo-reduction of Co^{III} to Co^{II}, the complex retaining its axial ligands.

If after the anaerobic photolysis of benzyl(pyridine)cobaloxime the oxygen is introduced without any further photolysis we obtain an ESR spectrum of nitroxide, arising from the attack of a benzyl radical on the dimethylglyoxime equatorial ligand.

For the other complexes, homolytic cleavage of the Co—C bond occurs and in the presence of oxygen gives rise to the superoxide cobalt complex adduct $Py(Co^{III})O_2^{\overline{\cdot}}$.

During photolysis of methyl(pyridine)cobaloxime in isopropanol homolytic cleavage of the Co—C bond occurs in preference to electron transfer reaction from the equatorial ligands.

The anaerobic photolysis of benzyl(pyridine)cobaloxime in isopropanol or in water at 113-133 K results in an electron transfer reaction. However, at 170 K we observe the formation of the Co^{II} complex arising from Co—C bond cleavage.

A mechanism for photo-induced insertion of oxygen in the Co—C bond is proposed.

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* Publication No. 132.

Introduction

In studies of the photolysis of alkyl cobaloximes [1] and analogous complexes [2-4] it has been noted that the presence of oxygen greatly increases the rate of cleavage of the Co—C bond. Irradiation of solutions of alkylcobaloximes saturated with oxygen results in the selective insertion of oxygen into the Co—C bond leading to the formation of stable alkyl peroxide complexes [5-7]. Since the mechanism of this insertion has not yet been elucidated, we have used the technique of electron spin resonance (ESR) spectroscopy to study the nature of the paramagnetic intermediates appearing during and after photolysis.

Materials and methods

The compounds were prepared as indicated previously [5-7] and were dissolved in $CHCl_3$ (0.75% C_2H_5OH) (Baker Chemical Co., Phillipsberg, N.J.) I-III 4×10^{-2} *M*; IV-XVI 4×10^{-3} *M*; in benzene, isopropanol or water (saturated solutions). The solutions were irradiated in the microwave cavity of a Varian E12 ESR spectrometer in 4 mm OD Supracil quartz tubes (for the $CHCl_3$ solutions) or in a Varian Model 248-1 narrow aqueous solution flat cell (for the isopropanol and water solutions). Illumination was from a Hanovia Model 997B 1kW Hg-Xe arc lamp in a Model LH-151N Schoeffel Lamp Housing. The light was focused through quartz lenses and filtered through a Corning 3-73 filter (transmits above 420 nm).

Results

For compounds I-VII aerobic photolysis in $CHCl_3$ between 198 K and 253 K resulted in the formation of ESR spectra analogous to those described earlier [8] for the anaerobic photolysis of the methyl- (I) and the benzyl(pyridine)cobaloximes (IV). We thus conclude that for compounds I-VII the photolysis results only in a photoreduction of Co^{III} to Co^{II} even in the presence of oxygen. For compounds I-VII no other paramagnetic species were detected during aerobic photolysis except for the benzyl(pyridine)cobaloxime (IV), which behaves differently.

If, after anaerobic irradiation of IV at room temperature in $CHCl_3$, the tube is opened to the air and shaken without any further photolysis, an ESR spectrum is obtained (Fig. 1) consisting of seven lines which can be analyzed in terms of a single nucleus of $I = 1$ with hyperfine splitting 15.0 ± 0.2 G and two equivalent nuclei with $I = 1/2$ with hyperfine splitting 8.2 ± 0.2 G*. The g factor (measured relative to DPPH**, $g = 2.0037$) is 2.0056 ± 0.0002. The observed g factor is characteristic of organic nitroxide compounds. Thus it is reasonable to assume that the nucleus with $I = 1$ is ^{14}N and the two nuclei with $I = 1/2$ are protons. The observed ESR parameters for this radical are very similar to nitrox-

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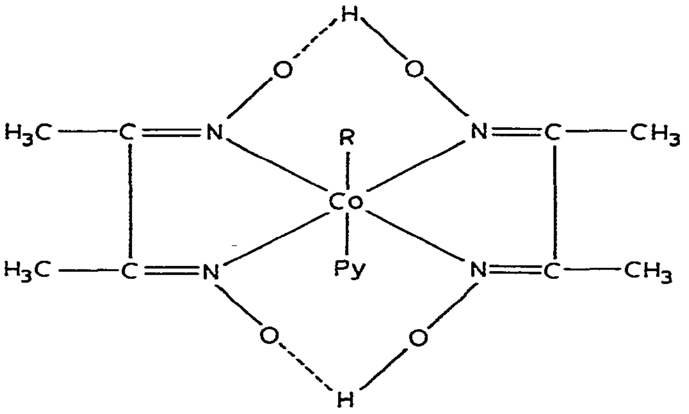
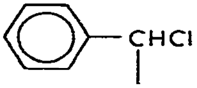
* It should be noted that the relative amplitudes of the outer two lines are not in the expected 1/2 ratio; however, the second line is broader than the first which accounts for the anomalous amplitude ratio. This is an example of an alternating line width effect, and indicates a small barrier to rotation about the CN bond in the radical structure proposed.

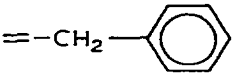
** DPPH = diphenylpicrylhydrazine.

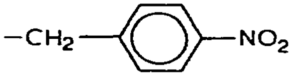


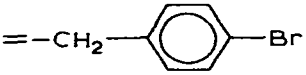
(I) R $= -CH_3$

(II) R $= -CH_2C{\equiv}N$

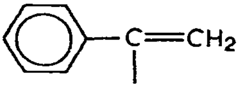
(III) R =


(IV) R =


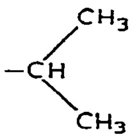
(V) R =


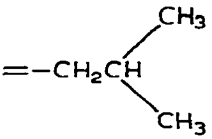
(VI) R =


(VII) R =

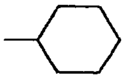

(VIII) R =


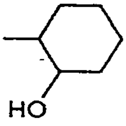
(IX) R $= -C_2H_5$

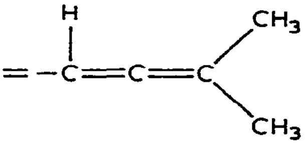
(X) R =

$-CH(CH_3)_2$

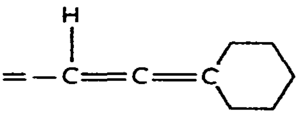
(XI) R =

$-CH_2CH(CH_3)_2$

(XII) R $= -CH_2(CH_2)_3CH_3$

(XIII) R =


(XIV) R =


(XV) R =

$-CH{=}C{=}C(CH_3)_2$

(XVI) R =


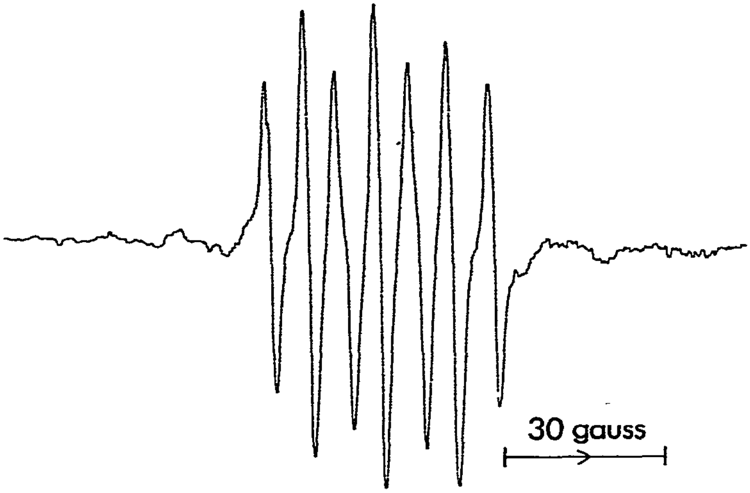
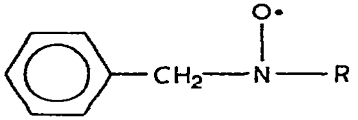
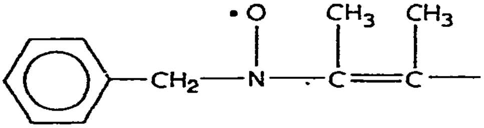


Fig. 1. ESR spectrum of the photolysis product of IV in chloroform just after adding oxygen after anaerobic photolysis at 263 K. Modulation amplitude 2.0 G; microwave power 10 mW; microwave frequency 9.130 GHz; receiver gain 8 × 10^3.

ide radicals of the type



For example, in the case of R = t-butyl a(N) = 14.25 G a(H) = 7.13 G in benzene [9]*. Thus we tentatively identify the radical as a product of the attack of a benzyl radical on the dimethylglyoxime ligand leading to a radical of the type



In support of this hypothesis we find that the radical is very stable at room temperature, as are nitroxides of this type. Even after degassing several times no hyperfine structure due to ^{59}Co ($I = 7/2$) 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 center**. We are puzzled by the fact that compounds V-VII do not give a similar benzyl-adduct ESR spectrum. It may be that the substituents on the benzene ring of the benzyl group reduce the stability of the benzyl radical.

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* The hyperfine splittings in nitroxides increase slightly as the solvent becomes more polar. Thus the slightly larger splittings we observe can be attributed to a solvent effect.

** If the irradiation is resumed the spectrum shown in Fig. 1 disappears and is replaced by the Co^{II} electron-transfer product.

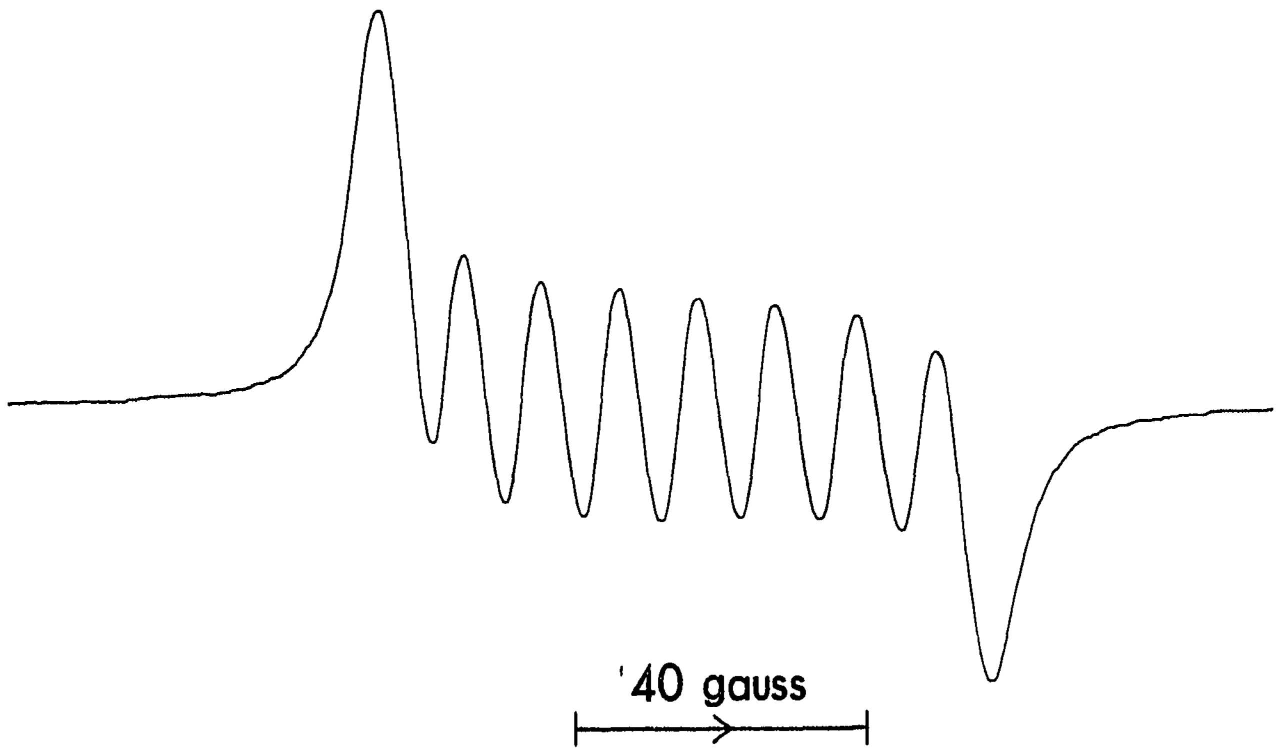
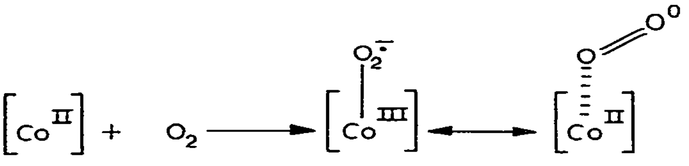


Fig. 2. ESR spectrum of the aerobic photolysis of XIII at 198 K in chloroform. Modulation amplitude 10 G; microwave power 5 mW; microwave frequency 9.130 GHz; receiver gain 2×10^3.

In the case of the alkylcobaloximes VIII-XIV the addition of oxygen to a sample previously subjected to anaerobic photolysis and maintained at 263 to 253 K or under direct aerobic photolysis produced an intense dark red color. Coincident with the formation of the red color there appears a characteristic ESR spectrum consisting of 8 equally intense lines (Fig. 2) with no evidence of any other hyperfine structure. We assume that the 8 lines arise from the ^{59}Co ($I = 7/2$) of a Co^{II} low spin complex, a(Co) = 11.46 G and $\langle g \rangle = 2.021$. When the sample is warmed to room temperature the red color disappears at the same time as the ESR signal.

Similar ESR spectra have been detected during the addition of oxygen to the complexes of Co^{II} and dimethylglyoxime [10] or analogous complexes [11, 14] and even in the course of the decomposition of the superoxide dimer [15].

It has been proposed [10-16] that this spectrum is that of a superoxide cobalt complex PyCoO$_2^{\overline{\cdot}}$ resulting from transfer of an electron to O$_2$ from a Co^{II} complex.



The superoxide structure must dominate as the g factor is characteristic of an O$_2^{\overline{\cdot}}$ species and the cobalt hyperfine splitting is much smaller than in most Co^{II} complexes.

As a check on the identification of the spectrum in Fig. 2 we have synthesized the compound Py(Co^{II})Py [15]. In the presence of oxygen it yields in the dark an ESR spectrum essentially identical to that in Fig. 2 which we have obtained for compounds VIII-XVI. Thus we feel confident in assigning the spectrum in Fig. 2 to the superoxide complex Py(Co^{III})O$_2^{\overline{\cdot}}$.

For compounds XV and XVI during aerobic photolysis an ESR spectrum similar to that in Fig. 2 is seen in the first second or two of illumination, but as

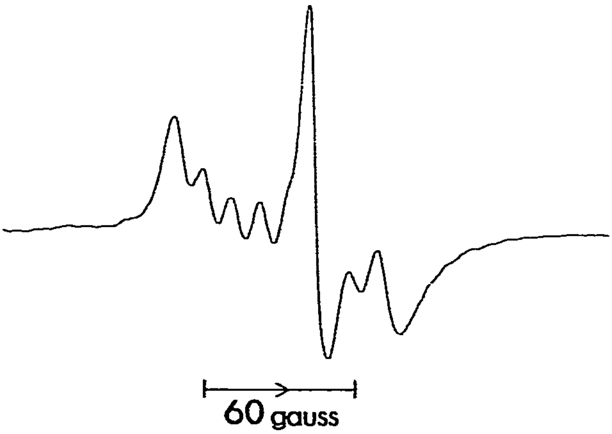


Fig. 3. ESR spectrum of the aerobic photolysis of XV at 203 K in chloroform. Modulation amplitude 8 G; microwave power 5 mW; microwave frequency 9.142 GHz; receiver gain 5 × 10^3.

the photolysis continues the ESR spectrum of an organic radical is detected (Fig. 3). The signal from this radical decays very rapidly when irradiation is stopped. No hyperfine structure is observed and $\langle g \rangle = 2.014 \pm 0.001$ for XV and for XVI. From the *g* factors we conclude that the radical formed is probably an alkyl peroxide.

The photolysis of the methyl(pyridine)cobaloxime I in isopropanol at 113 K exhibits quite different characteristics from the photolysis of the same compound in $CHCl_3$ or benzene. An ESR spectrum is seen which is very similar in line shape and *g* factor to that obtained from the photolysis of isopropyl(pyridine)cobaloxime and analogous complexes in $CHCl_3$ [8]. This spectrum is very different from that obtained in the photolysis of I in $CHCl_3$. There is strong evidence that the ESR spectrum in this case arises from a Co^{II} complex formed as the result of electron transfer from the equatorial ligands to the Co^{III} center. Since the ESR spectrum seen in the photolysis of I in isopropanol closely resembles that found for the photolysis of X in $CHCl_3$, where Co—C bond cleavage occurs, we conclude that in isopropanol cleavage of the Co—C bond occurs in preference to electron transfer.

From the first instant of photolysis of I in isopropanol a seven line ESR spectrum is seen (Fig. 4) with $g \simeq 2.003$ and a hyperfine splitting of 20 G. This spectrum is essentially the same as that observed in the UV photolysis of H_2O_2 in isopropanol [16], where the radical formed is known to be $(CH_3)_2\dot{C}OH$. The abstraction of the α-hydrogen of the isopropanol could arise either from hydrogen atoms ejected from the complex or from the methyl radicals produced as a result of the Co—C bond cleavage.

If the photolysis of I is carried out in water, the homolytic Co—C bond cleavage is not the only process possible, as a poorly resolved signal which corresponds to the Co^{II} complex formed by electron transfer is also observed. A confirmation of the cleavage is given by the addition of oxygen; for the reaction in isopropanol and in water, we observed a (poorly resolved) spectrum characteristic of the same superoxide cobalt complex found in the aerobic photolysis of X and analogous compounds.

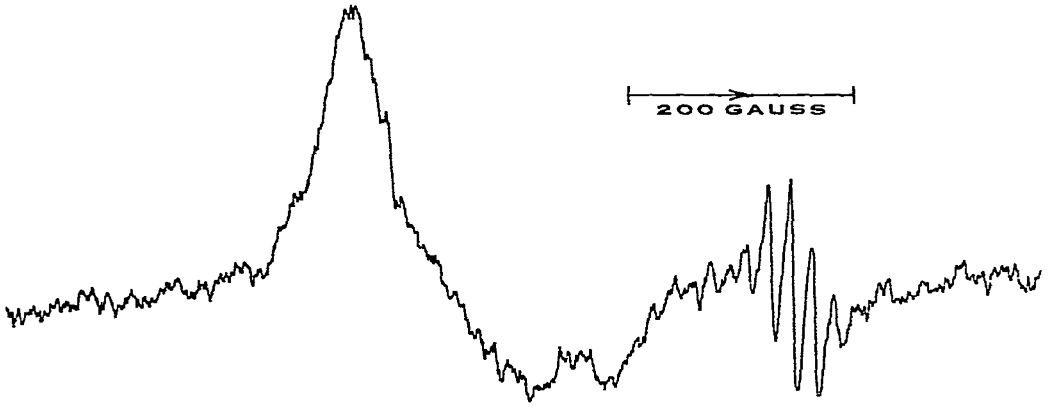


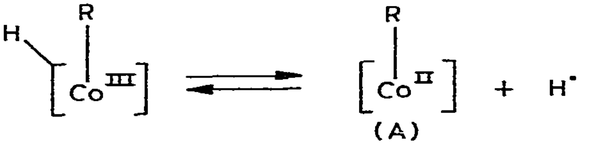
Fig. 4. ESR spectrum of the anaerobic photolysis of IV in isopropanol at 193 K. Modulation amplitude 4 G; microwave power 10 mW; microwave frequency 9.145 GHz; receiver gain 2.5×10^4.

Fig. 5. ESR spectrum of the anaerobic photolysis of I in isopropanol at 173 K. Modulation amplitude 4 G; microwave power 30 mW; microwave frequency 9.142 GHz; receiver gain 3.2 × 10^4.

The anaerobic photolysis of benzyl(pyridine)cobaloxime (IV) in isopropanol or in water at 113-133 K results in essentially the same electron transfer reaction as seen in the case of the anaerobic photolysis of IV in $CHCl_3$ or benzene. However at temperature ≃ 170 K we observe the formation of the Co^{II} complex arising from Co—C bond cleavage. If the photolysis is conducted in the liquid state at ~190 K we observe the immediate formation of an ESR spectrum which is characteristic of an organic radical (see Fig. 5). Perhaps the radical is the benzyl radical. On addition of oxygen at low temperatures, an ESR spectrum characteristic of the superoxide Co complex (Fig. 2) is observed confirming the presence of a Co^{II} without its alkyl axial ligand. With the compounds II, III, V-VII we observed only an electron transfer reaction between 113 K and 173 K for photolysis in isopropanol.

For compound VIII photolysis in isopropanol at 133 K gives almost exclusively the electron transfer product. However, as the temperature is raised to 173 K the Co^{II} complex arising from Co—C bond cleavage begins to appear as well. After 30 min of irradiation at 173 K the intensity of the two signals is about the same. But as the photolysis continues, the reaction of homolytic cleavage predominates (see Fig. 6).

In previous work we have examined the photolysis of methyl- and benzyl(pyridine)cobaloxime in the presence of the spin trap DMPO (5,5-dimethyl-1-pyrroline-1-oxide). By the use of selective deuteration and a BF_2 derivative we have demonstrated that a hydrogen atom ejected in the photolysis (as detected by the hydrogen atom adduct of DMPO) comes from the equatorial ligands [21] and thus we can write the first step of the mechanism as in eqn. 1.



$$\text{H}\left[\overset{\text{R}}{\text{Co}^{\text{III}}}\right] \rightleftharpoons \underset{\text{(A)}}{\left[\overset{\text{R}}{\text{Co}^{\text{II}}}\right]} + \text{H}^{\bullet} \qquad (1)$$

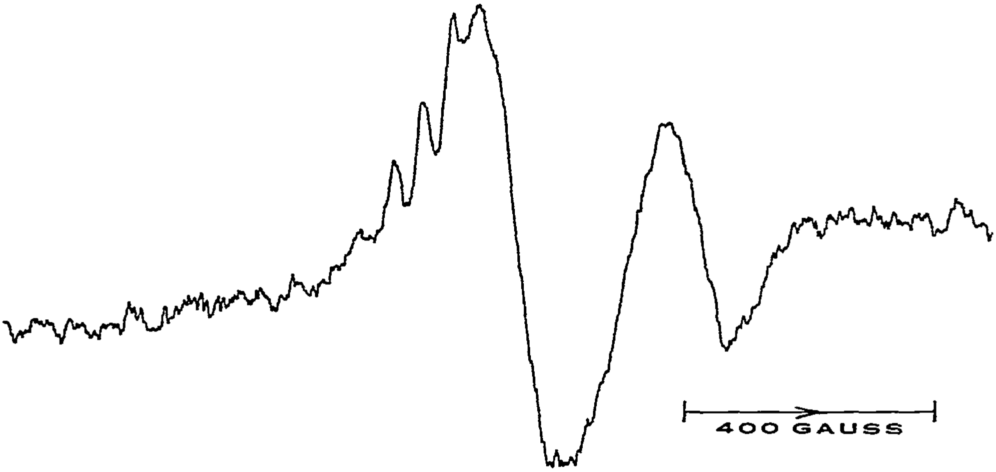
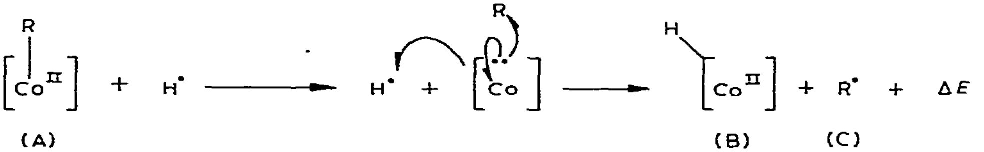


Fig. 6. ESR spectrum of an anaerobic photolysis of VIII after one irradiation for 30 min in isopropanol at —80°C. Modulation amplitude 3.2 G; microwave power 20 mW; microwave frequency 9.143 GHz; receiver gain 2 × 10^4.

The first step is written as a reversible process since we have observed that at low temperature (113 to 173 K) the formation of the electron transfer product is partially reversible [8]. After the initial step complex A, depending the conditions, may undergo a homolytic bond cleavage releasing the organic radical $R^•$ (eqn. 2).



(2)

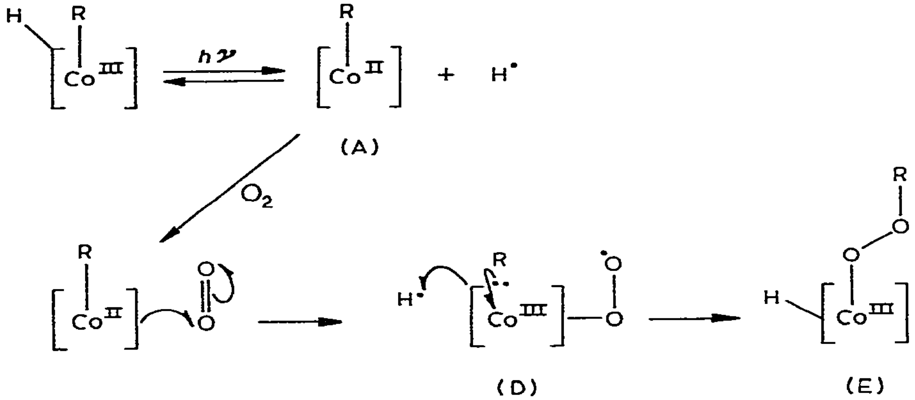
In the case of complexes I-VIII complex A is stable, and thus one observes the Co^{II} complex resulting from electron transfer. However, for complexes IX-XVI complex A is not stable and the reaction proceeds to forms B and C, which participate in other secondary reactions. All the compounds IX-XVI show an intense blue-green coloration when the photolysis is carried out at 130 K. We attribute this color to the formation of a Co^{I} species, which is assumed to come from hydrogen atom abstraction at the β position of the Co—C bond [17].

Discussion and conclusions

We have found that the anaerobic photolysis of compounds I-XVI brings about a ligand to metal electron-transfer reaction [8,18,19,21]. In the case of compounds I-VIII, the Co^{II} complex which is produced is relatively stable and retains all the original ligands [8,21]. However, in the case of the other complexes IX-XVI, homolytic cleavage of the Co—C bond occurs.

During the aerobic photolysis of compounds I-VII in aprotic solvents an electron transfer reaction is still detected by ESR. As noted earlier [5-7,20] the formation of a diamagnetic cobalt peroxide complex can be detected by NMR in the aerobic photolysis of these complexes. In the case of the benzyl(pyridine)-cobaloxime (IV) the addition of oxygen after anaerobic photolysis results in the expulsion of a benzyl radical which possibly then attacks the dimethylglyoxime ligand to form a stable nitroxide entity.

In the light of the observations above, we suggest that the photo-induced oxygen insertion into the Co—C bond for compounds I, IV-VII in aprotic solvents involves the mechanism of eqn. 3.



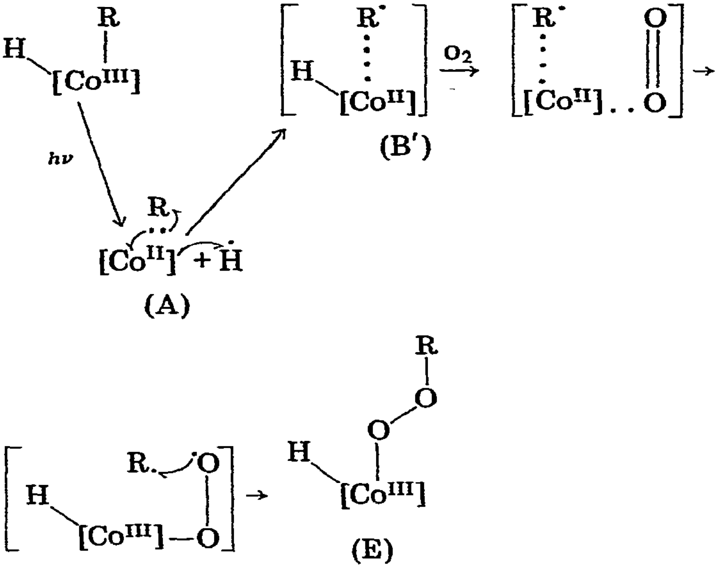
(3)

The cobalt(II) complex A gives an electron to oxygen to form the unstable superoxide D. The Co—C bond breaks homolytically. The cobalt gives up an electron to neutralize the charge on the equatorial ligands at the same time as the O—R bond is formed leading to the stable alkyl peroxide complex E.

During the aerobic photolysis of compounds VIII-XIV we have observed the formation of a superoxide—cobalt complex, and in the case of compounds XV and XVI we find in addition an organic peroxide radical. The NMR study of this oxygen insertion into the Co—C bond of these compounds (IX-XVI) [5, 6,20] shows that the product is essentially an alkyl peroxide—cobalt complex but the yield depends on the temperature at which the insertion is carried out [20].

The anaerobic photolysis of compounds I-VIII in isopropanol or water does not involve exclusively an electron transfer from an equatorial ligand to Co^{III} and it seems that homolytic cleavage of the Co—C bond also occurs. The nature of the photo-induced electron transfer reaction thus appears to depend markedly on the nature of the solvent, with aprotic solvents favoring equatorial electron transfer.

On the other hand for compounds IX-XVI in solvents such as $CHCl_3$ or benzene, or in polar solvents such as isopropanol or water, for compounds I, IV-VII, IX-XVI, we propose that in the first steps of the photo-induced insertion of oxygen a homolytic cleavage of the Co—C bond is involved. The resulting radical ($R^•$) remains in the solvent cage, and reacts with O_2 to form the diamagnetic peroxide (eqn. 4).



(4)

The entity B′ in eqn. 4 reacts rapidly with oxygen to form a superoxide complex of Co^{III} which may either liberate the radical $R^{\bullet}$ from the solvent cage or react with $R^{\bullet}$ to form the alkyl peroxide Co^{III} complex E. If the latter process has a significant activation energy, then at low temperatures the rate of diffusion of $R^{\bullet}$ away from the cobalt complex may exceed that of reaction of $R^{\bullet}$ with the cobalt superoxide complex. This would explain why the yield of the alkyl peroxide—cobalt complex is low at low temperatures. However, at higher temperatures the rate of reaction of $R^{\bullet}$ with the cobalt superoxide could exceed that of diffusion of $R^{\bullet}$ away since diffusion rates have a very low activation energy. Thus at higher temperatures ($\simeq$ —10 to 20°C) formation of the alkyl peroxide—cobalt complex is the predominant reaction and may proceed as a concerted process [22,6].

Concerning the photoexpulsion of the pyridine in the axial position, we have demonstrated that this process occurs during photolysis of alcoylcobaloximes under aerobic conditions [7,8,20]. We postulate that the complex, minus the pyridine base, could be the intermediate which undergoes the oxygen insertion into the Co—C bond. Unfortunately the ESR lines are too broad to show any possible hyperfine structure due to the pyridine ligand. Furthermore from the ESR experiments we cannot decide whether or not the pyridine remains attached during the oxygen insertion into the Co—C bond.

Acknowledgements

We are grateful to Professor E. Lederer for his interest in this work. We thank Dr. Kemp and Dr. M.D. Johnson for an interesting discussion of the results.

This work was supported by a National Research Council of Canada Grant (J.R.B.) and by a joint grant from CNRS (France) and NRC (Canada) (C.G.).

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