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ELECTRON SPIN RESONANCE STUDY OF THE ANAEROBIC PHOTOLYSIS OF ALKYLCOBALOXIMES; PHOTOCHEMICAL ELECTRON TRANSFER

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Summary

The anaerobic irradiation of alkyl(pyridinato)cobaloximes gives in the first instance the photochemical electron transfer reaction from the solvent or from the equatorial ligands for the methyl- and benzyl-(pyridinato)cobaloximes and homolytic cleavage for the isopropyl, isobutyl, n-pentyl and cyclohexyl compounds.

The photolysis of alkylcobaloximes in vacuo or under inert atmospheres has been the subject of earlier investigations [1—3]. It is generally assumed, by analogy with the photochemistry of Co^{III} complexes [4] and cobalamines [5], that the photolysis of alkylcobaloximes results in the homolytic cleavage of the Co—C bond. However, no physical evidence has previously been obtained for the production of a Co^{II} species in the primary photochemical step of alkylcobaloximes. In order to ascertain whether the Co^{II} species is the primary product we have undertaken an electron spin resonance (ESR) study of the anaerobic photolysis of some alkylcobaloximes.

The samples were degassed (to less than 10^{-3} Torr) on a vacuum line through at least five freeze-pump-thaw cycles. The samples were dissolved in chloroform (Fisher spectral grade containing ≈ 0.75% ethanol) and had a final concentration of $\approx 4 \times 10^{-3}$ *M*. I was a saturated solution ($\approx 4 \times 10^{-2}$ *M*). The degassed samples (in 4 mm quartz tubes) were irradiated in a Varian TE102 cavity with a Hanovia 977B1 1000 watt Hg—Xe arc lamp in a Schoeffel housing. The light was passed through a flowing water filter and a Corning 3-73 filter. Temperatures were maintained by a Varian Model E257 Variable Temperature System; the electron spin resonance apparatus was a Varian E-12.

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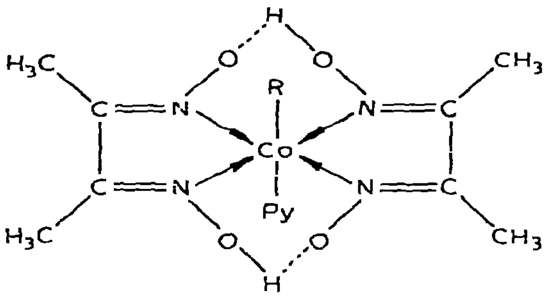

(Py = pyridine ;
I R = methyl ;
II R = isopropyl ;
III R = isobutyl ;
IV R = n-pentyl ;
V R = cyclohexyl ;
VI R = benzyl)

The results obtained can be divided into two groups. For the methyl- and benzyl-(pyridinato)cobaloximes I, VI, the photolysis results in the abstraction of an electron from the solvent producing a Co^{II} complex containing all of the original ligands; for the other alkyl(pyridinato)cobaloximes (II-V) the photolysis results in a homolytic cleavage of the Co—C bond with the formation of a Co^{II} complex and the corresponding alkyl radical.

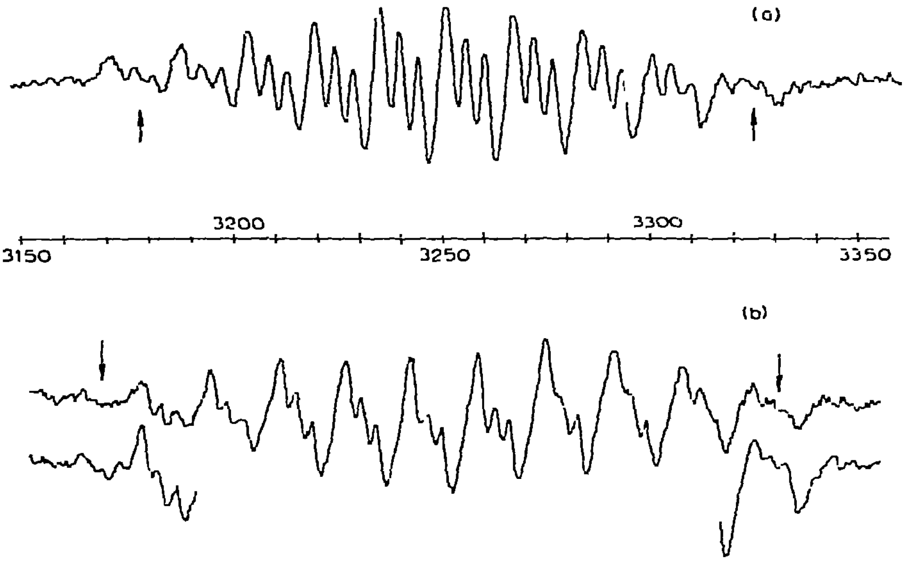

Fig. 1. ESR spectra of the photolysis products of VI(a) and I(b) at 253 K. Magnetic field is plotted in the middle (gradations 10 G). Modulation amplitude 2.0 g; microwave power 30 mW; microwave frequency 9.130 GHz; receiver gains 6.3×10^3 for (a) and 3.2×10^4 for (b). Insets in (b) were recorded at a gain of 8×10^4. The arrows indicate the outermost groups of lines in each spectrum.

The well-resolved ESR spectrum of the photolysis product of VI at —20° in chloroform is given in Fig. 1a. In the analysis the ten groups of lines are assumed to come from the accidental equality of the Co ($I = 7/2$) hyperfine splitting and the proton hyperfine splitting of the CH_2 group of the benzyl [$A^{Co} = A^{H}_{CH_2} = (15.3 \pm 0.3) \times 10^{-4}$ cm^{-1}]. The small triplet on each line arises from a single nitrogen ($I = 1$) [$A^{N} = (4.2 \pm 0.2) \times 10^{-4}$ cm^{-1}]; $\langle g \rangle = 2.009 \pm 0.001$. There is no doubt that this spectrum arises from a low-spin Co^{II} complex. The unpaired electron is probably in a d_{z^2} orbital, and hence large hyperfine splittings from the axial ligands are expected. Since both axial ligands present in VI contribute to the ESR spectrum, we assume that the photolysis has resulted in a simple electron transfer from the solvent.

The ESR spectrum of the photolysis product of the methyl(pyridinato)-cobaloxime (I) is shown in Fig. 1b. The spectrum is, however, much weaker than for VI. This appears to be due to a much lower quantum yield for photolysis of I. The spectrum is very similar to that in Fig. 1a except that there are eleven groups of lines instead of ten. This is expected, if the analysis of Fig. 1a is correct since a CH_3 group will add three groups of lines to the eight from the Co hyperfine splitting. In this case: $A^{Co} = A^{H}_{CH_3} = (15.1 \pm 0.4) \times 10^{-4}$ cm^{-1}; $A^{N} = (3.6 \pm 0.2) \times 10^{-4}$ cm^{-1}; $\langle g \rangle = 2.008 \pm 0.001$. Again we assume that a simple electron transfer has occurred. In support of this hypothesis we find that with both I and VI no other ESR spectrum is obtained at temperatures from —160 to 0°. Of course, the spectrum is considerably broadened at lower temperatures.

The ESR spectrum of the photolysis product of the isopropyl(pyridinato)-cobaloxime (II) at —160° is shown in Fig. 2. The spectrum is weak and there is a strong background signal; however, there is a sharp resonance in the free radical region ($\langle g \rangle = 2.003 \pm 0.001$) which we ascribe to the isopropyl radical and other lines which must arise from a Co^{II} complex. There is a clear set of eight parallel

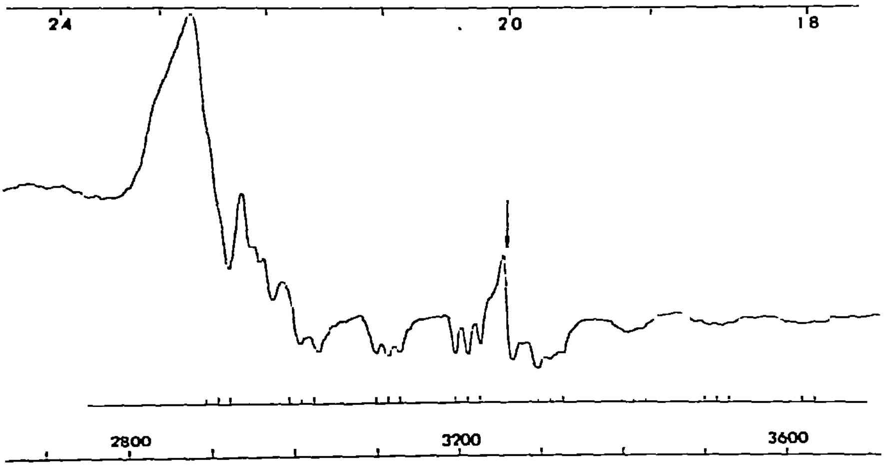

Fig. 2. ESR spectrum of the photolysis products of II at 113 K. Magnetic field is plotted at the bottom (gradations 100 G) and g is plotted at the top (gradations 0.1). The parallel components of the Co^{II} spectrum are indicated below the spectrum. Modulation amplitude 10 G; microwave power 20 mW, microwave frequency 9.137 GHz; receiver gain 3.2×10^{3}. The arrow indicates the resonance component assigned to the isopropyl radical.

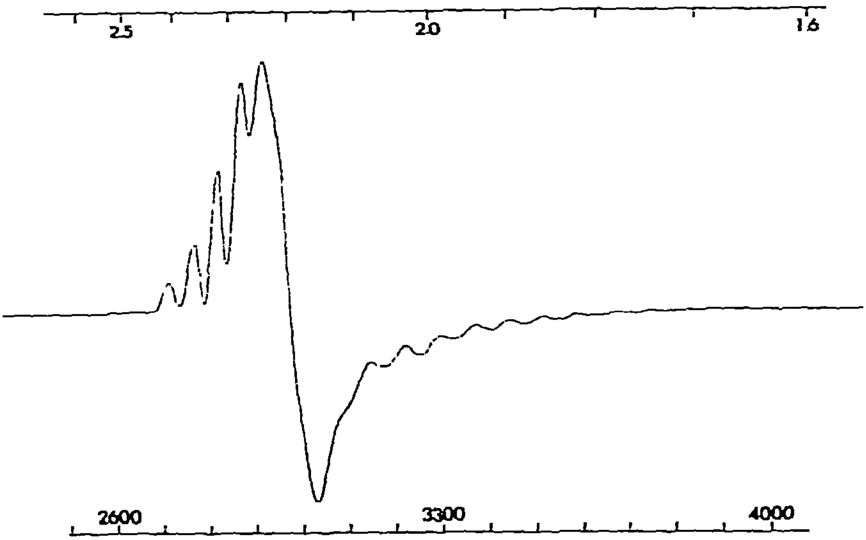

Fig. 3. ESR spectrum of the photolysis product of II at 173 K (spectrum taken at 113 K after photolysis at 173 K). Magnetic field is plotted at the bottom (gradations 100 G) and g is plotted at the top (gradations 0.1). Modulation amplitude 10 G, microwave power 5 mW; microwave frequency 9.133 GHz; receiver gain 8×10^2.

components in Fig. 2 with $g_\parallel = 1.986 \pm 0.005$; $A_\parallel^{Co} = (93 \pm 4) \times 10^{-4}$ cm^{-1}. In addition, each parallel component is split into three lines from one nitrogen ($I = 1$) with $A_\parallel^N = (13 \pm 2) \times 10^{-4}$ cm^{-1}. The perpendicular feature has some structure from which we obtain $g_\perp = 2.253 \pm 0.005$ and $A_\perp^{Co} = (13 \pm 2) \times 10^{-4}$ cm^{-1}. We assign this broad spectrum to the Co^{II} complex remaining after the removal of the isopropyl radical.

On warming the sample to −100° or on irradiation at −100° the ESR spectrum shown in Fig. 3 is obtained. It is characterized by the parameters $g_z = 1.86 \pm 0.01$, $g_y = 2.21 \pm 0.01$ and $g_x = 2.25 \pm 0.01$; $A_z = (66 \pm 3) \times 10^{-4}$ cm^{-1}, $A_y < 30 \times 10^{-4}$ cm^{-1}, $A_x = (54 \pm 3) \times 10^{-4}$ cm^{-1}. This Co^{II} complex may arise from loss of the pyridine ligand or substitution of a solvent molecule in the alkyl position. Almost identical results and spectra are obtained on the photolysis of III—V. The spectrum shown in Fig. 3 persists until ≈ 0°. We observe the same kind of signals in frozen toluene solutions.

The g factors for the Co^{II} species in the two low temperature spectra (Figs. 2 and 3) are characteristic of low-spin d^7 complexes with a strong tetragonal distortion of the octahedral field. For example, in cobalt(II) phthalocyanine in pyridine [6] $g_\parallel = 2.016$, $g_\perp = 2.268$ and $A_\parallel^{Co} = 78 \times 10^{-4}$ cm^{-1}, are in good agreement with our results.

We believe that our observations on II—V provide the first physical evidence for the hypothesis [1, 2] that the first step in the photochemistry of alkylcobaloximes is the homolytic cleavage of the Co—C bond. However, our observations on the photochemistry of I and VI show that the cleavage mechanism is not universal. Indeed, the nature of the initial photochemistry depends markedly on the nature of the alkyl ligand. There is evidence that the cleavage of the

Co—C bond in I is very difficult or impossible under strictly anaerobic conditions, but becomes easier when the photolysis is carried out under oxygen or a small concentration of oxygen [1, 2]. The benzyl substituent in VI may be stabilized by the phenyl group. Clearly electron transfer from the solvent or from the equatorial ligands is the primary photochemical step for I and VI, whereas the homolytic cleavage of the Co—C bond is the primary step for II—V.

We have carried out a wide variety of studies on the photochemistry of these compounds including rates of formation and decay of the Co^{II} species and effects of adding oxygen or in using polar solvents (isopropanol, ethanol). These will be reported in later publications.

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