PHOTOCHEMICAL ELECTRON TRANSFER REACTIONS IN ALKYLCOBALOXIMES

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Summary

It is shown that photolysis with visible light ($\lambda > 420$ nm) of any alkylcobaloxime procedes via a mechanism involving an initial electron transfer reaction from an equatorial ligand to the central metal to produce a cobalt(II) species which retains both original axial ligands. In a subsequent rearrangement of the equatorial ligand a hydrogen atom is ejected.

Introduction

In previous publications we discussed the electron spin resonance (ESR) spectra arising from the photolysis of several alkylcobaloximes [1—3]. We showed that with methyl- (I) and benzyl-pyridinecobaloxime (II) and analogous compounds, irradiation (λ above 420 nm) results in an electron transfer from the equatorial ligands to the central cobalt producing a cobalt(II) species containing the original axial ligands. A subsequent rearrangement of the equatorial ligands may result in the expulsion of a hydrogen atom. In the case of isopropylpyridine-cobaloxime (III) the photochemical behavior is different. We have shown that at —170°C, the products are a cobalt(II) complex without the axial alkyl ligand plus the free organic radical. On photolysis of III in the presence of the spin trap DMPO (dimethylpyrroline-N-oxide) there is also a detachment of a hydrogen atom [2], which could come either from the axial or equatorial ligands.

In this earlier work we discussed the question of whether photochemical electron transfer is a general primary step for the case of cobaloximes possessing a hydrogen atom β with respect to the Co—C bond. In order to provide further evidence on this matter we have extended our photolysis studies by use of ESR.

Experimental

The preparation of the compounds and the irradiation techniques and equipment were as described previously [1—3]. The irradiation at 77 K was carried out on a sample prepared by adding a chloroform solution of the cobaloxime (4×10^{-2} M) dropwise into liquid nitrogen contained in a Varian Model E 246-I Dewar insert. The flash photolysis techniques used in association with ESR have been described elsewhere [4].

Results

The photolysis of compounds III and IV at 8°C in perdeuterobenzene containing DMPO (0.05 M) produces an ESR signal identical to that which has been attributed to the species arising from detachment of a hydrogen atom in the photolysis [2]. We conclude that for compounds III and IV following the first step, the photolysis once again results in a detachment of a hydrogen atom from the equatorial ligands and not, as one might have supposed, from the axial alkyl ligand. In order to determine whether the hydrogen atom comes from the hydroxyl of the chelate or from the methyl groups of the dimethylglyoxime we prepared compound V. Irradiation of this compound as above in the presence of DMPO rapidly produced an ESR signal identical to that observed in the photolysis of compounds III or IV. We thus conclude that with isopropyl-d_7-pyridinecobaloxime (III) the detached hydrogen atom probably comes from the methyl groups of the dimethylglyoxime. We expect to obtain confirmation of this by using deuterated dimethylglyoxime.

We considered the possibility that the ESR signal following the addition of a hydrogen atom to DMPO might be due to a secondary thermal reaction. To test this hypothesis we employed the flash photolysis coupled with ESR detection. By setting the magnetic field at the hydrogen adduct ESR spectrum, we have shown that the signal appears in less than 1 ms after the flash, with no indication of a delay. Thus we conclude that the hydrogn atom spin adduct of DMPO is probably formed from hydrogen atoms liberated in the photolysis reaction and not as a result of secondary processes.

There is also the possibility that the hydrogen atom adduct of DMPO is formed by a direct reaction of DMPO with the cobalt(II) electron transfer product from the photolysis leading to an abstraction of an equatorial hydrogen atom to the DMPO. The ESR results do not allow us to reject this hypothesis. However, the mechanistic arguments which we put forward in previous publications and in this paper do not depend on whether or not the hydrogen atom is completely detached or remains associated with the cobalt-complex.

We have previously shown that the photolysis of isopropylpyridinecobaloxime (VI) between —170 and 0°C gives an ESR signal characteristic of the homolytic cleavage of the Co—C bond. However, this product is not detected below —170°C. We have repeated these investigations using photolysis of droplets of the CHCl₃ solutions of the cobaloxime frozen in liquid nitrogen in a quartz Dewar insert. Prolonged irradiation (about 1 h) of frozen droplets of isopropyl-morpholinecobaloxime (VII) gives rise to two signals at 77 K, one due to a cobalt(II) species resulting from electron transfer (species A) and the other to a
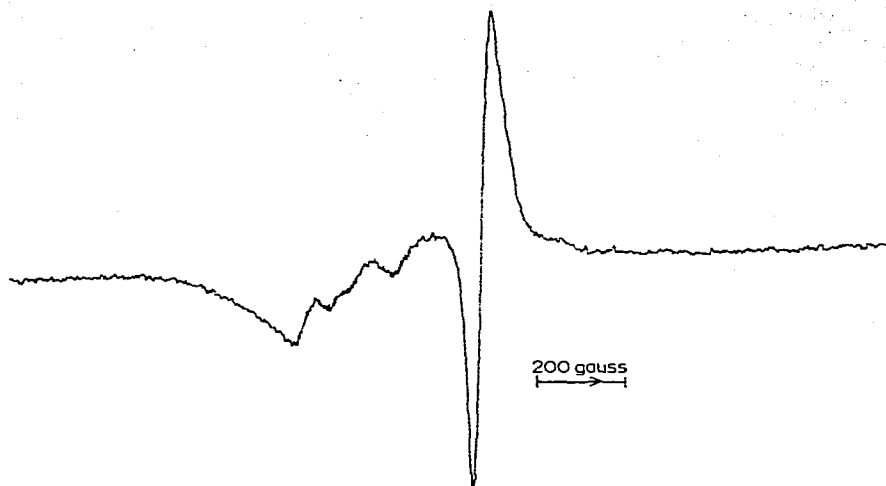
Fig. 1. ESR spectrum of the photoylsis of droplets of the $CHCl_3$ solution of the isopropylmorpholine-cobaloxime (VII) frozen in liquid nitrogen. Modulation amplitude 12.5 G, microwave power 1 mW; microwave frequency 9335 GHz, receiver gain 3.2×10^2.

cobalt(II) species resulting from the homolytic cleavage of the Co—C bond (species B) (Fig. 1). The ESR spectrum of species B was characterised earlier [1]. The spectrum we have labelled as species A is the same as that observed for the benzylpyridinecobalozime(II) under the same conditions.

Analogous spectra were obtained from isopropylpyridinecobaloxime (VI) and ethylpyridinecobaloxime (VIII). In the case of n-propylpyridinecobaloxime (IX) we observed only the formation of species A, that is the cobalt(II) species due to electron transfer without any trace of species B (Fig. 2). As before, photolysis at higher temperature and at 77 K of the benzylpyridinecobaloxime(II) gave only the electron transfer product, A.

We conclude that the photolysis at 420 nm of any alkylcobaloxime proceeds by an initial electron transfer from an equatorial ligand to the metal, and that this ligand then rearranges with the expulsion of a hydrogen atom. At low temp-
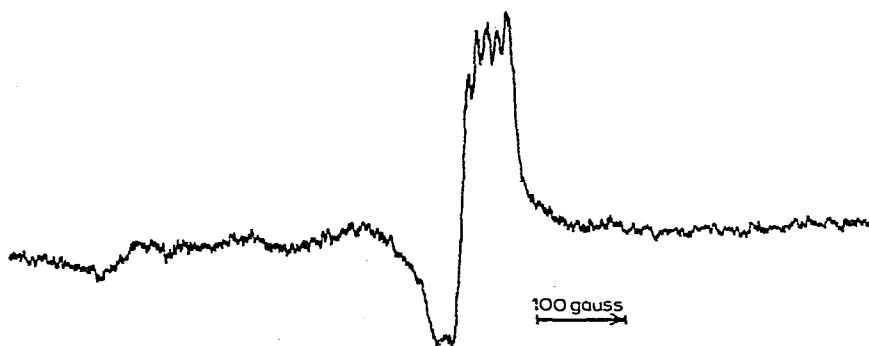

Fig. 2. ESR spectrum of the photolysis of droplets of the $CHCl_3$ solution of the n-propylpyridinecobal-oxime (IX). Modulation amplitude 0.5 G, microwave power 2.2 mw, microwave frequency 9335 GHz, receiver gain 10×10^3.

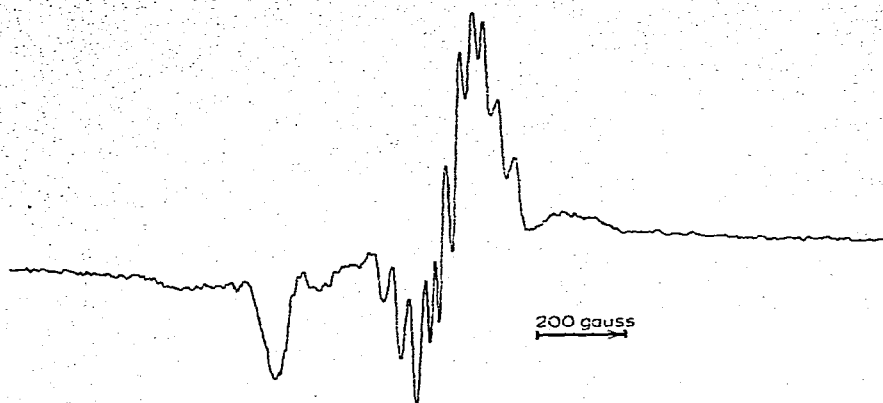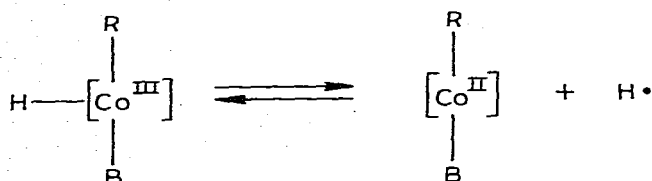Fig. 3. ESR spectrum of the anaerobic photolysis of the benzyl-2-methylpyrazinecobaloxime (XIII) in CHCl$_3$ at +20°C then cooled down rapidly at −100°C without further photolysis. Modulation amplitude 12.5 G, microwave power 15 mW, microwave frequency 9152 GHz, receiver gain 1.25 × 10^3.

erature the process is reversible, and can be formulated as follows:

The homolytic cleavage of the Co—C bond depends strongly on the nature of the alkyl groups, on the nature of the solvent and also on the temperature.

In the case of benzylpyridinecobaloxime, photolysis at temperatures between −160 and −10°C gives solely the electron transfer product, but if the photolysis is carried out at +20°C and the temperature suddenly lowered to −100°C, it is possible to detect the cobalt(II) species due to homolytic cleavage of the Co—C bond (Fig. 3).

The cleavage of the Co—C bond also depends strongly on the base lying in the axial position. The methylaquocobaloxime (X) and the benzylcobaloximes having 3-cyanopyridine (XI), 4-cyanopyridine (XII) and 2-methylpyrazine (XIII) respectively, as an axial base undergo homolytic cleavage of the Co—C bond on photolysis more easily than the benzylpyridinecobaloxime (II). Photolysis of the methylaquocobaloxime at −20°C (in CHCl$_3$) followed by ESR examination at −120°C shows a mixture of species A and B rather than exclusively species A as found for the benzylpyridinecobaloxime.

We suggest that the homolytic cleavage of the Co—C bond occurs via the mechanism previously suggested, i.e.:
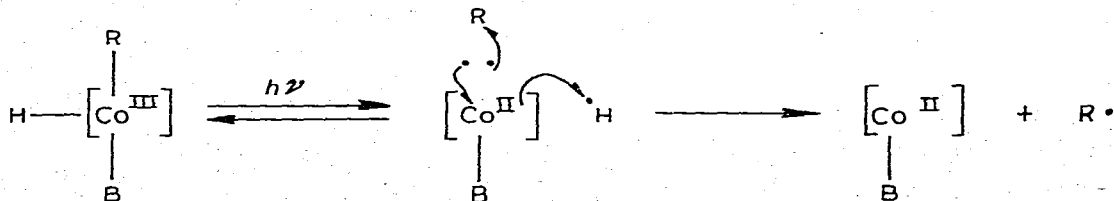
Discussion

It was previously suggested that an absorption band of alkylcobaloximes between 400 and 500 nm is due either to a transition involving charge transfer from the alkyl ligand to the cobalt [5—7] or to a metal d—d [8] transition. In the light of our results we conclude that the transition was probably incorrectly assigned. A better interpretation is that the transition is due to a charge transfer from the equatorial ligands to the cobalt. In the case of complexes containing saturated equatorial ligands the charge transfer Co—C bond is found in the UV region of the spectrum [9].

The cleavage of the Co^{III}—C bond could proceed through the intermediate formation of a Co^{II}—C bond by an initial electron transfer. If the Co^{II}—C is weak then cleavage will occur; otherwise the Co^{II}—C bond will remain intact, thus stabilizing the electron transfer product. Further optical studies will be necessary to characterize these transitions fully.
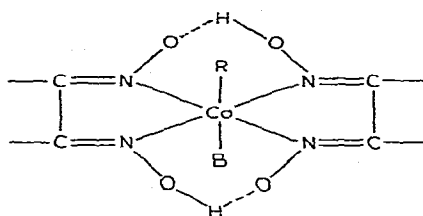
(I—IV, VI—XIII)
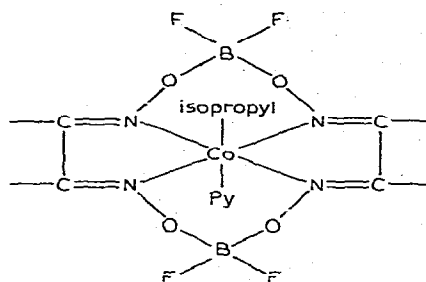
(V)

I , R = CH_3 , B = pyridine ;

II , R = CH_2—⬡ , B = pyridine;

III . R = CD<CD_3 / CD_3 , B = pyridine-d_5 ;

IV , R = CD_2—CD_3 , B = pyridine-d_5 ;

VI . R = CH<CH_3 / CH_3 , B = pyridine ;

VII R = CH<CH_3 / CH_3 , B = morpholine ;

VIII . R = C_2H_5 , B = pyridine;

IX , R = $(CH_2)_2CH_3$, B = pyridine;

X , R = CH_3 , B = H_2O;

XI , R = CH_2—⬡ , B = 3-cyanopyridine;

XII , R = CH_2—⬡ , B = 4-cyanopyridine;

XIII , R = CH_2—⬡ , B = 2-methylpyrazine

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