

ELECTRON SPIN RESONANCE STUDY OF FREE RADICAL INTERMEDIATES IN THE PHOTOLYSIS OF SOME ALKYLCOBALOXIMES AND PEROXYCOBALOXIMES USING THE TECHNIQUE OF SPIN TRAPPING

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Summary

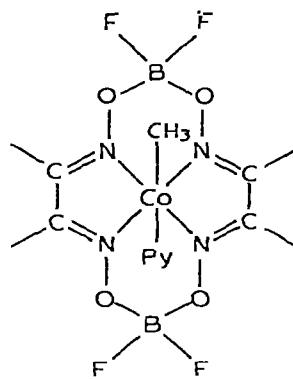
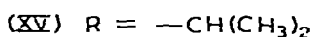
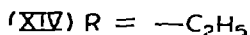
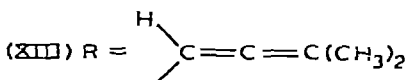
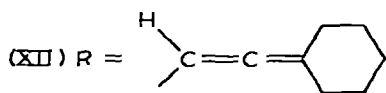
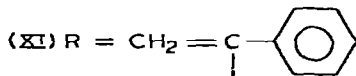
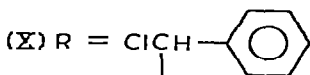
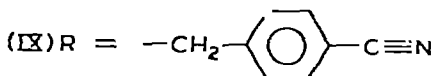
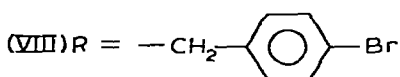
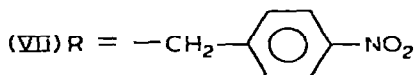
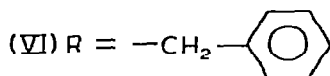
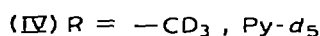
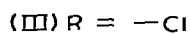
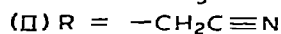
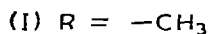
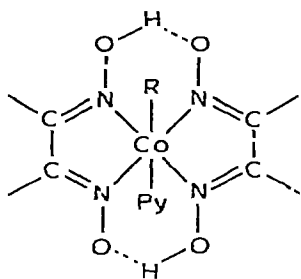
The anaerobic photolysis of methyl- and benzyl-pyridinecobaloximes and some analogous compounds proceeds via an electron transfer reaction to form a Co^{II} species containing the original axial ligands. Using the technique of spin trapping with 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) we have recorded an ESR spectrum which corresponds to the hydrogen atom adduct of DMPO. By use of selective deuteration and preparation of a BF_2 derivative we have shown that the ejected hydrogen atoms originate from the equatorial ligands of the complexes. The anaerobic photolysis of isopropylpyridinecobaloximes and analogous complexes also yields hydrogen atoms, but the products of photolysis arise from a $\text{Co}-\text{C}$ bond cleavage.

Anaerobic photolysis of alkylperoxycobaloximes in the presence of DMPO reveals the formation of both hydrogen atoms and RO^{\cdot} radicals.

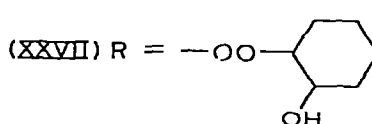
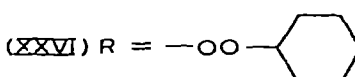
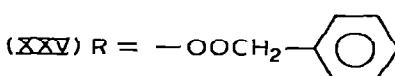
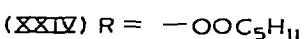
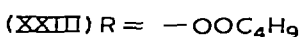
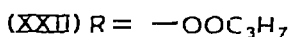
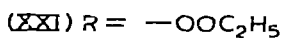
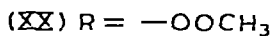
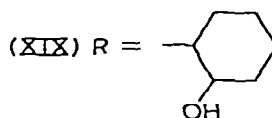
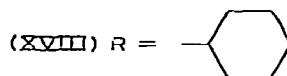
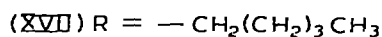
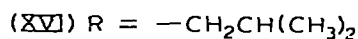
Introduction

Recently Schrauzer et al. [1, 2] proposed that the photolysis of methylcobaloximes in aqueous solution proceeds via the abstraction of hydrogen atoms, partly from the solvent and partly from the equatorial ligands of the complex. In a similar system we observed that the photolysis of methyl- and benzyl-pyridinecobaloximes [3] or analogous compounds [4], in chloroform or benzene, proceeds via an electron transfer reaction to a Co^{II} complex containing both of the original axial ligands; and we suggested that the electron necessary

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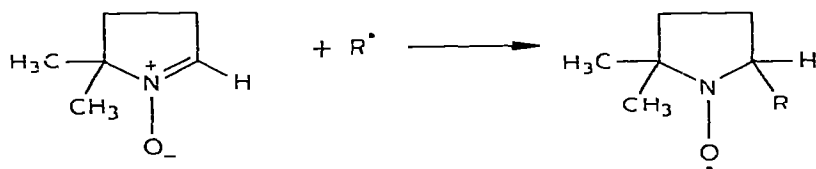
for this reduction comes either from the solvent or the equatorial ligands [3, 4].

In order to clarify the mechanism of these reactions, we have employed the technique of spin trapping [5], with electron spin resonance (ESR) spectroscopy to detect and identify any short-lived radical intermediates produced in the reaction. We have been able to show that hydrogen atoms are produced as

intermediates, and that they originate from the equatorial ligands of the complex.

Experimental

We used the spin trap 5,5-dimethyl-1-pyrroline-1-oxide [6, 7] (DMPO) which was synthesized and kindly donated to us by Dr. K.S. Chen. DMPO reacts rapidly with reactive free radicals R^\cdot to yield relatively stable nitroxides:



The ESR spectrum of the resulting nitroxide can be obtained, analyzed and in favorable cases enables identification of the intermediate R^\cdot .

In the experiments discussed below, DMPO (0.05 mol) was dissolved in chloroform or benzene (Baker Chemical Company, Phillipsberg, N.J.). The cobaloximes were dissolved [(I-V) 4×10^{-2} mol in CHCl_3 ; (VI-XXVII) 4×10^{-3} mol] in a solution containing DMPO and irradiated in the microwave cavity of a Varian E12 ESR spectrometer as described previously [3]. We also employed the technique of flash photolysis coupled to the ESR spectrometer [8].

CD_3I and pyridine- d_5 used in the synthesis of the deuterated compounds were obtained from Merck, Sharpe and Dohm, Montreal, Canada. Methyl- d_3 -pyridine- d_5 -cobaloxime was prepared as previously described for methylpyridine-cobaloxime [3].

Results and discussion

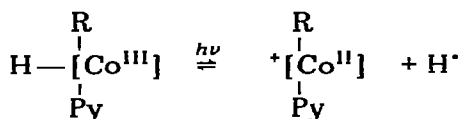
We attempted to trap radical intermediates at low temperatures ($\approx -196^\circ$ and $\approx -267^\circ$) and identify them by ESR, but no photolysis products were detected. However, with the spin trapping technique, the photolysis of compounds I-III and VI-XIII in benzene at 10° or chloroform at -75° in the presence of DMPO immediately produces an ESR spectrum of a nitroxide radical (Fig. 1) which can only have arisen from the reaction of a hydrogen atom with DMPO. The spectrum is analyzed in terms of $a_N = 14.3 \pm 0.3$ G and a_H (two protons) = 18.7 ± 0.3 g. This compares with $a_N = 14.4$ G and $a_H = 18.9$ G for the hydrogen atom adduct described by Janzen et al. in benzene solution [7]. Thus we are confident that hydrogen atoms are produced in the photolysis of the cobaloxime complexes, and the question is, "where do the hydrogen atoms come from?" To find the answer we used selective deuteration.

The irradiation of methyl- d_3 -pyridine- d_5 -cobaloxime in the presence of DMPO under the conditions described above yields exactly the same spectrum as in Fig. 1. Thus the hydrogen atom does not come either of the axial ligands. The irradiation of benzyl- or methyl-pyridinecobaloxime or methyl- d_3 -pyridine-cobaloxime in CDCl_3 or C_6D_6 also gives the same spectrum as in Fig. 1. Thus we conclude that the hydrogen atom does not come from the solvent but from the equatorial ligands of the complex.



Fig. 1. ESR spectrum of the hydrogen atom spin adduct to DMPO from the photolysis of methylpyridine-cobaloxime in benzene containing DMPO (0.05 mol). Modulation amplitude 1.0 G, microwave power 20 mW.

There are two possibilities for hydrogen atom abstraction from the equatorial ligands, either from one of the hydroxylic hydrogens or from the methyl hydrogens. In an attempt to deduce which we synthesized compound V, which does not contain any hydroxylic hydrogens. Irradiation of this compound in the presence of DMPO led to formation of the same hydrogen atom adduct, but the hydrogen abstraction was very slow. This result could be due to the nature of the compound or the fact that hydroxylic hydrogens are normally abstracted but in their absence methyl hydrogens can be abstracted less readily, so we cannot deduce which hydrogen is ejected; selective deuteration of the methyl group will be required to resolve this question. However, we do know that the hydrogen atom comes from the equatorial ligands and thus we can write the mechanism as follows:



This process is written as reversible since we have observed that at low temperatures (-160 to -100°) the formation of the electron transfer product is partially reversible. We attribute this to the fact that hydrogen atoms cannot diffuse very far away. This mechanism is in accord with the previous observation described [4] that if oxygen is admitted to a tube containing benzylpyridinecobaloxime which had been previously subjected to anaerobic photolysis exposure, an ESR spectrum can be recorded which corresponds to a stable nitroxide produced by the attack of a benzyl radical (released during the reaction with oxygen) on the equatorial ligand [4].

We applied the flash photolysis technique to this system by setting the magnetic field on one of the lines of the hydrogen atom adduct of DMPO, and found that the ESR spectrum develops within less than 1 ms after the initiation of the flash (flash duration $\approx 100 \mu\text{s}$). The signal decays relatively slowly (several seconds half life). We have not been able to follow the kinetics

of the formation of the Co^{II} species because the signal is very broad and this reduces the sensitivity.

We are extending the study of the kinetics of formation and decay of the Co^{II} species from the anaerobic photolysis of benzylpyridinecobaloxime using a steady-state light source and a fast shutter system. No ESR signal can be detected below $\approx -170^\circ$, but above -170° the signal increases in amplitude as the temperature is raised to $\approx -90^\circ$. This work will be described separately in a later communication.

In the case of compounds XIV-XIX in the presence of DMPO in CHCl_3 or benzene we observed in the first few seconds of photolysis the ESR spectrum shown in Fig. 1. Thus, although the photolysis of these compounds involves homolytic cleavage of the Co-C bond, hydrogen atoms are nevertheless ejected. At this stage we cannot say whether the hydrogen atom comes from an axial or an equatorial ligand. Specific deuteration studies are in progress.

In the case of the alkyl peroxide compounds XX-XXVII, we observed that photolysis accelerates the rate of a thermal reaction involving homolytic cleavage of the O-O bond. Using DMPO we have observed the spin adduct corresponding to the OR radical in addition to the spectrum corresponding to the hydrogen atom adduct [6, 7].

Acknowledgements

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