

PHOTOLYSIS IN APROTIC SOLVENTS OF SOME ALKYL CO^{III} COMPLEXES: AN ESR AND SPIN TRAPPING TECHNIQUE STUDY

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We have studied the anaerobic photolysis of samples of coordination complexes having a Co^{III}-C bond 1-13 in mixtures with nitrosodurene (1,2) Phenyl-t-butyl-nitrone (3,4,5) (PBN) or 5,5'-dimethyl-pyrroline-N-oxide (DMPO) (6) or the equimolecular mixture of DMPO-nitrosodurene and DMPO-PBN as a spin trap.

The ESR study of anaerobic solutions of (7) (220-300°K) containing nitrosodurene as spin trap exhibits instantaneously upon irradiation the characteristic spectra of alkyl free radical trapped adducts coming from the axial position of the complexes. If the photolysis is carried out with PBN, one can observe a rather more complicated ESR spectrum interpreted as the superposition of spectra of the alkyl and the hydrogen atom spin adducts (4,5) ($a_H = 7.33G$, $a_N = 14,66G$).

The photolysis of 1-7, 9-13 with DMPO instead of nitrosodurene or PBN, only gives the spectrum resulting from addition of one hydrogen atom to the spin trap, except in the case of adamantyl cobaloxime 8 (7) where a more complicated ESR spectrum corresponding to the superposition of ESR signals of one Hydrogen atom $a_H = 18,90G$, $a_N = 14,43G$ and adamantyl free radical spin trapped on the DMPO : $a_H = 21,00G$. $a_N = 13,66G$ (8) is obtained. The constants for adamantyl DMPO spin adduct are in the same order of those reported in literature for bulky free radicals (8).

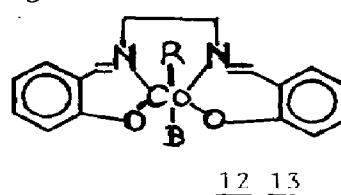
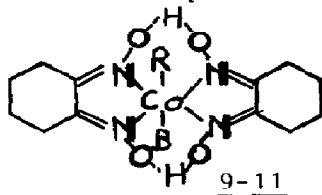
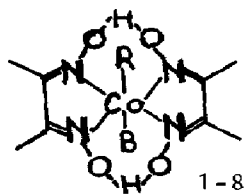
The photolysis of solutions of (1-7, 9-13) with equimolecular mixture of DMPO and nitrosodurene shows an ESR spectrum which can be interpreted as the superposition of ESR signals coming from the addition of one hydrogen atom and the alkyl free radical spin adduct respectively on DMPO and on nitrosodurene. If an equimolecular mixture of DMPO and PBN is used

one obtains a rather complicated ESR spectrum coming from one hydrogen atom spin adduct on DMPO and PBN and the alkyl free radical spin adduct on PBN.

Previously we have suggested that the hydrogen atom trapped by DMPO could be from the alkylcobaloxime equatorial ligand chelated hydrogen atom (9). To check this hypothesis we have studied the photolysis of some perdeuterated cobaloximes (2,4,6). The nature of the perdeuterated complex has been studied by IR and ^1H NMR spectroscopy.

One can observe in one hour the disappearance of the N-O-D stretch ($\nu_{2670\text{cm}^{-1}}$). The exchange is particularly fast and irreversible this rapid exchange explains why the photolysis of these compounds with DMPO in dry D_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$ solutions gives only the characteristic spectrum of hydrogen atom spin adduct on DMPO. We have checked that the deuterium atom produced by photolysis of toluene solution of $(\text{nC}_4\text{H}_9)_3\text{SnD}$ is spin trapped on DMPO : $g_{\text{iso}} = 2,0058 \pm 0,0002$, $a_{\text{N}} = 14,33\text{G}$, $a_{\text{H}} = 18,99\text{G}$, $a_{\text{D}} = 2,83\text{G}$.

The photolysis of the compounds 12-13 which do not contain any chelated hydrogen atoms, with DMPO, PBN, also gives alkyl radicals and hydrogen atom spin adducts, however with nitrosodurene, we get once more the free radical alkyl spin adduct. In this case hydrogen atom abstraction probably occurs from the α carbon atom of the equatorial ligand.



R	
CH_3	
CD_3 (dmg D_2 5 %)	
C_2H_5	
C_2D_5 (dmg D_2 5 %)	
$(\text{CH}_3)_2\text{CH}$	
$(\text{CD}_3)_2\text{CD}$ (dmg D_2 5 %)	
CNCH_2	
1-adamantyl	

B	
Py	<u>1</u>
PyD_5	<u>2</u>
Py	<u>3</u>
PyD_5	<u>4</u>
Py	<u>5</u>
PyD_5	<u>6</u>
Py	<u>7</u>
"	<u>8</u>

R	E	
CH_3	Py	<u>9</u>
$(\text{CH}_3)_2\text{CH}$	Py	<u>10</u>
$\text{C}_6\text{H}_5\text{CH}_2$	Py	<u>11</u>
CH_3	Py	<u>12</u>
CH_3	H_2O	<u>13</u>

In conclusion we have pointed out that during photolysis in benzene or toluene of alkylcobaloximes and related compounds (1-13), hydrogen atom and alkyl free radicals are formed. At the present time with our photochemical equipment coupled with ESR and spin trapping techniques it is not possible to precisely say which one is occurring first.

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