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PHOTOLYSIS IN APROTIC SOLVENTS OF SOME ALKYLCOBALT(III) COMPLEXES; AN ESR AND SPIN-TRAPPING TECHNIQUE STUDY

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Summary

Photolysis of several alkylcobalt(III) complexes in the visible region $\lambda > 420$ nm has been studied by ESR and spin-trapping techniques with nitrosodurene, phenyl-t-butylnitrone (PBN) and 5,5′-dimethylpyrroline-*N*-oxide (DMPO) and their mixtures. DMPO and PBN give spin adducts of two different radicals; the first is a hydrogen atom coming from the equatorial ligand, and the second is an alkyl-free radical coming from the axial position of the cobalt(III) complexes. This indicates that excitation of the complex is followed by the expulsion of one hydrogen atom and homolytic cleavage of the metal—alkyl bond.

Introduction

The use of spin-trapping techniques for quenching short lived intermediates has led to increased understanding of the mechanisms of photochemical reactions of transition metal complexes [1—7]. Photochemical activation of alkylcobaloximes [5,8—10] and analogous compounds [11] results in several reactions, and can be associated with the large absorption band in the UV-visible spectrum of these compounds [12—14] where several transitions overlap. On one hand the homolytic cleavage of the Co^{III}—C bond (which is catalysed by protic solvents [9] or acidic medium [8]) and photoexpulsion of the Lewis axial base [15], can be observed, and on the other hand excitation in the CTTM band of the equatorial ligand is followed by electron transfer to the metal and expulsion of one hydrogen atom [5,9], and probably one nitrogen atom is decoordinated [16].

In order to determine the precise nature of the intermediates produced during these photolyses we have irradiated samples of alkylcobalt(III) complexes in the presence of spin traps, inside the ESR cavity.

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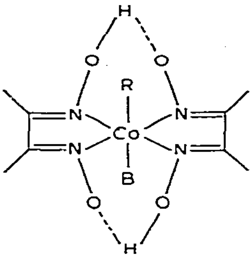
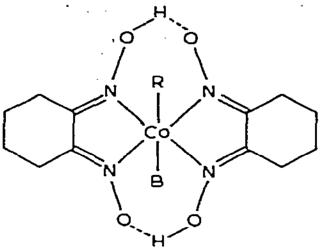
Experimental

The alkylcobaloximes, perdeuterated alkylcobaloximes, and salen compounds were prepared as indicated in the literature [9,12,14].

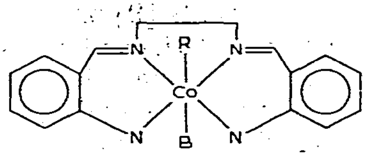
Solutions of alkylcobaloximes (5×10^{-3} M) in carefully purified benzene or toluene were introduced into a 4 mm cylindrical quartz ESR tube in the dark and deoxygenated by bubbling a slow stream of argon for 20 min. They were then introduced into an ER-400X-RL cavity of a Bruker ER-420 spectrometer equipped with a B-ST 100/700, B-MN12 and B-A6 accessories for variable temperature, magnetic field calibration, and frequency measurements, respectively. Irradiation was carried out with a Hanovia 977 B-0090, 1000 W Hg—Xe arc lamp in a Model LH 15 1H Schoeffel Lamp Housing. The light was focused through quartz lenses and filtered through a 15 cm flowing water filter and a Corning 3.73 filter. The spin traps used were 5,5'-dimethylpyrroline-*N*-xodie (DMPO), nitrosodurene and phenyl-t-butylnitrone (PBN) in 5×10^{-2} M concentration. The tri-n-butyltin hydride and tri-n-butyltin deuteride were prepared by reduction of tri-n-butyltin chloride or bis(tri-n-butyltin) oxide with lithium aluminium hydride and lithium aluminium deuteride in dry ether [1,18]. The ^{1}H NMR, UV and IR spectra were recorded, respectively on Varian T60 and Perkin—Elmer R12, Cary 14 and Perkin—Elmer IR 257 spectrometers.



	R	B
I	CH_3	Py
II	CD_3(DMG D_2 5%)	PyD_5
III	C_2H_5	Py
IV	C_2D_5(DMG D_2 5%)	PyD_5
V	$(CH_3)_2CH$	Py
VI	$(CD_3)_2CD$(DMG D_2 5%)	PyD_5
VII	$CNCH_2$	Py
VIII	$HOCH_2CH_2$	Py
IX	$C_6H_5CH_2$	Py
X	$C_6H_5CH_2$	H_2O
XI	$C_6H_5CH_2$	Morphiline
XII	*p*-$BrC_6H_4CH_2$	Py
XIII	*p*-$CNC_6H_4CH_2$	Py
XIV	*p*-$NO_2C_6H_4CH_2$	Py
XV	C_5H_{11}	Py
XVI	$C_{10}H_{21}$	Py
XVII	$C_{12}H_{25}$	Py
XVIII	$C_{12}H_{25}$	H_2O
XIX	$C_{16}H_{35}$	Py
XX	1-Adamantyl	Py



	R	B
XXI	CH_3	Py
XXII	$(CH_3)_2CH$	Py
XXIII	$C_6H_5CH_2$	Py
XXIV	$C_{10}H_{21}$	Py
XXV	$C_{12}H_{25}$	Py
XXVI	$C_{16}H_{33}$	Py



	R	B
XXVII	CH_3	Py
XXVIII	CH_3	H_2O
XXIX	CH_3	*p*-CNPy

Results

We have studied the anaerobic photolysis of samples of the coordination complexes I—XXIX in solutions containing nitrosodurene [19,20], phenyl-t-butylnitrone [21—23] (PBN) or 5,5'-dimethylpyrroline-*N*-oxide (DMPO) [24] or an equimolar mixture of DMPO/nitrosodurene or DMPO/PBN. We confirmed by UV and ^{1}H NMR spectroscopy that there is no reaction or association between the spin traps or their equimolar mixtures with the cobalt(III) complexes. We also confirmed that carefully degassed solutions prepared in the dark and introduced into the ESR cavity do not show any signal. On irradiation anaerobic solutions of I—XIX (220—300 K) containing nitrosodurene as spin trap immediately exhibits the characteristic spectra of trapped alkyl free radical adducts (Table 1) coming from the axial position of the complexes. If the photolysis is carried out with PBN, a rather more complicated ESR spectrum is observed and is interpreted as the superposition of spectra of the alkyl and the hydrogen atom spin adducts [22,23] (a(H) 7.33 G, a(N) 14.66 G (Fig. 1)).

The photolysis of I—XIX or XXI—XXIX with DMPO instead of nitrosodurene or PBN, gives only the spectrum resulting from addition of one hydrogen atom to the spin trap, except in the case of adamantylcobaloxime (XX) [25] where a more complicated ESR spectrum is obtained corresponding to the superposition of ESR signals of one hydrogen atom a(H) 18.90 G, a(N) 14.43 G and adamantyl free radical spin trapped on the DMPO: a(H) 21.00 G. a(N) 13.66 G [26] (Fig. 2). The constants for adamantyl DMPO spin adduct are in the range reported for bulky free radicals [26].

Photolysis of solutions of I—XIX and XXI—XXV) with an equimolar mixture of DMPO and nitrosodurene immediately shows an ESR spectrum which can be interpretated as the superposition of ESR signals coming from the addition

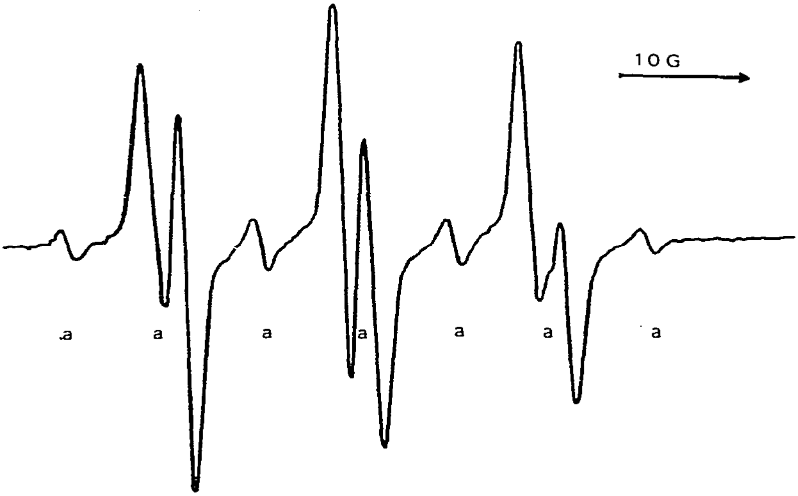


Fig. 1. ESR spectrum of the hydrogen atom spin adduct (a) and the isopropyl spin adduct (b) with PBN, obtained by photolysis of isopropylpyridinecobaloxime (V) in toluene containing PBN. (Microwave frequency 9.515 GHz, modulation intensity 1 G, microwave receiver gain 5 × 10^4, microwave power 25 mW.)

TABLE 1

HYPERFINE SPLITTING CONSTANTS FOR NITROXIDES PRODUCED BY RADICAL ADDITIONS TO NITROSODURENE AT ROOM TEMPERATURE IN TOLUENE

R	Radical source	g_{iso} ±0.0003	Splitting constants (G)		
			a(N)	a_{β}(H)	Other
CH_3	I, XXI, XXVII, XXVIII, XXIX	2.0062	13.65	12.17	
CD_3	II	2.0067	13.54		1.87(D)
C_2H_5	III	2.0058	13.50	10.99	
C_2D_5	IV	2.0060	13.65		1.66(D)
$CH(CH_3)_2$	V, XXII	2.0058	13.70	6.65	
$CD(CD_3)_2$	VI	2.0064	13.65		<0.9(D)
$CNCH_2$	VII	2.0056	13.17	8.33	
$HOCH_2CH_2$	VIII	2.0056	13.33	13.33	
$C_6H_5CH_2$	IX, X, XI, XXIII	2.0050	13.65	8.00	
p-$BrC_6H_4CH_2$	XII	2.0052	13.33	7.99	
p-$CNC_6H_4CH_2$	XIII	2.0057	13.16	7.99	
p-$NO_2C_6H_4CH_2$	XIV	2.0052	13.25	7.99	
C_5H_{11}	XV	2.0064	13.49	10.83	
$C_{10}H_{21}$	XVI, XXIV	2.0042	13.75	10.67	
$C_{12}H_{25}$	XVII, XVIII, XXV	2.0042	13.75	10.70	
$C_{16}H_{33}$	XIX, XXVI	2.0042	13.75	10.67	
1-Adamantyl	XX	2.0062	13.58		

of one hydrogen atom and the alkyl free radical spin adduct respectively, to DMPO and nitrosodurene (Fig. 3). If an equimolar mixture of DMPO and PBN is used, a rather complicated ESR spectrum is obtained, which comes from one hydrogen atom spin adduct with DMPO and PBN and the alkyl free radical spin adduct with PBN (Fig. 4).

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

The hydrogen of the hydroxyl group of the dimethylglyoxime itself deuterated

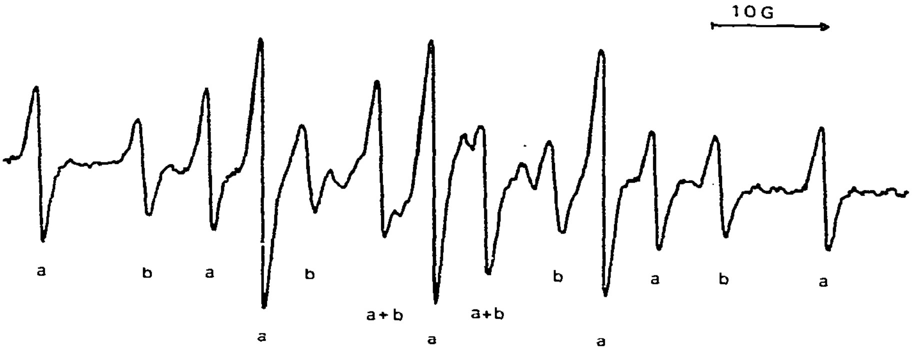


Fig. 2. ESR spectrum of the hydrogen atom spin adduct (a) and the 1-adamantyl spin adduct (b) with DMPO, obtained by photolysis of 1-adamantylpyridinecobaloxime (XX) in toluene containing DMPO. (Microwave frequency 9.518 GHz, modulation intensity 1 G, microwave receiver gain 2.5 X 10^5, microwave power 25 mW.)

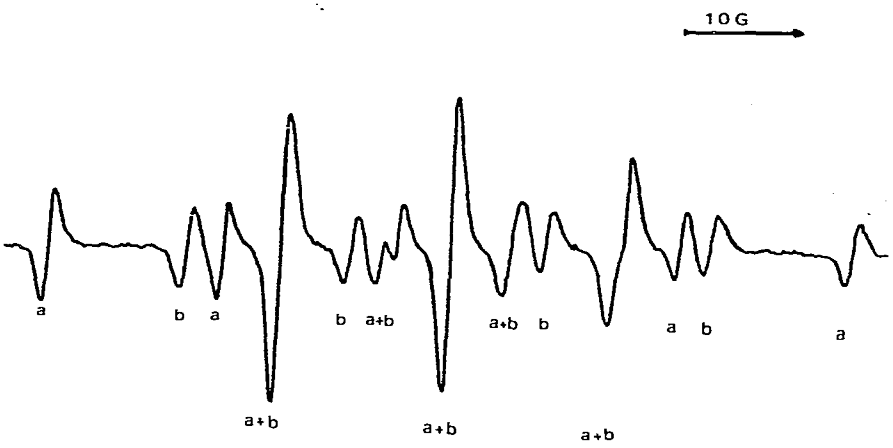


Fig. 3. ESR spectrum of the hydrogen atom spin adduct with DMPO (a) and the benzyl spin adduct (b) with nitrosodurene, obtained by photolysis of benzylpyridinecobaloxime (IX) in toluene containing an equimolar mixture of DMPO and nitrosodurene. (Microwave frequency 9.510 GHz, modulation intensity 8 G, microwave receiver gain 1.25 × 10^5, microwave power 25 mW.)

to the extent of more than 95% [8], but, surprisingly, the hydrogen in the chelated position of the complexes II, IV, VI was found by ^1H NMR to be <5% deuterated, and the methyl of the dimethylglyoxime equatorial ligand was 45% deuterated. We also studied the evolution of these complexes by taking an IR spectrum every ten minutes for one hour. The N—O—D stretch (ν 2670 cm^{-1}) disappears during this time. The exchange is particularly fast and irreversible (Fig. 5) this rapid exchange explains why the photolysis of these compounds with DMPO in dry C_6D_6 or $C_6D_5CD_3$ solutions gives only the characteristic spectrum of the hydrogen atom spin adduct with DMPO. We have confirmed that the deuterium atom produced by photolysis of a toluene solution of $(n\text{-}C_4H_9)_3SnD$ is spin trapped by DMPO: $g_{iso} = 2.0058 \pm 0.0002$, a(N) 14.33 G, a(H) 18.99 G, a(D) 2.83 G.

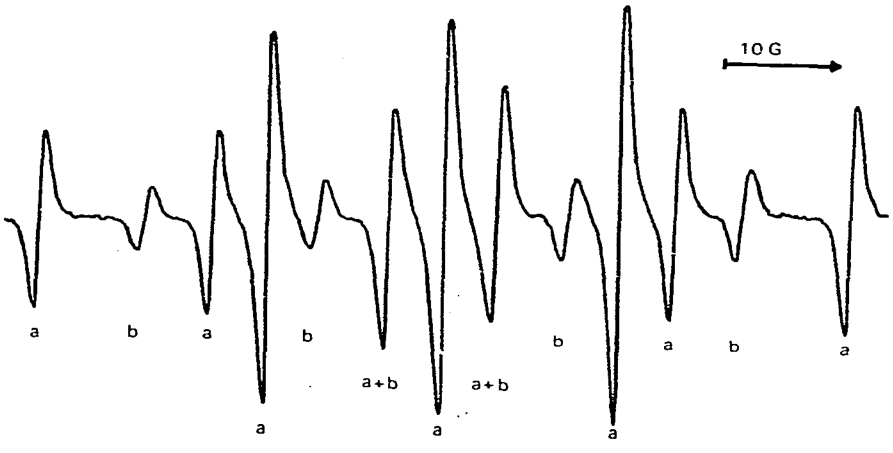


Fig. 4. ESR spectrum of hydrogen atom spin adduct with DMPO (a) the hydrogen atom spin adduct with PBN (b), and the methyl spin adduct with PBN (c), obtained by photolysis of methylpyridinecobaloxime (I) in toluene containing an equimolar mixture of DMPO and PBN. Microwave frequency 9.519 GHz, modulation intensity 1 G, microwave receiver gain 10^5, microwave power 25 mW.)

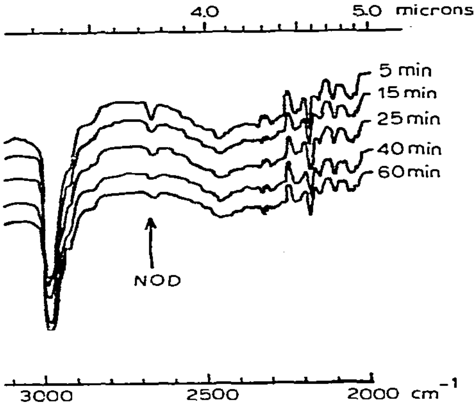


Fig. 5. Infrared spectrum of perdeuterated isopropyl-d_7-pyridine-d_5-cobaloxime-d_2, 5% VI in CDCl$_3$.

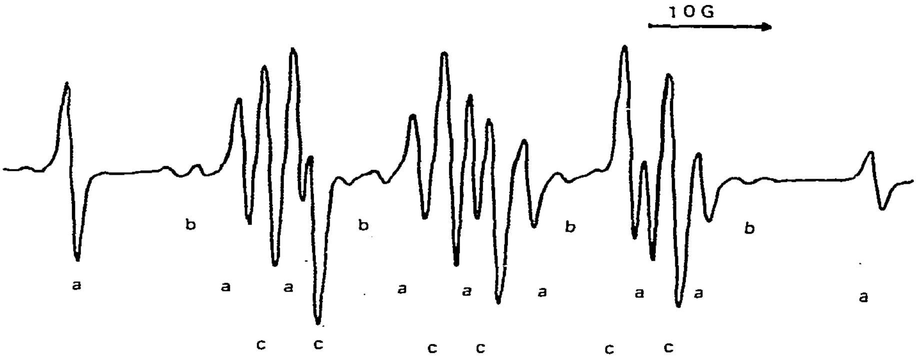


Fig. 6. ESR spectrum of the hydrogen atom (a) and methyl spin adduct (b) with DMPO, obtained by photolysis of methylpyridine-Salen (XXVII) in toluene containing DMPO. (Microwave frequency 9.460 GHz modulation intensity 0.63 G, microwave receiver gain 6.3 × 10^4, microwave power 25 mW.)

TABLE 2

HYPERFINE SPLITTING CONSTANTS FOR NITROXIDE PRODUCED BY RADICAL ADDITIONS TO PHENYL-t-BUTYLNITRONE AT ROOM TEMPERATURE IN TOLUENE

R	Radical source	g_{iso} ±0.0003	Splitting constants		
			a(N)	a_β(H)	a_β(D)
H	I, XXIX and (n-$C_4H_9)_3$SnH	2.0053	14.99	7.49	
D	(n-C_4H_9)SnD	2.0070	14.66	7.44	1.25
CH_3	I, XXI, XXVII, XXVIII, XXIX	2.0061	14.91	3.66	
$C_6H_5CH_2$	IX, X, XI, XXIII	2.0047	14.41	2.83	
$CH(CH_3)_2$	V, XXII	2.0072	14.66	2.58	
$CD(CD_3)_2$	VI	2.0072	14.66	2.58	
$CNCH_2$	VII	2.0065	14.41	3.58	
$HOCH_2CH_2$	VIII	2.0070	14.66	3.58	
C_5H_{11}	XV	2.0065	14.66	3.41	
$C_{10}H_{21}$	XVI, XXIV	2.0071	14.66	3.33	
$C_{12}H_{85}$	XVII, XVIII, XXV	2.0070	14.66	3.33	
$C_{16}H_{33}$	XIX, XXVI	2.0072	14.66	3.31	
1-Adamantyl	XX	2.0058	14.75	2.21	

The photolysis of compounds XXVII—XXIX, which do not contain any chelated hydrogen atoms, in presence of DMPO or PBN also gives alkyl radical and hydrogen atom spin adducts (Fig. 6); however, with nitrosodurene, the free radical alkyl spin adduct is again observed. In this case the hydrogen atom abstraction is probably from the α-carbon atom of the equatorial ligand.

Discussion

We have shown that during the photolysis of a large number of alkylcobalt complexes in organic aprotic solvents, two radical species are involved: alkyl radicals and hydrogen atoms.

With DMPO, it is possible to observe hydrogen atom abstraction under visible photolysis even at very low temperature (150 K). The abstraction of the hydrogen atom has been found to occur in less than 10^{-3} sec [4]. When nitrosodurene is used with alkylcobaloximes VII, IX—XIV, the alkyl free radical spin adduct can be detected below 220 K, but if the photolysis is carried out at lower temperature (180—210 K) and detection is made at 230 K without any further photolysis the spectrum resulting from the addition of the alkyl free radical to nitrosodurene is clearly observed. This spectrum disappears again if the temperature is lowered below 220 K, but reappears above 220 K. This can account for by assuming that the free radical spin adduct dimerises below 220 K but dissociates again above 220 K without photolysis.

Literature reports [26,27] reveal that DMPO does act as a spin trap for alkyl free radicals and hydrogen atoms. We find that except for the compounds XX, XXVII—XXIX, DMPO does not simultaneously trap on alkyl free radical and a hydrogen atom, but only the latter spin; this can be attributed to the fact that hydrogen atoms react so fast that trapping of alkyl free radicals by DMPO is precluded. It is noteworthy that the reaction of the alkyl free radical with DMPO is in competition with the recombination process with the cobalt(II) [8,11,28], to reform the initial Co^{III}—C bond, and with other secondary reactions, and so the spin density is very low and DMPO may not trap enough alkyl radicals to give significant signals. In the case of compound XX, the bulky adamantyl free radical does not easily undergo secondary reactions and is stable enough to be detected directly by ESR in solution [29,30] but it reacts readily with DMPO to give the corresponding spin adducts. In the case of the photolysis of Salen complexes XXVII—XXIX it is possible to detect the adducts between DMPO and the hydrogen atom and the alkyl free radical. This hydrogen atom coming from the α-carbon of the equatorial ligand would come off more slowly than the chelated hydrogen atom of the dimethylglyoxine complex derivatives and so the DMPO can trap the alkyl free radicals more effectively.

Nitrosodurene was found not to trap hydrogen atoms in previous studies [19,20]. We carried out photolyses of a mixture of nitrosodurene with $(n\text{-}C_4H_9)_3SnH$ and $(n\text{-}C_4H_9)_3SnD$, but no stable hydrogen or deuterium atom spin adducts were detected. It is possible that nitrosodurene can spin trap one hydrogen atom, to give a very short lived free radical which can either react with another hydrogen atom to give the corresponding hydroxylamine or undergo other reactions. After continuous photolysis of a sample containing an alkylcobaloxime (I,V) and equimolar amount of nitrosodurene, an aromatic hydroxylamine and additional unidentified compounds were detected by IR (ν(N—OH), ν(NO) at 3540, 1540 cm^{-1} respectively) and ^{1}H NMR spectroscopy (m at δ 5.2 and 5.5 ppm). A sample of nitrosodurene photolysed on its own with $(n\text{-}C_4H_9)_3SnH$ gave approximately the same mixture.

Recently we showed that in the photolysis of methylcobaloxime in the presence of nitrosodurene the homolytic cleavage of the cobalt—carbon bond and the recombination process are rather slow and spin trapping by nitrosodurene is quite efficient [28]. If the expulsion of the hydrogen atom is a very fast process, that could explain why DMPO reacts virtually exclusively with the hydrogen atom in the case of most of the cobaloximes.

We have pointed out in previous publications [4,5,6,10] that cleavage of the cobalt—carbon bond is not easily detected and identified during the photolysis of alkylcobaloximes at low temperature and in aprotic solvents, such cleavage is more easily detected at room temperature. This could be explained by the fact that recombination is temperature- and viscosity-dependent, and that low temperature and high viscosity promote recombination. The nitrosodurene or PBN at room or low temperature quenches the recombination process $Co^{II} + {}^{\bullet}R \rightarrow Co^{III}$—R by diffusion in the solvent cage, and so it is possible for the alkyl radical spin adducts to be formed more easily.

Abstraction of the hydrogen atom from crystalline dimethylglyoxime is brought about by γ-irradiation [32]. The facility with which the hydrogen atom formed by photolysis of alkylcobaloximes trapped by DMPO and PBN favours the proposed resonance form of the hydrogen atom of the OH group of the dimethylglyoximate anion in metal complexes [33,34,35].

In conclusion, while we have shown that during photolysis in benzene or toluene of alkylcobaloximes and related compounds (I—XXIX) hydrogen atoms and alkyl free radicals are formed, we cannot at present say which of these processes occurs first after the initial light excitation.

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