E.S.R. Spectra of Radicals formed in the System Formaldehyde–Diaquacobaloxime–Nitroso-compound; Methylene or Oxymethylene Trapping

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Diaquacobaloxime promotes formation of radicals from formaldehyde; products of trapping of these radicals by nitroso-compounds have unusually small methylene hyperfine coupling constants.

Electron transfer from paramagnetic transition metal compounds onto formaldehyde, which would give rise to co-ordinated $[CH_2O]^{\bullet-}$, $\bullet CH_2$–O–metal or $\bullet O$–CH_2–metal, species has not been reported previously. Such species could have interesting reactivity. Deoxygenation of formaldehyde giving rise to methylene has recently been achieved in the gas phase by atomic carbon,[1] the methylene formed being trapped by cyclohexene. Methylene was also trapped at 4.2 K by nitric oxide, giving the methyleneamine *N*-oxyl radical $CH_2{=}N{-}O^{\bullet-}$.[2] However, no other potential methylene traps, such as paramagnetic transition metal nitroxides, have been described.

Diaquacobaloxime, $Co(Hdmg)_2(H_2O)_2$ (H_2dmg = dimethylglyoxime), reacts in polar solvents such as methanol, acetone, acetonitrile, or dimethyl sulphoxide (DMSO) with nitrosobenzene, giving rise to the known phenylcobaloxime-nitroxide radical[3] $Co^{III}(Hdmg)_2N(Ph)O^{\bullet}$. We have found that a solution of $Co(Hdmg)_2(H_2O)_2$ (1 mmol) and PhNO (1—2 mmol) (or a substituted nitrosobenzene) reacts with aqueous formaldehyde (3 mmol; 30 cm^3 of solvent; Ar; room temp.;

Table 1. Hyperfine coupling constants (a/G)[a] and g values for the radicals detected in the systems containing diaquacobaloxime, formaldehyde, and nitroso-compounds in acetone.

Nitroso-compound	a(N)	$a(CH_2)$	$a(H_{o,p})$	$a(H_m)$	g
PhNO	10.40	4.12	2.69	0.94	2.0048
p-BrC_6H_4NO	11.20	4.3	3.20	1.0	2.0047
3,5-$Cl_2C_6H_3NO$	9.83	4.06	2.73	—	2.0056
2,6-$Cl_2C_6H_3NO$	12.70	7.62	0.95	0.7	2.0063
2,4,6-$Br_3C_6H_2NO$	12.63	7.89	—	0.5	2.0061

[a] 1 G = 10^{-4} T.

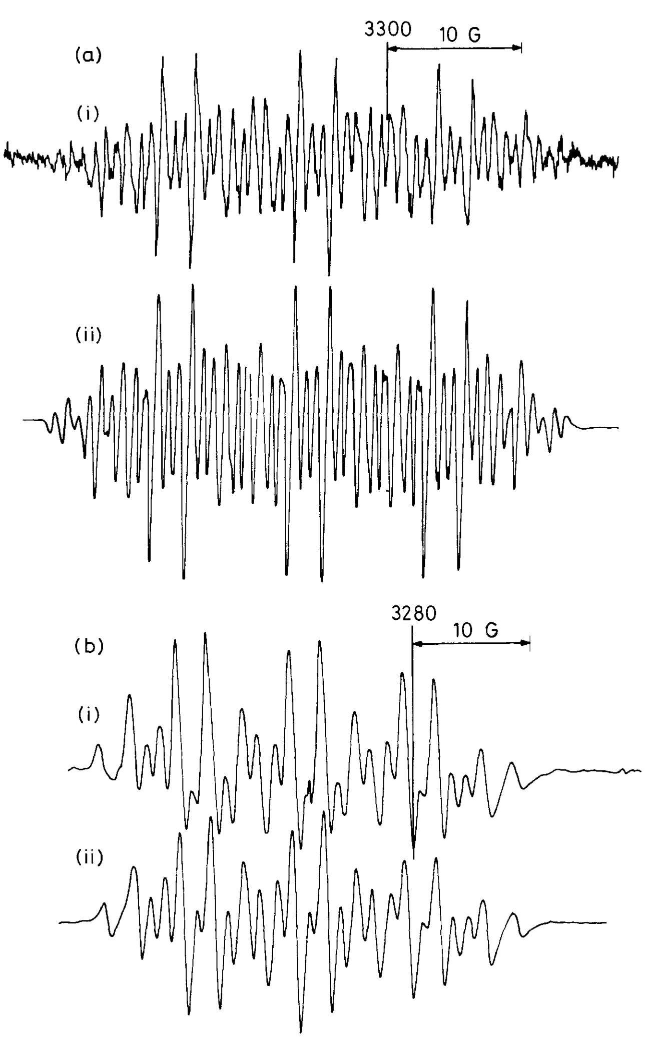

Figure 1. E.s.r. spectra of the radicals formed in the system aqueous formaldehyde–diaquacobaloxime–nitroso-compound: (a) nitrosobenzene; (b) 3,5-dichloronitrosobenzene; (i) experimental; (ii) computer simulated.

few minutes) giving rise to radicals, examples of the e.s.r. spectra of which are shown in Figure 1. All the spectra could be stimulated (Figure 1, ii) by use of the parameters given in Table 1.† The observed coupling constants could be interpreted in terms of two structures: (**1**), the radical anion of the nitrone formed by reaction (1), or (**2**), the nitroxide of oxymethylenecobaloxime formed by reaction (2). However, the same signal was observed from aqueous formaldehyde and PhNO in the absence of $\mathrm{Co(Hdmg)_2(H_2O)_2}$ after a prolonged reaction time (24 h), the rate of appearance of the signal being about 200 times slower than in the presence of $\mathrm{Co(Hdmg)_2(H_2O)_2}$. The observation of this signal without $\mathrm{Co(Hdmg)_2(H_2O)_2}$ excludes structure (**2**).

$$\mathrm{Co(Hdmg)_2N(Ar)O\cdot + CH_2O \rightarrow \underset{(\mathbf{1})}{[ArN(O){=}CH_2]^{\cdot -}} + Co^{III}(Hdmg)_2{}^{+}\ or\ Co^{III}(Hdmg)_2O^{+}} \tag{1}$$

$$\mathrm{Co(Hdmg)_2N(Ar)O\cdot + CH_2O \rightarrow \underset{(\mathbf{2})}{Co^{III}(Hdmg)_2OCH_2N(O\cdot)Ar}} \tag{2}$$

A structure analogous to (**2**), the radical $\mathrm{PhN(O^{\cdot -})}$-$\mathrm{CH_2OH}$, has been described by Chachaty,[4] but the coupling constants for this radical, a (N) 11.1, a ($\mathrm{CH_2}$) 8, a ($\mathrm{H}_{o,p}$) 3 G, particularly a($\mathrm{CH_2}$), are very different from the observed values (Table 1), providing further evidence in favour of structure (**1**). Indeed, the possible existence of radical ions of nitrones has been mentioned by Symons.[5]

It is known that photolysis of nitroso compounds in solution gives aryl radicals Ar•,[6] and so it is likely that the observed reaction involves radical-promoted formation of nitrone radical ion. As formation of radicals with diaquacobaloxime is faster than in its absence, either phenylcobaloximenitroxide radical is a more effective promoter than Ar•, or the concentration of Ar• formed during visible light photolysis of the nitrosobenzene is much smaller than the concentration of $\mathrm{Co^{III}(Hdmg)_2N(Ph)O\cdot}$.

The addition of $\mathrm{CF_3CO_2H}$ does not affect the e.s.r. spectra of radicals formed from $\mathrm{Co(Hdmg)_2(H_2O)_2}$, PhNO, and aqueous formaldehyde [$\mathrm{CF_3CO_2H : Co(Hdmg)_2(H_2O)_2}$, 2 : 3], whereas addition of $\mathrm{CF_3CO_2H}$ to bis(*p*-methoxyphenyl) nitroxide gives a protonated radical different from that originally formed;[7] it is known that the paramagnetic centres in 2,2,6,6-tetramethylpiperidine *N*-oxyl are destroyed by HCl, $\mathrm{H_2SO_4}$, or $\mathrm{CF_3CO_2H}$.[8]

The coupling constants for the radicals obtained from $\mathrm{Co(Hdmg)_2(H_2O)_2}$, PhNO, and aqueous formaldehyde are only slightly affected by a change of solvent from DMSO to $\mathrm{Me_2CO}$, MeCN, or MeOH. a (N) values for some radicals are affected by solvent and others are not,[9] so solvent dependence is of little value in distinguishing between the radical species.

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† A simulation program for e.s.r. spectra was developed for an EMU-11 type KFKI (Hungary) minicomputer. The spectra are built up by superposition of the first derivative Lorentzian lines, where the line positions are derived by the second order perturbation solution of the isotropic spin Hamiltonian:

$$\mathcal{H} = \beta H_g S_z + a(\mathrm{N})S_z I_z(\mathrm{N}) + S_z \sum_j a(\mathrm{H_j}) I_z(\mathrm{H_j})$$

where S_z denotes the electron spin, $I_z(\mathrm{N})$ and $I_z(\mathrm{H}_j)$ stand for the nuclear spin of $^{14}\mathrm{N}$ and the j-th proton, respectively, while a(N) and $a(\mathrm{H})_j)$ are the corresponding hyperfine coupling constants.