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ELECTRON SPIN RESONANCE STUDIES OF AN IRON NITROXIDE, $[(CN)_5FeN^{\bullet}(Ph)OH]^{3-}$ AND SOME RELATED RADICALS

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Summary

Methanolic solutions containing the complex ion $(CN)_5FeN(Ph)O^{3-}$, on exposure to ^{60}Co γ-rays at 77 K, gave a well-defined ESR spectrum assigned to the nitroxide $(CN)_5FeN^{\bullet}(Ph)OH^{3-}$, having ESR parameters similar to those for the well-known cobalt analogue, the unpaired electron being largely localised on the NO group. In contrast, nitrosobenzene alone gave $PhN^{\bullet}O(OMe)$ in methanol. In acetonitrile, a species thought to be the negative ion, $PhN^{\bullet}O^-$ was formed from nitrosobenzene.

On annealing above 77 K, the iron nitroxide was lost irreversibly and a new ESR spectrum, characteristic of an iron d^7 complex was obtained. We suggest that this is formed by electron transfer from the paramagnetic ligand into the d_{z^2} (Fe) orbital with concurrent loss of the *trans*-cyanide ligand.

Introduction

A range of nitroxides of the type $(CN)_5CoN^{\bullet}(R)O$ where R is either alkyl [1] or aryl [2] have been reported since the first examples were discovered [3, 4]. We have also reported results for the solid state ESR spectra for radicals of this type [5]. Because of the large number of stable pentacyanoferrate derivatives, it seemed likely that the analogous iron nitroxide radical could be formed [6]. Our approach has been to expose the complex $Na_3[Fe(CN)_5N(Ph)O]$ to ^{60}Co γ-rays, in the expectation that electron addition would occur.

We also report results of γ-radiolysis of the parent compound PhNO in various solvents for comparative purposes. We know of no previous solid-state radiolysis studies of this compound. However, the products of one-electron reduction of nitrosobenzene has been the subject of conflicting reports. Good agreement exists for the solution ESR parameters assigned to $PhN^{\bullet}O^-$ and $PhN^{\bullet}(H)O$ [7,8]. Also, the species $PhN^{\bullet}OH$ has been postulated in a number of reports, the

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ESR parameters being similar to those for the anion. This species has also been proposed as an unstable intermediate in the autoxidation of phenylhydroxylamines in methanol [9,10], and solution ESR parameters for a species formed in the reaction of phenylhydrazines with hydroperoxide have been assigned to this radical [11,12]. In addition, an equilibrium between PhN˙O⁻ and PhN˙OH has been proposed [8] for reduction products of nitrosobenzene in a deaerated sodium ethoxide/ethanol mixture. Other workers [13] have challenged the assignment of the observed ESR spectrum to PhN˙OH and have proposed PhN(O)-ON(H)Ph as being preferable. Recently [14,15], alkyl derivatives of PhN˙OH have been reported.

Experimental

$Na_3Fe(CN)_5H_2O$ was prepared by the method of Hofmann [16] and reacted with nitrosobenzene to form the Baudisch [17] complex by the method of Dezsi et al. [18]. All other chemicals used in this work were of reagent grade quality.

Solutions of this compound or of nitrosobenzene in methanol, methyl cyanide or their deuterated analogues were deaerated and cooled to 77 K as small spheres. These were exposed to ^{60}Co γ-rays at 77 K in a Vickrad cell having a dose rate of ca. 1.7 *M* Rad h^{-1} for periods of ca. 1 h. ESR spectra were recorded on a Varian E-3 spectrometer at 77 K. Samples were annealed directly in the insert Dewar with continuous monitoring of the ESR spectrum and were re-cooled to 77 K whenever significant changes occurred. In other experiments a Varian variable temperature accessory was used.

Results and discussion

Our results show that the species formed from the iron complex differs markedly from those formed from nitrosobenzene, particularly with respect to the *g*-values. Before proceeding to a discussion of the iron complex, we consider briefly the results for nitrosobenzene.

Nitrosobenzene

Although only very poorly defined spectra were obtained for the irradiated pure material, solutions in methanol and methyl cyanide (or CD_3OD and CD_3CN) gave good spectra (Fig. 1) with well-defined "parallel" features for the *g*- and ^{14}N *A*-tensors of species which are clearly nitrogen centred π-radicals. The central region was uninformative because of dominating features from solvent radicals. However, after annealing to remove these species, and re-cooling, the spectra were dominated by the species responsible for the initial parallel lines, and this enabled us to put limits to the value of "$A_\perp$". (It is unlikely that the *A* and *g*-tensors are truly axial but, since we are unable to estimate any loss of axial symmetry, it is convenient to use this nomenclature.)

On controlled annealing, just before the softening points of the glasses were reached, quite well resolved isotropic lines were obtained (Fig. 2). The results thereby obtained fit in well with the low temperature data (Table 1), and we conclude that these spectra are all due to the same species.

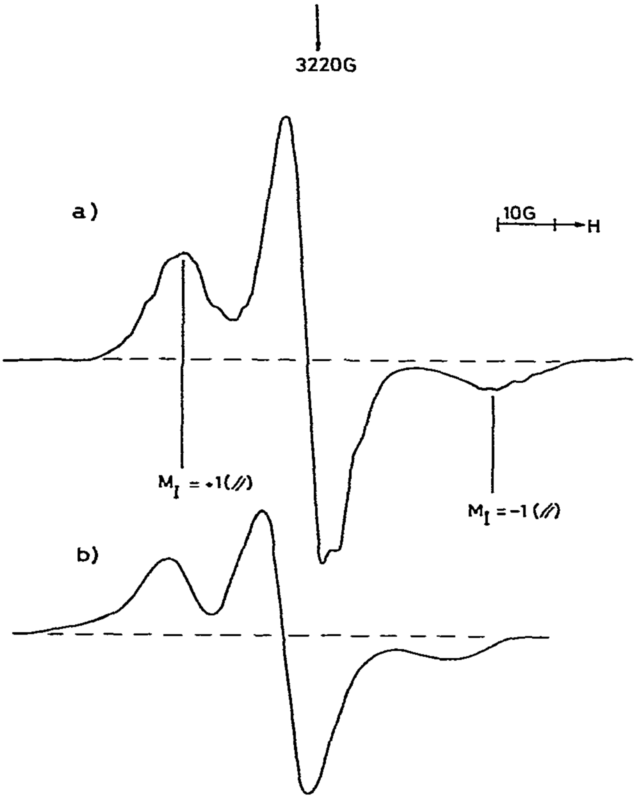
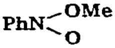
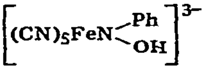
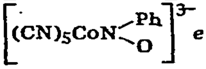


Fig. 1. First derivative X-band ESR spectra for nitrosobenzene in *a* CD_3OD and *b* CD_3CN glasses at 77 K after exposure to ^{60}Co γ-rays and slight annealing to remove solvent radicals, showing features assigned to *a* $PhN^{\cdot}O_2CD_3$ and *b* $PhN^{\cdot}O(CD_2CN)$ or $PhN^{\cdot}O^-$ radicals.

TABLE 1

ESR DATA FOR VARIOUS NITROXIDE RADICALS

Radical	Medium	^{14}N hyperfine coupling (G)[a]			^1H hyperfine coupling (G)			g-values		
		$A_{\parallel}$	$A_{\perp}$	A_{iso}	*ortho/para*	*meta*	Other	g_{xx}	g_{yy}	g_{zz}[b]
 $PhN\begin{smallmatrix}OMe\\O\end{smallmatrix}$	CH_3OH/CD_3OD	30.0	ca.7	15.1	3.1	1.0	1.0(CH_3)[c]	2.003	2.008	2.008
 $PhNO^-$ or $PhN\begin{smallmatrix}R\\O\end{smallmatrix}$	CD_3CN	25.5	0 ± 4	10.3	4	1		2.003	2.007	2.007
 $\left[(CN)_5FeN\begin{smallmatrix}Ph\\OH\end{smallmatrix}\right]^{3-}$	CH_3OH/CD_3OD	30.0	ca.5	ca.13.3	4.2	0 ± 1	4(OH)[d]	1.999	2.007	2.019
 $\left[(CN)_5CoN\begin{smallmatrix}Ph\\O\end{smallmatrix}\right]^{3-}$ [e]		32.0	5	13.4	3.2	1.1		1.999	2.007	2.012

[a] 1 G = 10^{-4} T. [b] Axial symmetry is assumed. [c] 1/3/3/1 in CH_3OH, singlet in CD_3OD. [d] Doublet in CH_3OH, singlet in CD_3OD. [e] Ref. 5.

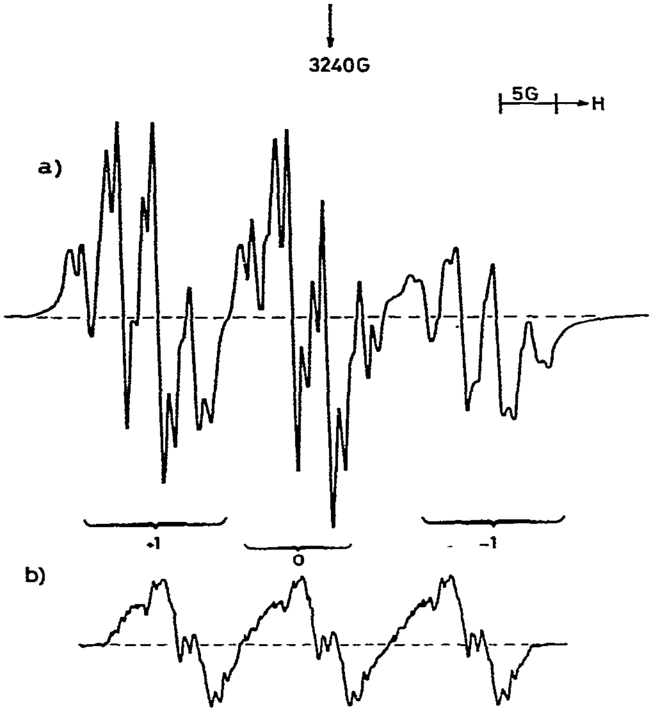


Fig. 2. As Fig. 1, after warming close to the softening point for the glasses, showing isotropic features for *a* $PhN^{\bullet}O_2CD_3$ and *b* $PhN^{\bullet}O(CD_2CN)$ or $PhN^{\bullet}O^-$ radicals.

Chemically reasonable products include $PhNO^-$, $PhNO^+$, $PhN^{\bullet}(H)O$, $PhN^{\bullet}$-OH, and $PhN^{\bullet}(R)O$, where R is some radical derived from the solvent. The species $PhNO^+$ can be ruled out, since this has an "iminoxyl" type structure and would exhibit a far larger isotropic ^{14}N coupling. The data for the radical in CD_3CN are quite reasonable for $PhN^{\bullet}O^-$ or $PhN^{\bullet}(R)O$ (we suggest $PhN^{\bullet}(CD_2CN)O$). The species in methanol has a far larger isotropic coupling to ^{14}N, and we therefore suggest that this is $PhN^{\bullet}(OMe)O$ formed by attack of methoxy radicals. ($MeO^{\bullet}$ radicals are not directly detected in irradiated methanol, but there is good indirect evidence for their formation [19].) It is well established that alkoxy-nitroxide radicals have a considerably greater ^{14}N hyperfine coupling than the corresponding alkyl nitroxides.

The iron nitroxide

A typical ESR spectrum for this complex in CD_3OD at 77 K, obtained after removal of $\dot{C}D_2OD$ and $D\dot{C}O$ radicals by annealing, is given in Fig. 3. Although some motional averaging of these features could be achieved on warming, we were not able to detect an isotropic spectrum. By careful annealing, a considerable improvement in spectral resolution has been obtained relative to that in our preliminary study [6], and we have considerably modified our original interpretation. The more accurate data are listed in Table 1. The present analysis was confirmed by comparing spectra at X- and Q-band frequencies. The data com-

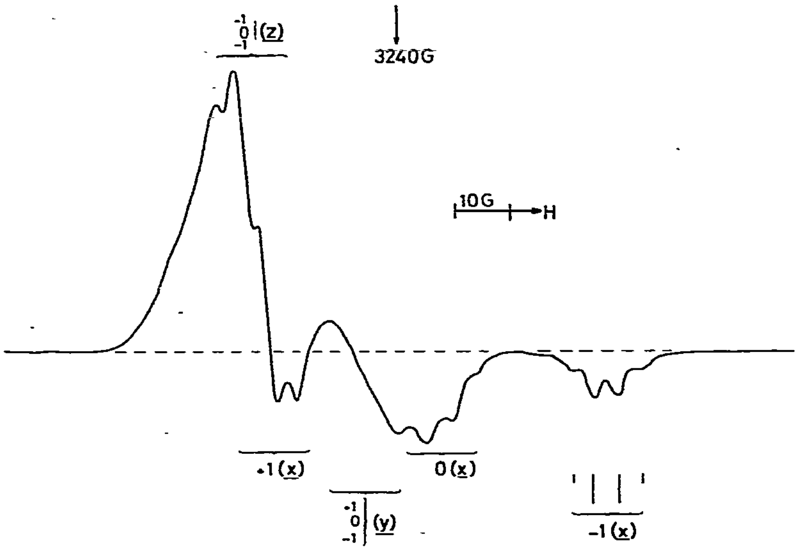


Fig. 3. First derivative X-band ESR spectrum for $Na_3(CN)_5FeNO(Ph)$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K and annealing to remove solvent radicals, showing features assigned to $(CH)_5FeN^{\bullet}O(Ph)(OD)^{3-}$ radicals.

pare favourably with those for the cobalt nitroxide, $(CN)_5CoN(O)Ph^{3-}$ (Table 1). Since the violet colour of trapped electrons normally found for irradiated methanol was suppressed by the iron complex, we suggest that the paramagnetic species is formed by electron capture.

$$(CN)_5FeN(O)Ph^{3-} + e^- \rightarrow (CN)_5FeN(O)Ph^{4-} \qquad (1)$$

However, as shown in Fig. 3, there is an extra line in the "parallel" features for this complex in CH_3OH compared with CD_3OD. The quartet for the latter solvent is assigned to coupling to the nearly equivalent *ortho* and *para* positions of the benzene ring. The extra coupling must come from a readily replaceable proton and so we suggest that the complex is $(CN)_5FeN^{\bullet}(Ph)OH^{3-}$ rather than $(CN)_5FeN^{\bullet}(Ph)O^{4-}$, with the OH proton responsible for a coupling of 4 G. The high negative charge would explain why this protonation occurs in the neutral medium, in contrast with the behaviour of alkyl nitroxides.

The hyperfine coupling of 4 G is quite reasonable for such a species, but is not diagnostic because its magnitude is a strong function of the geometry of the radical. If the proton lies in the radical "plane" a small negative coupling is expected but, if it were constrained out of this plane, the coupling would become progressively more positive. Its mean location will be a function of several constraints and cannot be predicted. When dialkyl nitroxides are protonated, the isotropic hyperfine coupling to ^{14}N increases by ca. 5 G [20]. This is because the proton pulls negative charge onto oxygen thereby forcing the unpaired electron more onto nitrogen. This effect is greatly reduced in the present case because of increased delocalisation into the aromatic ring and, also, probably, because of increased delocalisation onto the iron atom (see below). Hence A_N remains comparable with that for the cobalt complex, which is probably not protonated.

We have previously [5] supported the contention of Swanwick and Waters [2] that the cobalt nitroxides are properly viewed as being quite comparable to their purely organic analogues. In the present case, the larger shift in g_{zz} suggests that some real d_π—p_π delocalisation of the unpaired electron on to iron is occurring. This has the effect of putting electron spin into the $3d_{xz}$ orbital, and magnetic field along z will then couple the d_{xz} and d_{yz} levels. Since the closest level containing d_{yz} is filled, this will cause a positive shift in g_{zz} as observed. The value for g_{yy} is normal and the small high-field shift in g_{xx} can be thought of as stemming from coupling to the d_{xy} and the σ^* level containing $d_{x^2-y^2}$.

On melting the glasses this species was irreversibly lost, being replaced by a species with properties almost indistinguishable from those assigned to $(CN)_5Fe$-NO^{3-} [or more probably, $(CN)_4FeNO^{2-}$] [21,22]. [A_{iso} (^{14}N) 14.7 G and g_{av} 2.0264, compared [21] with A 14.8 G and g 2.0260]. We suggest that this species is the d^7 analogue of the substrate d^6 complex. This could be formed by an irreversible electron transfer from the π-ligand system into the $3d_{z^2}$ iron orbital, with the accompanying loss of the *trans*-cyanide. This complex is then structurally very similar to $(CN)_4FeNO^{2-}$, and could well have comparable ESR parameters. If this is correct, then it constitutes an example of electron-transfer proceeding via an organic ligand, similar to that previously found for sodium nitroprusside [23].

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