EPR Study of Iron–Nitrosyl Clusters in the Oxidation of Fe(NO)₂(CO)₂

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The oxidation of Fe(NO)₂(CO)₂ by tetracyanoethylene (TCNE), by the nitrosium ion (NO⁺), or by electrolysis in polar solvents was studied by EPR spectroscopy. A number of long-lived (t1/2 of the order of hours) free radicals were detected in the early stages of reaction, all having similar isotropic g-factors and 14,15N hyperfine interactions. These have been identified as the mononuclear cations, Fe(NO)₂(CO)₂−St⁺ (St = solvent molecule). They slowly disappear and are replaced by persistent radicals (t1/2 of the order of days) that show equal isotropic hyperfine interactions with four-, six-, or eight-nitrogen nuclei. Infrared and EPR spectroscopic data suggest that two of these species are trinuclear nitrosyl clusters, Fe₃(NO)₆(CO)₆−₃aₙ (n = 3, 4), in which the unpaired spin is localized on one iron nucleus, but which are fluxional on the EPR time-scale. The third nitrosyl radical with four equivalent NO ligands is tentatively identified as a binuclear intermediate that may be a precursor of the trinuclear clusters.

KEY WORDS  EPR; ESR; iron–nitrosyl radicals; cluster nitrosyls; Fe(NO)₂⁺

INTRODUCTION

The recent realization that nitric oxide is an important neurotransmitter has brought about a renewed interest in its chemistry, particularly the chemistry of its iron complexes that are central to the role of nitric oxide in the body. Iron nitrosyls are also implicated in an ongoing controversy over the health aspects of nitrate ingestion, in which their carcinogenicity is in question. The dramatic upsurge of interest in nitric oxide in the research community has earned it a reprieve from its lowly status as a boisterous pollutant, and the title 'molecule of the year' from the Editors of Science.

In the biochemical chemistry of non-heme iron, much attention has been paid to a group of paramagnetic iron nitrosyl complexes dubbed 'Fe(NO)₂⁺', or '2.03 complexes', because of the value of their isotropic g-factor. There is even evidence to suggest that certain complexes of this type constitute the endothelium-derived relaxing factor (EDRF), rather than nitric oxide itself. Certain of these organometallic free radicals are also effective initiators of oligomerization and cycodimerization processes. Eaton and Bryar have recently reviewed the structures of Fe(NO)₂⁺ species in the light of EPR spectroscopic data, and have suggested a correlation between structure and such catalytic activity. Thiolato ligands confer stability upon this type of radical, yielding Fe(NO)₂(SR)₂⁺ species that play pivotal roles in biological chemistry. The apparent tendency of such radicals to cluster, as in the formation of Roussin's red and black salts, together with a suggested implication of cluster nitrosyl radicals in septic shock, captured our attention and led us to initiate an investigation by EPR spectroscopy of the oxidation of certain simple metal nitrosylcarbonyls. In this paper we describe EPR studies of the oxidation of iron dinitrosylcarbonyl in tetrahydrofuran (THF), dimethoxyethane (DME) and diethyl ether solutions.

EXPERIMENTAL

Iron dinitrosylcarbonyl, Fe(NO)₂(CO)₆, was prepared and purified according to the method of Seel. Isotopically labelled Fe(NO)₂(CO)₆ was prepared directly from the reaction of NO⁻ (99% enrichment) with Fe(CO)₅ and from the reaction of NO with Fe(CO)₅ enriched to 99% in ¹³C. All solvents were dried according to standard procedures before use. Fe(CO)₅ and Fe(CO)₃ were purchased from the Aldrich Chemical Co., and were used without further purification. EPR spectra were recorded at X-band and at Q-band, on Varian E-12 and Bruker ESP300 spectrometers, respectively, with the usual accessories for readout of the magnetic field, microwave frequency and temperature. The spectrometers were operated at a modulation frequency of 25 kHz and g-values were calculated directly from the frequency and the magnetic field. Infrared data were obtained on a Nicolet 7000 FTIR spectrometer using NaCl solution cells.

RESULTS AND DISCUSSION

On mixing a well degassed solution of Fe(NO)₂(CO)₅ in THF with tetracyanoethylene (TCNE) at room temperature, an EPR spectrum developed within about 30 min. It consisted of a very broad line centred near
$g = 2.03$ together with the expected $^{14}$ sharp, nine-line spectrum of TCNE$^-$ near the free-spin $g$-value. When cooled to $-50^\circ$C, the broad line at high $g$ resolved into three components: a pair of partially overlapped quintets, each with intensity ratios of $1:2:3:2:1$ and line-widths ca. 0.1 mT, and a broad (ca. 1.5 mT peak-to-peak) incompletely resolved resonance to lower field (Fig. 1). Upon standing at ambient temperature, the latter component of the spectrum at $-50^\circ$C gained very slowly in intensity at the expense of the two narrow components. After approximately 1 week, it was the major component of the EPR spectrum, but it remained broad and unresolved. At ambient temperature, this component completely dominated the EPR spectrum, and it persisted for weeks in a sealed tube. Unfortunately, resolution to an unambiguous $^{14}$N hyperfine pattern was not achieved for this species at any temperature in liquid THF. However, when the same experiment was carried out with 99% enriched $^{15}$NO$_2$, a useful resolution of the $^{15}$N manifold was apparent (Fig. 2). Furthermore, measurements and spectral simulations of the narrow components in the $^{15}$N spectrum confirmed the presence of overlap-

![Figure 1](image1.png)

**Figure 1.** First-derivative EPR spectrum at 235 K and 8985 MHz in the early stages of oxidation of Fe(NO)$_2$(CO)$_3$ in THF.

![Figure 2](image2.png)

**Figure 2.** (a, b) First-derivative EPR spectra together with (c, d) spectral simulations for cluster radicals (a, c) Fe$_8$(NO)$_2$(CO)$_3$ and (b, d) Fe$_8$(NO)$_2$(CO)$_3$. Spectra observed in THF at 300 K after several days of reaction.

Very similar observations were noted when using DME as solvent, except that the high-field part of the spectrum was now clearly a superposition of three components, each due to a radical showing two equal $^{14}$N or $^{15}$N hfss. Similar spectra were also observed during the early stages of oxidation of Fe(NO)$_2$(PF$_6$)$_2$, FeCP$_2$ (ferrocene) and Fe$_3$(NO)$_2$(SET)$_2$ (Rousin's red ester). The isotropic $g$-values and $^{14}$N hfss of these species are summarized in Table 1. No EPR spectra were detected when the reactions were carried out in CH$_2$Cl$_2$ or in hydrocarbon solvents, suggesting strongly that the radicals observed in polar solvents were charged.

**Mononuclear nitrosyls**

The values (Table 1) of the isotropic $g$ and the $^{14}$N coupling constants for the narrower, high-field spectra are reminiscent of the 2.03 iron-dinitrosyl complexes and we have little hesitation, therefore, in making an assignment to that class of radicals. Tetra-coordination is the norm for this type of radical, although penta- and hexacoordinated examples have been documented when the ligands include single-electron donors. Since it is well established that THF can slowly replace the CO ligands in the substrate, a scheme such as that shown in Scheme 1 can account for the observation of two radicals in THF solvent, Fe(NO)$_2$(CO)$_3$ and Fe(NO)$_2$(CO)(THF)$_2$.

A third species would be expected through substitution of the second CO by a solvent molecule, and was clearly observed in the case of DME. A very weak third species was also observed in THF, and is tentatively assigned to Fe(NO)$_2$(THF)$_2$. Qualitative observations on the growth of the radicals led to the assignment given in Table 1. Apart from the two equal $^1$N hfss, no hyperfine coupling to ligand or solvent nuclei was resolved even in $^{13}$C-enriched materials. However, an additional isotropic coupling of 1.51 mT was observed (Fig. 3) for a Fe(NO)$_2$ radical that was formed free of interfering species early in the oxidation of $^{57}$Fe-enriched (22% $^{57}$Fe, $I = \frac{1}{2}$) Fe(NO)$_2$(CO)$_2$ by NOPF$_6$ in THF (Table 1). Such a large coupling to $^{57}$Fe is indicative of an unpaired electron essentially confined to Fe d-orbitals, and accounts for the very small hfss with ligand nuclei. This observation supports the contention of Eaton and Breyer that these Fe(NO)$_2$ radicals are best described as 17-electron Fe $^2p$ complexes in which the metal atom is formally Fe$^-$ and the nitric oxide ligands bind as NO$^+$. The alternative for-
Table 1. Isotropic g and 14N hyperfine interactions for Fe(NO)2+ radicals at 223 K

<table>
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<tr>
<th>Reagent</th>
<th>Oxidant</th>
<th>$g_{av}$</th>
<th>$g_{av}$</th>
<th>$a_{iso}(14N)$</th>
<th>Assignments</th>
</tr>
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<tr>
<td>Fe(NO)2(CO)2</td>
<td>TCNE</td>
<td>2.0276</td>
<td>0.32</td>
<td>2.0276</td>
<td>Fe(NO)2(CO)2+</td>
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<td>0.32</td>
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<td>0.32</td>
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<td>Fe(NO)2(CO)2+</td>
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<td>2.0249</td>
<td>Fe(NO)2(CO)2+</td>
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</table>

* Isotropic hyperfine interaction of two equivalent Ns in mT.
* $a_{iso}(14N)$ calculated from $14N$ measurements.
* Some two radicals observed independent of reagents.
* Fe(NO)2(NX)2+, where X is unknown.

The magnetic equivalence of the two nitrogen nuclei in low-symmetry situations, such as Fe(NO)2(CO)2+ and Fe(NO)2(CO)2+, is understandable in view of the known isotropic $g$-factor ($<2.00$) and very small metal hyperfine interactions in such species.\textsuperscript{17,18} It also runs counter to our observations on the electrochemical generation of radicals from Fe(NO)2(CO)2+, which indicated the formation of the radicals at the anode, but not at the cathode.

The magnetic equivalence of the two nitrogen nuclei in low-symmetry situations, such as Fe(NO)2(CO)2+ and Fe(NO)2(CO)2+, was not an unexpected result. Many of the metal carbonyl and nitrosyl radicals, fluxional motion in the ligand phase often causes rapid interchange of ligands and an averaging of associated hfs, e.g. Fe(NO)2(CO).\textsuperscript{19} The small values of the isotropic hfs in N of species such as Fe(NO)2(CO)2+-$\sigma$Fe+ (Table 1) is an indication that there is very little direct spin density in N of this species, as is also apparent from the unusually large 13C hfs. Unpaired spin density on ligand nuclei in Fe(NO)2+ radicals is undoubtedly due to indirect contributions from polarization of the metal-ligand bonds by the Fe d orbitals that dominate the semi-occupied molecular orbital (SOMO). The d-orbital composition of this type of complex has been discussed in detail elsewhere,\textsuperscript{14,15} and our present results reinforce the conclusions reached there. In such a metal-dominated SOMO, small variations in the electronic configuration at the metal nucleus, arising from changes in the nature and number of ligands L in Fe(NO)2+L, will significantly affect the g-tensor components through changes in the position and overlap of the Fe d-orbitals, but will have little effect on the N hfs. Hence we have the somewhat unusual situation (Table 1) of significant variations in $g$ within a family of very similar radicals, without attendant variations in N hfs.

Cluster nitrosyls

Spectral simulation of the septet observed at low field (Fig. 2[a]) shows that it is due to a radical with six equal $^{14}$N hfs of 0.24 mT and an isotropic $g$ value of 2.0350 in THF, or 2.0353 in DME. Since a mononuclear hexanitrosyl would be very unstable even for high oxidation states of the iron, we were forced to consider an assignment to a nitrosyl cluster species. A number of questions had to be answered before proposing a plausible structure: (i) are the nitrosyls bridged or terminal? (ii) are bridging or terminal CO ligands present? and...
(iii) how many iron nuclei are present and do they all bear unpaired spin? These questions were addressed through IR and EPR spectroscopy.

Enrichment to 99% in $^{13}$C of the substrate resulted in small but significant changes in the cluster spectrum [Fig 2(b)]. It no longer had a line at the centre, and all lines were significantly broader than for the singly enriched starting material. There are, therefore, two groups of carbonyls in this radical, one containing an odd number showing resolved hfs and the other containing an unknown number with $^{13}$C hfs lost in the linewidth. Spectral simulation suggests that the resolved $^{13}$C structure is due to a single nucleus with a hfs of 0.19 mT, although because of the large linewidth we cannot entirely eliminate alternative possibilities of equal interactions from $(2n+1)$ $^{13}$C nuclei $(n \geq 1)$. IR spectroscopy of oxidized Fe$^{2+}$NO$_3^-$(CO)$_3$ at long reaction times supports the presence of two kinds of carbonyl ligand in the radical. CO stretching frequencies measured for the reaction product [at elapsed times corresponding to Fig 2(n)] of 1940 and 2009 cm$^{-1}$ represent a decrease compared with the starting material, while that at 2095 cm$^{-1}$ represents an increase (Table 2). The latter are well within the range of frequencies for terminal carbonyl ligands. The increase in frequency compared with Fe(NO)$_3$(CO)$_3$ is expected if the metal acquires positive charge. We tentatively assign the two lower stretching frequencies to singly bridging COs; positive charge on the iron together with electron withdrawal by NOs will certainly shift such modes to higher frequencies than normal. The IR absorption spectrum also clearly showed that the nitrosyl ligands were all terminal and linear. Once again, the small increase in NO stretching frequency (Table 2) is an indication of a positive charge on the metal nuclei, i.e. the species is a radical cation.

The donated-electron count from six linearly bound nitrosyls and (at least) two carbonyls clearly points to a cluster radical containing three of more metal nuclei. Fe$_2$(NO)$_3$(CO)$_3$ is a 32-electron cation, and more metal nuclei are clearly required to accommodate a further two carbonyls in a stable structure. It was therefore with some surprise that we observed interaction of the unpaired electron with a single iron nucleus in the spectrum generated from Fe$(^{15}$NO)$_3$(CO)$_3$ enriched to 92% in $^{15}$Fe (Fig 4). The size of the $^{57}$Fe isotropic coupling ($a_{\gamma} = 1.35$ mT at 240 K in DME) clearly indicates$^{16}$ that the unpaired spin is essentially localized in the d-orbitals of a single iron nucleus. Localization of the unpaired spin on one Fe nucleus is established for the binuclear iron carbonyl radicals$^{23,24}$ Fe$_2$(CO)$_3$-µ-PPh$_3$ and Fe$_2$(CO)$_3$ -

![Figure 4. Second-derivative EPR spectrum at 9160 MHz and 240 K in DME after 1 week's delay in the reaction of TCNE with $^{67}$Fe$(^{15}$NO)$_3$(CO)$_3$ enriched to 92% in $^{67}$Fe and to 99% in $^{15}$N.

(one isomer) and for$^{25}$ Fe$_4$(CO)$_3$+ Intramolecular carboxyl exchange in Fe$_2$(CO)$_3$-µ-PPh$_3$ in liquid solution renders five of the carbonyls equivalent on the EPR time-scale via a process of making and breaking CO bridges. However, that process is concomitant with a shuttling of the unpaired spin between the metal nuclei. In the cluster carbonyl nitrosyl under consideration, nitrosyl exchange evidently occurs without sharing of the unpaired spin between its iron nuclei.

An assignment to the 47-electron cation radical Fe$_3$(NO)$_3$(CO)$_2$-µ-C$_6$H$_5$CO$_2$+ can account for our observations (Fig. 5). Its structure is closely related to that of Fe$_3$(CO)$_2$-, in which rapid carbonyl scrambling is believed to occur by a process of concerted bridge opening and closing.$^{22}$ We propose that rapid nitrosyl exchange occurs in our proposed cluster radical by such a process.

Table 2. Infrared absorption frequencies for Fe$(^{15}$NO)$_3$(CO)$_3$ + TCNE in THF

<table>
<thead>
<tr>
<th>Initially ($t = 0$)</th>
<th>1726</th>
<th>2020</th>
</tr>
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<tbody>
<tr>
<td>Finally*</td>
<td>1744</td>
<td>2088 (broad)</td>
</tr>
<tr>
<td></td>
<td>1717</td>
<td>1940</td>
</tr>
<tr>
<td></td>
<td>1748</td>
<td>2009 (v. broad)</td>
</tr>
<tr>
<td></td>
<td>1796</td>
<td>2065 (ab)</td>
</tr>
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</table>

*At long reaction times corresponding to the spectra in Fig 2.
should show a relatively large $^{15}$N hfi and the axial CO a very small $^{13}$C hfi.

Related cluster radicals

It is curious that the trinuclear cluster Fe$_3$(NO)$_6$(CO)$_3$* is formed to the exclusion of other cluster radicals in the oxidation of Fe(NO)$_2$(CO)$_2$. In this regard, the intriguing possibility arises of making a binary iron nitrosyl radical cation, Fe$_3$(NO)$_5^+$, by the substitution of three COs in Fe$_3$(NO)$_6$(CO)$_3$* with two NOs. We have, in fact, generated a binary iron nitrosyl radical with an EPR spectrum (Fig. 6) appropriate for eight equivalent $^{15}$N nuclei ($g_{iso} = 2.036; 8 A_{15}$ at 0.43 mT in THF at 240 K) that we tentatively assign to Fe$_3$(NO)$_5^+$. This radical is obtained in polar solvents by the oxidation of Fe(PF$_3$)$_2$(NO)$_2$ or Fe$_2$(μ$_2$-SE)$_2$(NO)$_4$ by TCNE, by the oxidation of Fe(NO)$_2$Cl or Fe$_2$(CO)$_2$ by NOPF$_5$ or NOCl and by the anodic oxidation of Fe(NO)$_2$(CO)$_2$. Mysteriously, the EPR spectrum of this species generated with naturally abundant materials (Fig. 6) is not that of eight equivalent $^{15}$N hfis and, further, has nearly the same spectral width as that of the fully labelled $^{15}$N species (3.58 vs. 3.47 mT). Such a situation can only arise if the radical is undergoing a non-mutual exchange process between two or more isomers at a rate intermediate between slow (where the frozen structure would be revealed) and fast (where an averaged structure would be revealed). In such circumstances, the central component ($m_I = 0$) of a $^{14}$N ($I = 1$) manifold will remain sharp, but outer components may broaden beyond detection. By contrast, exchange in the intermediate regime for the same radical labelled with $^{15}$N ($I = \frac{1}{2}$) will result in broadening, but no loss of lines. It is thus possible, in principle, to observe a $^{14}$N spectrum that is significantly narrower than expected in relation to that of $^{15}$N. Measurements at Q-band (34 GHz) reveal the presence of two radicals ($A_g/q = 0.003$) in reversible equilibrium with each other ($\Delta H \approx 5.9$ kJ mol$^{-1}$) that we assume represent the extrema of the exchange process. The more stable of these isomers has the lower $g_{iso}$ and the narrower spectral width. Unfortunately, at Q-band they are both broad featureless resonances that give no structural information. Further studies of this unusual phenomenon are under way in an effort to establish the structure of Fe$_3$(NO)$_5^+$ and the nature of the exchange processes.

![Figure 5. Proposed structure of Fe$_3$(NO)$_6$(CO)$_3$* and merry-go-round mechanism of nitrosyl exchange.](image)

![Figure 6. First-derivative EPR spectra of cluster nitrosyl radicals observed at 200 K after a 30 min delay in the reaction between TCNE and Fe(NO)$_2$(PF$_3$)$_2$. Top, $^{14}$N spectrum obtained with natural reagents; bottom, $^{15}$N spectrum from reagent enriched to 95% in $^{15}$N.](image)
When the oxidation of Fe(NO)₄(CO)₂ with TCNE was conducted in diethyl ether solvent, a broad, persistent (r₁/₂ of the order of weeks) resonance was detected that resolved at 253 K into a spectrum characteristic of interactions of an unpaired electron with four equivalent ¹⁵N nuclei (g = 2.0376; 4 a₁₅ at 0.30 mT). No further hyperfine splitting was detected for the spectrum generated with material enriched to 99% in ¹³C, but the linewidth was significantly larger. It is tempting to assign this spectrum to a radical cation, such as Fe₂(NO)₄(CO)₆⁺, a 47-electron analogue of the clusters discussed above. However, we are inclined to think that such a trinuclear cluster is an unlikely product, since cluster formation appears to occur through association of Fe(NO)₄⁺ moieties that are stable with respect to nitrosyl loss. Accordingly, we feel that a more likely carrier of this spectrum is the 33-electron biunuclear nitrosyl carbonyl, Fe₂(NO)₄(CO)₆⁺, that may well be a precursor of the trinuclear clusters.

Acknowledgement

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REFERENCES