Reactions of Matrix Isolated Iron Atoms with Nitric Oxide

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Abstract

The matrix isolated binary nitrosyls, $Fe(NO)_x$, $x \leqslant 4$, formed upon co-condensation of iron with nitric oxide have been studied by infrared and Mössbauer spectroscopies. Infrared data suggest that the unsaturated complexes ($x = 1, 2$) contain linear NO ligands. The isomer shifts of all four complexes are consistent with covalently bonded Fe(0). In 100% NO, $Fe(NO)_4$ is the major product and gives the identical Mössbauer spectrum as $Fe(NO)_4$ made from the high pressure reaction of $Fe(CO)_5$ with NO. In addition, a second product, probably $Fe(NO)_3$ is detected in the Mössbauer spectrum of $Fe(NO)_4$ made by both procedures. Evidence is seen for a partially reversible temperature dependent equilibrium between $Fe(NO)_3$ and $Fe(NO)_4$, with $Fe(NO)_4$ favored at low temperatures. The unusal reactivity of NO with iron atoms is discussed.

Introduction

A wide variety of compounds containing a transition metal–nitrosyl bond are now known [1–4]. In recent years, the nitrosyl compounds which have been most studied are those which contain other ligands such as CO as well [1–4]. Binary metal–nitrosyl complexes, unlike the related metal–carbonyl complexes, are rather uncommon, and are generally difficult to characterize due to their instability [5]. Under matrix isolation conditions, however, it should be possible to prepare and study such compounds with relative ease. Until now, there have been several matrix isolation studies involving organometallic nitrosyls [6, 7], but very few concerning reactions of metal-containing complexes with NO [8, 9]. We now report the preparation and detection by Mössbauer spectroscopy of several binary iron–nitrosyl complexes. To the best of our knowledge, this is the first report of a simple binary transition metal–nitrosyl complex formed by co-condensation of the metal with nitric oxide under cryogenic conditions.

Experimental

Detailed descriptions of the Mössbauer and infrared experimental procedures have been previously described [10]. Kr (99.995%) and NO (99.9%) supplied by Linde, were used for both the IR and Mössbauer without further purification. Infrared spectra were recorded on a Perkin-Elmer 683.

Mössbauer spectra were computer fit with a least-squares routine to a sum of quadrupole doublets and singlets with Lorentzian lineshapes. The standard statistical tests, χ^2 and MISFIT were used as quantitative measures of the quality of the fits. Isomer shifts are reported relative to α-Fe at room temperature.

'$Fe(NO)_4$' for use in comparison to the matrix-isolated iron–nitrosyl products was prepared by a modification of a procedure previously described [11]. An infrared spectrum of the crystals in KBr indicated the absence of any carbonyl ligands and matched that of the previously reported '$Fe(NO)_4$'. For use in the Mössbauer experiments, '$Fe(NO)_4$' crystals were mixed with iron-free graphite powder under nitrogen and the mixture was then packed into a graphite container. The sample was stored in dry ice until its spectrum could be obtained. The Mössbauer apparatus used for characterization of this sample was similar to but not identical to the one already described for use with the matrix-isolated samples.

Results and Discussion

Mössbauer spectra were obtained on several samples of iron co-condensed with 100% NO at 20 K. Typical results are shown in Fig. 1. The best fit to the data is a singlet with isomer shift, δ, of +0.14 ±

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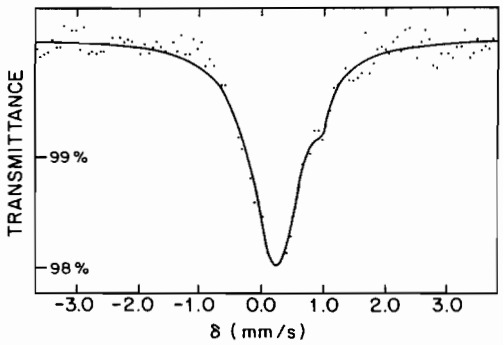

Fig. 1. ^{57}Fe Mössbauer spectrum of iron (0.6%) in a 100% NO matrix deposited at ~15 K.

0.10 mm/s, and linewidth, Γ, of about 0.9 mm/s. The data may also be fit satisfactorily with a quadrupole doublet centered at +0.14 mm/s with a quadrupole splitting, Δ, of about 0.4 mm/s and linewidth of 0.7 mm/s. As the doublet is not resolved, the first fit is the preferred one. Both fits are improved if a shoulder at approximately +0.80 mm/s is included.

The major component seen in the Mössbauer spectrum is assigned to **A**, a product of the reaction between iron and nitric oxide, whereas the minor component is assigned to **B**, an iron-containing side product. The peaks due to **A** and **B** appear in the region of the Mössbauer spectrum where covalently bound Fe(0) molecules normally absorb. Upon warming of the sample to 40 K and recooling, no changes in the Mössbauer spectra occurred, demonstrating the relative thermal stability of products **A** and **B**. Above this temperature, significant desorption of the sample occurred due to evaporation of the matrix material.

For Mössbauer absorption, the area of the peak is proportional to the product of the number of absorbers multiplied by the recoil-free fraction (probability that a ^{57}Fe nucleus will absorb the γ-ray without recoil). A log–log plot of the area of a Mössbauer peak *versus* iron concentration should then yield a straight line with the slope equal to the number of metal atoms in the product which gives rise to the absorption. When this is done for the peak at +0.14 mm/s, the slope was +0.9, indicating that **A** contains one iron atom. Changes in **B** could not be determined with any degree of accuracy.

There was no evidence for unreacted iron atoms in any of the experiments, as demonstrated by the absence of the characteristic absorption at $\delta = -0.71$ mm/s. Furthermore, absorptions which may be assigned to unreacted iron dimers, clusters or products of clusters with NO were not observed, even when the iron content of the sample was so large that such species might be expected to form (that is, when the concentration of iron is above 1%). In other words, regardless of the iron deposition rate only two products were ever seen, the mononuclear species, **A**, and the side product, **B**. The Mössbauer spectra were essentially identical for all of the Fe/100% NO experiments.

The absence of other products or unreacted iron atoms in the 100% NO matrices is one of the most significant features of these experiments. This means that virtually every iron atom in the matrix reacts with NO, and reacts with NO in preference to other iron atoms as well. In contrast, in a pure CO or N_2 [10, 12] matrix, there is evidence for unreacted iron atoms, as well as evidence for formation of dinuclear complexes when iron deposition rates are high. These results have been interpreted to mean that a small but finite activation energy exists for these reactions, due to the promotion energy from the unreactive ground state $(3d)^6(4s)^2$ of the iron atom to the reactive $(3d)^8$ state. NO is a free radical, so that the reaction of iron with NO is fundamentally different than the reaction with CO and N_2. For example, iron in the $(3d)^7(4s)^1$ state can use the unpaired $4s^1$ electron to interact with the unpaired π^* electron in NO. If this is the case much less promotion energy is required.

Unfortunately, it was not possible to obtain satisfactory infrared data on the 100% NO system due to the fact that nitric oxide and nitric oxide dimers absorb strongly in relevant parts of the IR spectrum.

The low temperature Mössbauer spectrum of '$Fe(NO)_4$' made according to the procedure of Wilkinson *et al.* [11], is shown in Fig. 2a. A fitting procedure similar to that used for the matrix isolation Fe/100% NO experiments was employed, and, again, a fit to a single peak with a shoulder gave the best results. The major absorption occurs at $\delta = +0.065$ mm/s, with a Γ of approximately 0.7 mm/s, identical within error to the isomer shift seen for matrix-isolated iron in NO. A somewhat more pronounced shoulder is seen in Fig. 2a than is seen in Fig. 1, and appears at approximately the same position (+1.00 mm/s). It appears that the two species, **A** and **B**, present when iron is co-condensed with 100% NO at 20 K are identical to the two species seen in '$Fe(NO)_4$'.

The infrared spectrum of '$Fe(NO)_4$' in a KBr pellet at room temperature showed three bands at 1810 cm^{-1}, 1730 cm^{-1}, and 1140 cm^{-1}, identical to that reported by Wilkinson. The very weak 1140 cm^{-1} was never detected in the IR spectra of samples of iron co-condensed with 100% NO, despite the fact that neither NO nor NO dimers absorb in this region of the infrared. Although this may be due to a concentration problem, we suggest that the 1140 cm^{-1} peak seen in the Wilkinson preparation is due to trace amounts of a minor product. At any rate, this band appears at too low a frequency to be attributable either to bent NO or to NO^- [3, 8].

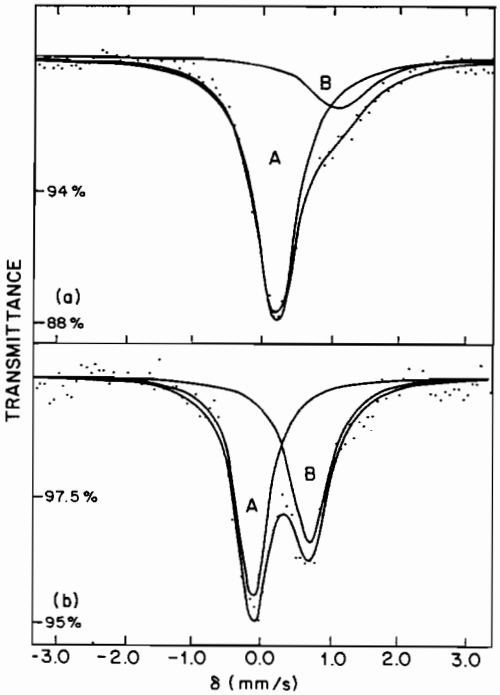

Fig. 2. ^{57}Fe Mössbauer spectrum of $Fe(NO)_4$ made by the high pressure reaction of $Fe(CO)_5$ with NO. (a) at ~20 K. (b) after warming to room temperature, under vacuum.

The structure of '$Fe(NO)_4$' made by the high pressure reaction of $Fe(CO)_5$ with NO has never been determined. The elemental analysis is high in iron for the empirical formula $Fe(NO)_4$. (Wilkinson found 33.08% Fe *versus* 31.75% calculated) [11]. The IR data, as well as the eighteen electron rule, predict that this complex has one bent and three linear NO ligands in a tetrahedral arrangement around the iron atom. However, in the past, it has been pointed out that a dimeric compound with a bridging hyponitrite ligand, $(NO)_3Fe(ONNO)Fe(NO)_3$, is also consistent with the IR data (and may explain the 1140 cm^{-1} band in the IR) [5]. Additionally, it has been suggested that this complex is actually ionic, $[Fe(NO)_3]^+[NO]^-$ [13]. However, it is now known that the 1140 cm^{-1} band is too low to be assigned to NO^- [8].

A comparison of Figs. 1 and 2 shows that the major product formed when iron is co-condensed with nitric oxide is the same as that formed using the Wilkinson method. Therefore, information obtained on the matrix-isolated system is applicable to '$Fe(NO)_4$' and may be helpful in elucidating its structure. First, the stoichiometric studies indicate that **A** is a mononuclear complex, effectively ruling out a dimeric structure as a possibility for '$Fe(NO)_4$'. The Mössbauer spectrum shows a singlet (or, possibly a doublet with a very small quadrupole splitting), suggesting that **A** has high symmetry [14]. A pseudo-tetrahedral $Fe(NO)_4$ with three linear and one bent nitrosyl ligand seems to be a reasonable structure for **A**, the major product seen in '$Fe(NO)_4$'. Such a structure would probably be fluxional, with the bent and linear nitrosyls exchanging rapidly. Since the characteristic time of the Mössbauer experiment is 10^{-7} s, there could be averaging of the four NO ligands, increasing the effective symmetry.

TABLE I. Mössbauer Parameters of Matrix-isolated Iron–Nitrosyl Complexes

Species	δ (mm/s)	Δ (mm/s)	Assignment[a]
1[b]	−0.71	0.0	Fe_1
A[c]	+0.14 ± 0.10[d]	0.0[e]	$Fe(NO)_4$
A[f]	+0.065	0.0[e]	$Fe(NO)_4$
A[g]	−0.10	0.0[e]	$Fe(NO)_4$
B[c]	~+0.4	~0.6	$Fe(NO)_3$
B[f]	~+0.4	~0.9	$Fe(NO)_3$
B[g]	~+0.3	~0.8	$Fe(NO)_3$
C[h]	+0.24 ± 0.05[d]	0.87 ± 0.16[d]	Fe(NO) or $Fe(NO)_2$
D[h]	+0.52 ± 0.11[d]	1.34 ± 0.24[d]	Fe(NO) or $Fe(NO)_2$

[a]Assignments tentative except for $Fe(NO)_4$. [b]At 20 K, 0.1–2% NO/Kr matrices. [c]At 20 K, 100% NO matrices. [d]Errors expressed as standard deviations of the mean of the values obtained in several experiments. [e]Fit to a singlet. See text for explanation of fitting procedure. [f]Made from the high pressure reaction of $Fe(CO)_5$ with NO as described in the text. Spectrum obtained at 20 K. [g]Made from the high pressure reaction of $Fe(CO)_5$ with NO as described in the text. Spectrum obtained at room temperature. [h]At 20 K, 0.1–10% NO/Kr matrices.

The second feature observed in the Mössbauer spectrum of both the matrix-isolated samples and in the '$Fe(NO)_4$' made from iron pentacarbonyl was an ill-defined shoulder at a more positive shift than $Fe(NO)_4$ itself, assigned to complex **B**. This has been listed in Table I as a quadrupole doublet with the second half of the doublet lying underneath the peak for compound **A**, since an isomer shift of +1.0 mm/s would be high for a covalent complex.

When '$Fe(NO)_4$' made by the Wilkinson method was warmed to room temperature under vacuum, several changes occurred in the Mössbauer spectrum (Fig. 2b). First, there was a slight shifting of both absorptions to more negative δs and a decrease in absorbance, both of which can be attributed solely to temperature effects. The second order Doppler shift (displacement of the isomer shift with respect to temperature) is about 0.2 mm/s, a typical value [14]. Furthermore, the shoulder attributed to **B** in the low temperature spectrum increased greatly in magnitude relative to the **A** peak. Upon recooling the sample to 20 K, spectrum 2a was reproduced. The sample underwent several temperature cycles without noticeable change occurring, giving spectrum 2a at low temperature and 2b at room temperature.

After standing at room temperature for a prolonged period of time (more than 12 h), however, the sample did not return to spectrum 2a upon recooling, but gave a spectrum intermediate between that of 2a and 2b. There was no net decrease in the sum of the absorbances of the two peaks when compared to the sum of the absorbances in the low temperature spectrum of the fresh sample.

If **B** has a greatly different Debye temperature than **A**, this would lead to a different dependence of recoil-free fraction upon temperature, and may explain the spectral changes seen upon warming and recooling. The decrease in absorbance by approximately 75% for **A** and 20% for **B** upon warming gives estimated Debye temperatures of 150 K and 400 K [14] for **A** and **B** respectively. It is highly unlikely that two related compounds in the same matrix would have such different properties. However, if a partially reversible, temperature-dependent equilibrium between **A** and **B** is occurring, this would lead to the observed changes in the absorbances without the necessity of postulating radically different Debye temperatures. (It must be noted that this interpretation does not exclude the possibility that some of the observed change in absorbance is due to recoil-free fraction effects).

Added evidence for such an equilibrium process is the fact that these changes are not entirely reversible (*i.e.*, an intermediate spectrum was obtained when the sample was warm for a long time). Bent NO is known to be labile [15, 16], and it is not unlikely that $Fe(NO)_4$ can lose one nitrosyl ligand to give $Fe(NO)_3$ (eqn. (1)).

$$\underset{\mathbf{A}}{Fe(NO)_4} = \underset{\mathbf{B}}{Fe(NO)_3} + NO \qquad (1)$$

Uncoordinated nitric oxide may eventually and slowly diffuse away from the product cystals, so that the process is not entirely reversible, and $Fe(NO)_3$ is trapped, even upon recooling.

Apparently, '$Fe(NO)_4$' is not a pure compound, but contains some $Fe(NO)_3$. This complex is a 17 electron species and is expected to be very reactive in the presence of nucleophiles (e.g. O_2, Br^-). The presence of about 20% $Fe(NO)_3$ in '$Fe(NO)_4$' would lead to an elemental analysis somewhat high in iron for formula $Fe(NO)_4$ and may provide a pathway for the observed decomposition at room temperature when not under vacuum. Additionally, the 1140 cm^{-1} peak seen in the IR of '$Fe(NO)_4$' may belong to a decomposition product of $Fe(NO)_3$.

Finally, Mössbauer spectra were obtained for samples of iron in matrices varying in composition from 0.1% NO to 10% NO in Kr. The most satisfactory fit to all of the spectra consisted of two overlapping quadrupole doublets, both differing in position from compounds **A** and **B** found in 100% NO. These are due to two new iron-nitrosyl complexes, **C** and **D**. Table I is a summary of the Mössbauer parameters for all of the species observed in the iron nitric oxide reactions. In addition, a single peak at −0.71 mm/s, characteristic of unreacted iron atoms in a symmetrical environment was seen in the more dilute matrices. As would be expected, the relative concentration of the unreacted iron atoms, as measured by the relative area of the peak at − 0.71 mm/s, decreased as NO content of the matrix increased. No simple relationship exists between the NO content of the matrix and the ratio of the concentration of **C** to **D**.

In the infrared, a new band at about 1820–1825 cm^{-1} appears when iron is co-condensed in matrices of 0.1–2% NO in Kr. This band is not present in the absence of iron and is consistent with an iron–nitrosyl complex in which NO is linearly bonded. This may be either compound **C** or **D**. Again, much of the relevant portion of the infrared spectrum is obscured by NO and NO dimers. Further characterization of **C** and **D** was not possible, although, it may be assumed that they are the unsaturated nitrosyl complexes, Fe(NO) and $Fe(NO)_2$.

Conclusions

Although the inability to obtain IR data for this system hampered identification of the iron complexes formed in NO and NO/Kr matrices, the Mössbauer spectra provided some clarification. Four different iron–nitrosyl complexes, A, **B**, **C** and **D** are seen, depending upon the nitric oxide content of the matrices. The isomer shifts of all four complexes are consistent with covalently bound iron compounds. These observations lead to $Fe(NO)_4$, $Fe(NO)_3$, $Fe(NO)_2$, and Fe(NO) as possible formulations for **A**, **B**, **C** and **D** respectively. The Mössbauer spectrum of iron co-condensed with 100% NO matched that of '$Fe(NO)_4$' made earlier by Wilkinson and coworkers and poorly characterized. The results obtained upon the matrix-isolated samples show that this product is monomeric. Furthermore, the Mössbauer spectra indicate that this complex has high symmetry, suggesting that it is $Fe(NO)_4$ with one bent and three linear nitrosyl ligands with a pseudotetrahedral geometry. The 18 electron rule and IR spectrum of '$Fe(NO)_4$' made according to Wilkinson's procedure support this structure. At room temperature, **A** converts to **B**, whereas at low temperature **A** is favored. It is possible that this conversion takes place via loss of a bent nitrosyl from **A** yielding the three-coordinate **B** complex. This also suggests a possible pathway for the observed decomposition of '$Fe(NO)_4$' above 0 °C, in the presence of adventitious air, and may explain some of the anomalous observations such as the high iron analysis.

Finally, the observed reactivity of NO with iron atoms at low temperatures is significant and may have useful consequences. The matrix isolation experiments suggest that metal atom vaporization techniques [17] could be used to synthesize iron tetranitrosyl readily, and, perhaps, could be extended to the preparation of other binary metal nitrosyls as well.

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