allowed to stand in contact with aqueous solution for 3 days, but this was necessary in order to get appreciable exchange into the solid blues previously prepared with ^{56}Fe in the lattice sites (carbon and nitrogen holes). Further verification of the fact that the interstitial iron is, indeed, Fe^{3+} for aged Turnbull's blue is demonstrated by the fact that no peak is found at or above $+1.5$ mm/sec. This peak is one of a pair of peaks centered at about $+0.8$ mm/sec and with quadruple splitting of about 1.7–3.0 mm/sec which are normally encountered for high-spin Fe^{2+}. The peak at about -0.3 mm/sec would be obscured by the nitrogen hole Fe^{3+} peak. The $+1.5$-mm/sec peak is also missing from the spectrum of Turnbull's blue shown in Figure 7 of Milligan's work,[2] in which the sample was prepared quickly and then frozen and in which there was a very large percentage absorption. Therefore we can clearly state that Prussian and Turnbull's blues are the same compound upon aging. There may be some low-oxidation preparation circumstances in which the Turnbull's blue could be kept with interstitial Fe^{2+} rather than Fe^{3+}, but for an aqueous preparation requiring more than 30 min, the high-spin field at this position causes the iron to be oxidized to the Fe^{3+} state. Either traces of some oxidizing agent such as dissolved oxygen or hydronium ions from the water itself must be the oxidizing agent since only the nitrogen hole Fe^{2+} would be oxidized by the $Fe^{III}(CN)_6^{3-}$ ion. Since the preparations reported here and those of Milligan, *et al.*,[2] were done under nitrogen, the hydronium ion is the most likely oxidizing agent.

Close study of the spectra show that the absorption peaks are somewhat broader and the quadrupole splitting is less for the interstitial Fe^{3+} than for the nitrogen hole Fe^{3+}. However, the isomer shift of $+0.10$ mm/sec and the quadrupole splitting of 0.47 mm/sec are close enough to those of the nitrogen hole Fe^{3+} that in a preparation with both these positions Mössbauer active the spectrum would appear to be a single pair of peaks. The less concentrated interstitial iron positions would be submerged under the more prominent nitrogen hole Fe^{3+} peaks. The absorption of these interstitial ions cannot be added to those of the nitrogen hole Fe^{3+} to give the asymmetry observed in insoluble Prussian blue. That asymmetry must be due to some other influences of the interstitial ions upon the nitrogen hole Fe^{3+}.

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Mössbauer and Electron Paramagnetic Resonance Studies of Some Iron Nitrosyl Complexes

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Fluorocarbon-bridged ligands react easily with $Fe(NO)_2(CO)_2$ to give the complexes $(L\text{-}L)Fe(NO)_2$ ($L\text{-}L = (CH_3)_2AsCCF_3{=}CCF_3As(CH_3)_2$, $(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(C}F_2)_n$ ($n = 2, 3, 4$)). The mixed ligand $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ gives both chelate and monosubstituted derivatives. Mössbauer data for compounds of the sort $(L\text{-}L)Fe(NO)_2$, $LFe(NO)_2X$, $[Fe(NO)_2X]_2$, and $LFe(CO)(NO)_2$ are reported. The spectra of the compounds $LFe(CO)(NO)_2$ indicate that the π-acceptor strengths of L increase in the order $(C_6H_5)_3P < (C_6H_5)_2(CH_3)P \sim (C_6H_5)_3As < (C_6H_5O)_3P < CO < NO$. The π-acceptor strengths of the ditertiary phosphines in the compounds $(L\text{-}L)Fe(NO)_2$ are approximately equal to $(C_6H_5)_3P$ and it is predicted that the sign of V_{zz} is positive for the fluorocarbon-bridged derivatives. The epr spectra of the paramagnetic compounds $(C_6H_5)_3PFe(NO)_2Br$ and $(C_6H_5)_3AsFe(NO)_2Br$ show hyperfine interactions with the phosphorus (or arsenic) and the bromine atoms with a greater spin density on the iron atom in the case of the phosphorus compound. The dimer $[Fe(NO)_2Br]_2$ gives a weak epr signal in CCl_4 solution which intensifies and alters on the addition of complexing agents. The nitrosyl iodide dimer gives a signal in CCl_4 solution which can be attributed to $Fe(NO)_2I(CCl_4)$.

Introduction

In recent years increasing attention has been paid to the chemistry of transition metal–nitric oxide complexes. These compounds are of interest from the theoretical standpoint of the bonding involved as well as from their chemical and biochemical properties.[1-4]

Complexes between iron and nitric oxide have been known for a long time and have been subjected to a number of electron paramagnetic resonance (epr) studies.[5-9] These studies have indicated that in most cases the NO ligand is acting as NO^+ and that most of the spin density resides on the central iron atom. The

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two exceptions to this, in which the NO group appears to donate two electrons and retains the odd electron, are $Fe(NO)(CN)_5^{3-}$ and the nitric oxide complex of haeme.[2] It seems that NO can act as a σ acceptor as in the ion $IrI(CO)(NO)(P(C_6H_5)_3)_2^+$ which has a bent Ir–N–O bond (125°).[10]

The first systematic study of the so-called "brown ring compounds" appears to have been carried out by McDonald, *et al.*[7] Their epr results suggest that in the presence of a wide variety of coordinating ligands (L) the reaction between Fe(II) and NO leads to tetrahedral complexes of the form $Fe(NO)_2L_2$. The dependence of the intensity of the epr line on the complexing ligand concentration suggests that many of the paramagnetic complexes exist in equilibrium with a diamagnetic complex involving two iron atoms which are antiferromagnetically coupled. It was also found by these workers that it is not always possible to resolve the ^{14}N hyperfine splitting. Subsequently Burlamacchi, *et al.*,[9] confirmed these conclusions with studies on iron–nitrosyl–halide compounds.

In the present work we describe epr studies on the previously known[3] complexes of the form $Fe(NO)_2BrL$ where L is triphenylphosphine or triphenylarsine. The complexes have been synthesized and their spectra generally confirm the conclusions based on *in situ* reaction of NO with Fe(II) in the presence of complexing ligands.[7,9] We have also investigated the behavior of the dimers $[Fe(NO)_2Br]_2$ and $[Fe(NO)_2I]_2$[3] in carbon tetrachloride in the presence of complexing ligands.

Mössbauer studies of a number of five-coordinate derivatives of $Fe(CO)_5$ suggest[11-14] that the isomer shift δ is not very sensitive to the nature of the attached ligands. This is in contrast to results for low-spin Fe(II) compounds.[15] On the other hand, the $Fe(CO)_5$ derivatives do show significant differences in quadrupole splittings.[11] However, even with complete knowledge of the *efg* tensor a detailed interpretation of such results is hampered by the fact that the observed splittings contain an inherently large contribution from the $3d^8$ electronic configuration of the iron atom.

It therefore seemed attractive to investigate a number of four-coordinate derivatives of $Fe(CO)_2(NO)_2$. In these compounds the formal oxidation state of iron is Fe(−II). This implies a $3d^{10}$ electronic configuration, which is spherically symmetric and should not contribute to the electric field gradient. Therefore to a first approximation Δ will depend only upon the dispositions and relative strengths of the ligands. Furthermore, very few data are available on such compounds[16] and we wished to see if δ for Fe(−II) complexes were sensitive to the nature of the ligand. At the same time, since NO usually appears to be a very strong π acceptor,[17] it seems reasonable to attempt to correlate changes in s-electron density at the iron nucleus with the N–O stretching frequency. This paper reports the Mössbauer parameters for a number of complexes of the sort $LFe(NO)_2(CO)$, $L_2Fe(NO)_2$, and $(L\text{-}L)Fe(NO)_2$, as well as for the nitrosyl halide dimers $[Fe(NO)_2X]_2$ and their paramagnetic derivatives $LFe(NO)_2X$ (L is a monodentate and L-L is a bidentate ligand).

Experimental Section

Volatile reagents were handled in a standard vacuum system. Mass spectra were measured with an AEI MS-9 spectrometer with direct introduction of solid samples. The Mössbauer spectrometer and attendant experimental details have been described previously.[11] Microanalyses were done by Mr. P. Borda of this department and the results are listed in Table I.

The preparations of the fluorocarbon-bridged ligands **1** and **2** have been described previously;[11,18,19] however one method[20] has been modified and is given again below. The other ligands used were commercially available. Iron dicarbonyl dinitrosyl was prepared as described by King[21] and was used to prepare the previously known $L_2Fe(NO)_2$ and $(L\text{-}L)Fe(NO)_2$ derivatives.[3] The paramagnetic halide complexes $LXFe(NO)_2$ (X = halogen) were made by the method of Hieber and Kramolowsky[22] involving the reaction of the ligand with iron dinitrosyl halide dimer. The latter was made by the reaction of iron dicarbonyl dinitrosyl and the halogen in dichloromethane solution and was purified by sublimation.[23]

Samples were prepared for epr studies by transferring the compounds, under dry nitrogen, to the degassed solvent contained in a silica tube. The solvent employed was carbon tetrachloride in order to minimize solvent influence. The samples were then further degassed carefully by the usual "freeze–thaw" method. The epr spectra were recorded on a 100-kHz X-band spectrometer, similar to the Varian V-4500 unit, equipped with a Varian V-4012 12-in. magnet. The magnetic field was measured with a proton resonance magnetometer. The microwave frequency was measured using a Hewlett-Packard 5245L frequency counter with a 5255A frequency converter.

1. **Preparation of *cis*-2,3-Bis(dimethylarsino)hexafluorobut-2-ene (2).**—Tetramethyldiarsine (20 g, 95 mmol) and hexafluoroacetone (30 g, 180 mmol (excess)) were sealed together under vacuum in a Pyrex tube. The tube was allowed to stand (with occasional shaking) for 2 hr at 20°. The tube was opened and hexafluorobut-2-yne was added (16 g, 99 mmol); the tube was resealed and the contents were allowed to react for 2 days. Then the tube was opened and the hexafluoroacetone was taken into the vacuum system. The least volatile liquid product was distilled in a semimicro apparatus, bp 98° (15 mm) (lit.[20] bp 98° (15 mm)) (yield 27 g, 75%).

2. **Preparation of $L_2Fe(NO)_2$ and $(L\text{-}L)Fe(NO)_2$ Complexes.** (a) **$f_n$fosFe(NO)$_2$.**—The ligand $f_4$fos, **1a** (1.4 g, 29 mmol), and iron dicarbonyl dinitrosyl (0.5 g, 29 mmol) were sealed in a Pyrex tube in acetone solution (15 ml) and allowed to stand for 1 day at 20°. The tube was then opened, and the acetone was removed under reduced pressure. The product was recrystallized from acetone–hexane solution to yield $f_4$fosFe(NO)$_2$ (1.4 g, 75%) as black shiny crystals. $f_6$fosFe(NO)$_2$ and $f_8$fosFe(NO)$_2$ ($f_6$fos = **1b**, $f_8$fos = **1c**) were prepared by an analogous route using equimolar quantities of reactants.

$f_6$fosFe(NO)$_2$ was also formed when a large excess of ligand was present. The product and excess $f_8$fos were separated by repeated recrystallization until elemental analysis indicated that the product was pure.

(b) **$(CH_3)_2AsC(CF_3){=}C(CF_3)As(CH_3)_2Fe(NO)_2$.**—The ligand **2** (0.8 g, 21 mmol) and iron dicarbonyl dinitrosyl (0.4 g, 22 mmol) were sealed in hexane solution (10 ml) in a Pyrex tube. The tube was irradiated using a 200-W ultraviolet lamp at a distance of 20 cm for 4 hr. The tube was opened, and the purple crystals

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TABLE I
ANALYTICAL DATA FOR NEW COMPOUNDS

Complex	% calcd C	H	N	% found C	H	N
$(C_6H_5)_2PC{=}CP(C_6H_5)_2CF_2CF_2Fe(NO)_2$	55.2	3.3	4.6	55.0	3.4	4.5
$(C_6H_5)_2PC{=}CP(C_6H_5)_2(CF_2)_2CF_2Fe(NO)_2$	52.8	3.0	4.3	52.9	3.2	4.5
$(C_6H_5)_2PC{=}CP(C_6H_5)_2(CF_2)_3CF_2Fe(NO)_2$	50.8	2.8	4.0	51.2	2.9	3.8
$[(C_6H_5)_2PCH_3]_2Fe(NO)_2$	60.6	5.0	5.5	60.5	4.9	5.4
$(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2Fe(NO)_2$	55.8	4.2	5.0	55.7	4.2	4.7
$(CH_3)_2AsCCF_3{=}CCF_3As(CH_3)_2Fe(NO)_2$	19.7	2.5	5.7	19.5	2.4	5.2
$(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2Fe(CO)(NO)_2$	55.4	4.1	4.8	55.1	4.0	4.6
$(C_6H_5)_3SbFeBr(NO)_2$	39.3	2.7	5.1	39.1	2.6	5.1

of product which had been deposited during irradiation were collected, washed with hexane, and dried (0.6 g, 60%). The product decomposed when attempts were made to recrystallize it.

(c) **ffarsFe(CO)(NO)$_2$.**—Attempts to make ffarsFe(NO)$_2$ (ffars = **1d**) by methods similar to and more extreme than those described produced only an oily black air-sensitive liquid, which had an infrared spectrum in the region 1600–2000 cm^{-1} that could be ascribed to ffarsFe(CO)(NO)$_2$ (ν(C=O) 2010 cm^{-1}; ν(N=O) 1770, 1730 cm^{-1}).

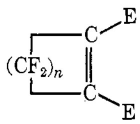
(d) **arphosFeCO(NO)$_2$ and arphosFe(NO)$_2$.**—arphos ($(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$) (1.0 g, 0.2 mmol) and Fe(CO)$_2$(NO)$_2$ (0.4 g, 0.2 mmol) were sealed in a Carius tube in acetone solution and heated to 85° for 3 hr. The tube was opened and the contents were chromatographed on Florisil. arphosFe(CO)(NO)$_2$ was eluted with petroleum ether–ether (20:1) and recrystallized from hexane as red crystals (0.2 g, 15%). arphosFe(NO)$_2$ was eluted with ether and recrystallized from acetone–hexane as brown crystals (0.6 g, 45%).

(e) **$[(C_6H_5)_2PCH_3]_2Fe(NO)_2$.**—Diphenylmethylphosphine (1 g, 5 mmol) and iron dicarbonyl dinitrosyl (0.4 g, 2.2 mmol) were heated at 60° in hexane in a sealed tube for 3 hr. The product was recrystallized from dichloromethane–hexane as red-brown crystals (1.2 g, 85%).

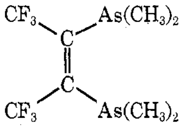
3. **Preparation of $(C_6H_5)_3SbFeBr(NO)_2$.**—Triphenylstibine (1.5 g, 4.2 mmol) in dry tetrahydrofuran solution (5 ml) was added to iron dinitrosyl bromide dimer (0.8 g, 4.0 mmol) also in THF solution (10 ml). The mixture turned from red to green on reaction. The THF was removed at reduced pressure and the residue dissolved in ether and filtered. The filtrate was concentrated to about 10 ml and then cooled (−10°): green-black crystals of product (10 g, 45%) separated. The ether was decanted and the product was washed with a small amount of hexane, dried, and stored under nitrogen.

Results and Discussion

The ditertiary phosphines **1a–c** react easily with iron dicarbonyl dinitrosyl to displace both carbon monoxide groups and give the chelated derivatives **3** (n = 2, 3, 4).



1a, E = $(C_6H_5)_2P$, n = 2, f$_4$fos
b, E = $(C_6H_5)_2P$, n = 3, f$_6$fos
c, E = $(C_6H_5)_2P$, n = 4, f$_8$fos
d, E = $(CH_3)_2$ As, n = 2, ffars



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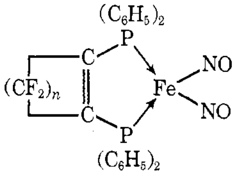

3

These derivatives are formed even in the presence of excess ligand indicating that there is little or no strain present in the chelate ring. The closely related ligand ffars **1d** seems to form only the monosubstituted compound ffarsFe(CO)(NO)$_2$. This is not at all unexpected in view of its failure to give the chelate complex ffarsFe(CO)$_3$.[11,24,25] What is surprising is that the acyclic ditertiary arsine **2** *does* form a chelate derivative when treated with Fe(NO)$_2$(CO)$_2$. A chelate Fe(CO)$_3$ complex is also obtained by treating **2** with Fe(CO)$_5$.[26] These results establish the cis geometry of the ligand which previously was inferred from spectroscopic results.[20]

The mixed ligand arphos $(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$ reacts easily with Fe(CO)$_2$(NO)$_2$ to give both the chelate and monosubstituted complexes arphosFe(NO)$_2$ and arphosFe(CO)(NO)$_2$. It is probable that the more basic phosphorus atom is coordinated to the iron atom in the latter case. In the course of this investigation we also prepared for the first time $((C_6H_5)_2PCH_3)_2Fe(NO)_2$ from Fe(CO)$_2$(NO)$_2$ and $(C_6H_5)_3SbFeBr(NO)_2$ from [FeBr(NO)$_2$]$_2$.

Analytical data for all new compounds are listed in Table I. The figures together with the spectroscopic data to be discussed below leave little doubt that the compounds are formulated correctly. The mass spectra of the Fe(NO)$_2$ derivatives of ligands **1a**, **1b**, **1c**, and **2** all showed parent peaks at the expected m/e values. The crystal structure of f$_6$fosFe(NO)$_2$ has been determined[27] and is essentially as indicated in **3** (n = 3). The main points of interest in this structure are the large deviations from the expected tetrahedral angle of 109° in both P–Fe–P and N–Fe–N angles. The P–Fe–P angle of 87° is not necessarily imposed upon the molecule by the geometry of the ligand (the P···P distance is 3.08 Å) since the P···P distance in the monodentate complex π-$C_5H_5Fe(CO)(f_6fos)Sn(CH_3)_3$ is 3.60 Å[28] so that the angle could conceivably be wider. The N–Fe–N angle in f$_6$fosFe(NO)$_2$ is 125° which is much greater than the expected 109°.

Mingos and Ibers[29] recently reported the structure of $[((C_6H_5)_3P)_2Ir(NO)_2]^+ClO_4^-$ a species where the metal is isoelectronic with the iron atom in f$_6$fosFe(NO)$_2$. In this compound both P–Ir–P and N–Ir–N angles are unexpectedly large, a result the authors attribute to the iridium atom tending toward a d^6 electronic configura-

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[24] This particular ligand, however, shows a strong tendency to bridge two metal atoms as in ffarsFe$_2$(CO)$_8$,[11] ffarsFe$_3$(CO)$_{10}$,[25a] (ffars)$_2$Ru$_3$(CO)$_8$,[25b] and ffarsCo$_2$(CO)$_6$.[25c]

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TABLE II

MÖSSBAUER AND INFRARED DATA FOR SOME IRON NITROSYLS $LYFe(NO)_2$

L (and/or Y)	δ,[a,b] mm sec^{-1}	Δ,[b] mm sec^{-1}	ν(NO),[c] cm^{-1}	ν(CO),[c] cm^{-1}
$[(C_6H_5)_3P]_2$	0.33	0.70	1723,[d] 1679	
$[(C_6H_5)_2PCH_3]_2$	0.30	0.60	1720, 1676	
$[(C_6H_5O)_3P]_2$	0.29	0.50	1770, 1719	
$[(C_6H_5)_3As]_2$	0.42	0.59	1732, 1692	
$(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2CF_2C}F_2$	0.35	0.29	1746, 1702	
$(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(CF_2)_2C}F_2$	0.33	0.29	1746, 1702	
$(C_6H_5)_2P\overline{C{=}CP(C_6H_5)_2(CF_2)_3C}F_2$	0.29	0.32	1746, 1706	
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$	0.29	0.54	1726, 1679	
$(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$	0.36	0.58	1730, 1686	
$(CH_3)_2AsCCF_3{=}CCF_3As(CH_3)_2$	0.37	0.42	1746, 1700	
$(C_6H_5)_2PCH_2CH_2As(C_6H_5)_2$, CO[e]	0.28	0.47	1764, 1722	2010
$(C_6H_5)_3As$, CO	0.34	0.64	1770, 1729	2012
$(CO)_2$	0.32	0.34	1810, 1769	2084, 2037
$C_5H_{11}N$, Br	0.60	1.12	1797,[f] 1731	
$(C_6H_5)_3P$, Br	0.50	1.02	1790, 1734	
$(C_6H_5)_3As$, Br	0.52	1.28	1795, 1740	
$(C_6H_5)_3Sb$, Br	0.55	1.49	1795, 1745	
$(C_6H_5)_3P$, I	0.49	1.09	1789, 1738	
$(C_6H_5)_3As$, I	0.50	1.28	1792, 1745	
$[BrFe(NO)_2]_2$	0.67	1.76	1826, 1764	
$[IFe(NO)_2]_2$	0.60	1.68	1810, 1771	

[a] Isomer shift relative to sodium nitroprusside. [b] Measured at 80°K, ±0.01 mm sec^{-1}. [c] Spectra recorded on a Perkin-Elmer 457 spectrometer. [d] In C_6H_{12} solution. [e] Only phosphorus is bonded to iron here. [f] In CCl_4 solution.

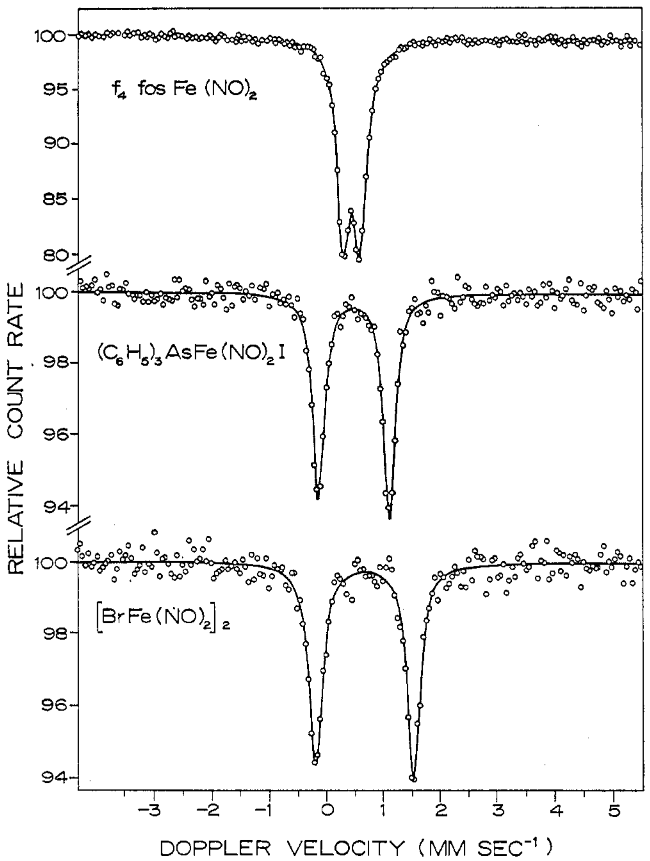

Figure 1.—Mössbauer spectra at 80°K of $f_4fosFe(NO)_2$, $(C_6H_5)_3AsFe(NO)_2I$, and $[BrFe(NO)_2]_2$. The velocity scale is relative to sodium nitroprusside, and the solid lines represent least-squares fits to Lorentzian line shapes.

tion. This however does not appear to occur in $f_6fosFe(NO)_2$ as evidenced by the linearity of the nitrosyl groups. The structure of $f_6fosFe(NO)_2$ shows that the cyclopentene ring is in an "envelope" configuration, and one fluorine atom is much nearer to a nitrogen atom than the other fluorine atoms. This inequivalence is not observed in the fluorine nmr spectrum of the molecule[30] probably because the pentene ring is flipping in solution and averaging the environment of the fluorine atoms.

Infrared data in the range 2100–1600 cm^{-1} were collected for the newly prepared complexes as well as for some previously reported. These results together with Mössbauer data are presented in Table II and representative Mössbauer spectra are shown in Figure 1. For the purpose of discussing these infrared and Mössbauer data, it is convenient to divide the complexes into three groups: (1) the diamagnetic Fe(−II) complexes $Fe(NO)_2(CO)_2$, $LFe(NO)_2(CO)$, $L_2Fe(NO)_2$, and (L-L)-$Fe(NO)_2$; (2) the paramagnetic derivatives $LFe(NO)_2X$; (3) the dinitrosyliron halide dimers $[Fe(NO)_2X]_2$.

1. Fe(−II) Complexes.—In a tetrahedral crystal field the iron 3d shell is split into a doubly degenerate e level lying below a triply degenerate t_2 level. Since the splitting is small, the compounds would not be expected to be diamagnetic (as found) unless the electronic configuration were $3d^{10}$; otherwise the electrons should adopt a high-spin arrangement. We shall therefore assume that the $3d^{10}$ assignment is correct.

The isomer shifts of these complexes show only very small differences, and it is clear that the total s-electron density at the iron nucleus varies only slightly from compound to compound. The magnitude of the isomer shift is influenced by the extent of both ligand-to-metal σ bonding and metal-to-ligand π back-bonding.[31] As the σ-donor strength of the ligands increases, the "metal character" of the a_1 bonding orbital will increase, with a concomitant decrease in δ. If the ligands have low-lying π^* or d orbitals available, increased bonding between these and the iron 3d orbitals will cause the latter to become more delocalized, thereby decreasing the shielding of the metal s electrons. Thus, δ will decrease with both increasing σ-donor power and increasing π-acceptor power of the ligands, and we might

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[30] The spectrum was run in an acetone-d_6 solution using a Varian HA 100 instrument. It was very similar to that of the free ligand.[11]

[31] B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *Trans. Faraday Soc.*, **64**, 620 (1968).

have anticipated larger variations in δ than observed here.

Owing to the near constancy of the δ values, there is no apparent correlation between δ and the N–O stretching frequency. If the latter is taken as a measure of the iron–nitrosyl π back-donation, we must conclude that the effects of changes in the σ-donor and π-acceptor properties of the ligands are simply absorbed by the nitrosyl groups with only a very small affect on the total s-electron density at the iron nucleus. More will be said about this point below. It is interesting to note that the ν(N–O) values are higher in the carbonyl-containing complexes than in the disubstituted derivatives (with the single exception of the bis(triphenyl phosphite) complex).

We turn now to a consideration of the quadrupole splitting parameter Δ, which is given by

$$\Delta = {}^1/_2 eQV_{zz}(1 + {}^1/_3\eta^2)^{1/2} \tag{1}$$

where eQ is the quadrupole moment of the $I = {}^3/_2$ excited state of ^{57}Fe. It is usually possible to choose a "principal" set of axes such that the off-diagonal elements of the *efg* tensor vanish.[32] These axes are conventionally labeled so that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, and the asymmetry parameter is then defined as

$$\eta = (V_{xx} - V_{yy})/V_{zz} \tag{2}$$

In cases where the d orbitals of the Mössbauer atom which are not involved in σ bonding are occupied so as to constitute a spherically symmetric set or subset, a simple point-charge treatment appears to provide an adequate description of the *efg* tensor. Such a model has proved quite successful in calculations on low-spin Fe(II) complexes[33] and Sn(IV) compounds,[34,35] and Mazak and Collins[36] have very recently applied this model to Fe(–II) complexes of the type reported here. We should add that such a treatment is *not* expected to apply when there are contributions to the *efg* from a nonspherically symmetric d_ϵ or d_γ subset.

In general, $V_{zz} = eq$ will depend both on noncubic distributions of the iron valence electrons and on external charges,[15] *i.e.*

$$q = (1 - R)q_{\text{valence}} + (1 - \gamma_\infty)q_{\text{lattice}} \tag{3}$$

where R and γ_∞ are the Sternheimer antishielding factors, and

$$q_{\text{valence}} = -\sum_i p_i\langle(3\cos^2\theta_i - 1)r_i^{-3}\rangle \tag{4}$$

$$q_{\text{lattice}} = \sum_{\text{L}} q_{\text{L}}(3\cos^2\theta_{\text{L}} - 1)r_{\text{L}}^{-3} \tag{5}$$

p_i is the effective population of the ith iron 3d orbital, and the expectation value for this orbital in (4) is taken over the electron coordinates θ_i, r_i; q_{L} is the charge on ligand L with polar coordinates θ_{L}, r_{L}. In the strict point-charge model, only q_{lattice} is considered. However, it has recently been shown[15] that q_{valence} also follows the predictions of the point-charge model, which allows one to approximate this term as shown by[37]

$$q_{\text{valence}} = \Sigma q_l(3\cos^2\theta_{\text{L}} - 1)r_l^{-3} \tag{6}$$

q_l being an effective charge on the Fe–L bond axis, representing the electron "hole" density in the appropriate orbital. Thus, V_{zz} becomes

$$V_{zz} = \sum_{\text{L}} [\text{L}](3\cos^2\theta_l - 1) \tag{7}$$

where

$$[\text{L}] = e[(1 - R)q_l r_l^{-3} + (1 - \gamma_\infty)q_{\text{L}} r_{\text{L}}^{-3}] \tag{8}$$

is the contribution of ligand L to the *efg*. The magnitude of Δ will depend upon differences in [L] values for the ligands involved in the same way as for the strict point-charge model, but the interpretation of [L] will differ. Indeed, we might expect q_{valence} to dominate the splitting because of the r^{-3} dependence of q, and this appears to be so.[38] Mazak and Collins[36] have computed the *efg* tensor components for Fe(–II) molecules of the types FeA_2B_2, FeA_3B, and FeA_2BC assuming tetrahedral symmetry. In the first two cases they also considered distortions from tetrahedral symmetry which maintain constant bond lengths. Some of their results are reproduced in Table III. In the FeA_3B case V_{zz} is positive if $|[\text{A}]| > |[\text{B}]|$ and *vice versa.* In the FeA_2B_2 case $\eta = 1$ for strict tetrahedral symmetry, which according to eq 2 means that the sign of the *efg* is indeterminate. However, η decreases as the bond angles change from tetrahedral, and it is found that V_{zz} is negative if the ligands with the larger $|[\text{L}]|$ move apart and positive if they approach each other.

TABLE III

POINT-CHARGE PREDICTIONS FOR CASES OF TETRAHEDRAL SYMMETRY[a]

Case		V_{zz}	η
FeA_2B_2		$2([\text{A}] - [\text{B}])$	1
FeA_2B_2	$[\text{A}] < [\text{B}] < 0;\ \alpha > 0$	<0	<1
FeA_2B_2	$[\text{A}] < [\text{B}] < 0;\ \alpha < 0$	>0	<1
FeA_3B	$[\text{A}] < [\text{B}] < 0$	$2([\text{B}] - [\text{A}]) > 0$	0
FeA_3B	$[\text{B}] < [\text{A}] < 0$	$2([\text{B}] - [\text{A}]) < 0$	0
FeA_2BC	$[\text{A}] < [\text{C}] < [\text{B}] < 0$	>0	<1
FeA_2BC	$[\text{C}] < [\text{B}] < [\text{A}] < 0$	<0	<1

[a] The second and third cases represent distortions from tetrahedral symmetry. α is the departure of the A–Fe–A angle from tetrahedral, and $\alpha > 0$ corresponds to an increase in this angle. These results are taken from ref 36.

Since the nitrosyl group bonds by first donating an electron to the iron atom to become the nitrosonium ion, we can assume that σ bonding occurs only through sp^3 hybrids. Then the "effective" populations of the iron 3d orbitals (hence q_{valence}) will depend almost entirely on the extent of π back-bonding from the filled metal d orbitals to empty π^* and/or d orbitals on the various ligands. In this case differences in σ-donor power among the ligands should have little or no effect upon the splitting,[39] and the Δ values should measure directly the π-acceptor capacity of the ligands. Note that a strong π acceptor will reduce the effective iron d-orbital population (lowering p_i) and also tend to delocalize the d-orbital charge density (increasing r_i). Both effects reduce $|q_{\text{valence}}|$ and we therefore expect the best π acceptor to show the smallest $|[\text{L}]|$.

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[32] R. L. Collins and J. C. Travis, "Mössbauer Effect Methodology," Vol. 3, Plenum Press, New York, N. Y., 1967, pp 123–161.

[33] R. R. Berrett and B. W. Fitzsimmons, *J. Chem. Soc. A*, 525 (1967).

[34] B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *ibid.*, 143 (1969).

[35] R. V. Parish and R. H. Platt, *ibid.*, 2145 (1969).

[36] R. A. Mazak and R. L. Collins, *J. Chem. Phys.*, **51**, 3220 (1969).

[37] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1970).

[38] G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 200 (1970).

[39] This is in contrast to the low-spin octahedral Fe(II) situation, where there is σ donation into the empty e_g orbitals of the iron d shell.

Using the magnetic perturbation technique[40] Mazak and Collins[36] have determined the signs of V_{zz} and magnitudes of η for $KFe(CO)_3(NO)$ [$V_{zz} > 0, \eta \approx 0$], $Fe(CO)_2(NO)_2$ [$V_{zz} < 0, \eta \approx 0.85$], and $Fe((C_6H_5)_3P)_2(NO)_2$ [$V_{zz} < 0, \eta \approx 0.76$]. The positive V_{zz} for $KFe(CO)_3NO$ implies $|[CO]| > |[NO]|$. The small quadrupole splitting ($\Delta = 0.35$ mm sec^{-1}) observed for this compound and for $Fe(CO)_2(NO)_2$ shows that the difference in $|[L]|$ values for CO and NO is not large, and the negative V_{zz} for the latter compound implies that the C–Fe–C angle is greater than 109°. The larger splitting found for $Fe((C_6H_5)_3P)_2(NO)_2$ shows that $|[(C_6H_5)_3P]| > |[CO]|$. Assuming that only the distortion of the ligand with larger $|[L]|$ is important, the sign of V_{zz} and magnitude of η lead to the inference that the P–Fe–P bond angle is approximately 116°.

The $|[(C_6H_5)_3P]| > |[CO]| > |[NO]|$ ordering is just the reverse of the previously suggested π-acceptor strengths of these ligands,[13,41] in agreement with the bonding ideas outlined above. Although the exact degree of distortion from tetrahedral symmetry cannot be determined with high accuracy, we *can* tell the sign of α if we know the sign of V_{zz} (see Table III). Conversely, if we know the crystal structure and the ranking of the ligands in the [L] series, we can infer at once the sign of V_{zz}.

Now let us return to the other $L_2Fe(NO)_2$ complexes listed in Table II. Although the detailed geometry of these compounds is not known, it seems reasonable to assume $\alpha > 0$, as was found for the $((C_6H_5)_3P)_2$ and $(CO)_2$ derivatives, and that V_{zz} will be negative. With this assumption, we can rank the ligands according to their $|[L]|$ values: $|[(C_6H_5)_3P]| > |[(C_6H_5)_2CH_3P]| \simeq |[(C_6H_5)_3As]| > |[(C_6H_5O)_3P]| > |[CO]| > |[NO]|$. If, as we suggested above, a smaller $|[L]|$ corresponds to a better π acceptor, this ranking is not unreasonable, although $[(C_6H_5)_3As]$ might be expected to lie above $[(C_6H_5)_3P]$.[41] Since the Δ values do not show a wide variation, it could well be that the ordering might be changed if the distortion from tetrahedral symmetry is much larger in the $((C_6H_5)_3As)_2$ derivative than in the $((C_6H_5)_3P)_2$ case. A detailed analysis of this point would require a knowledge of the η values. We should also point out that the above ordering of ligands correlates quite well with the N–O stretching frequencies. As the difference $|[L]| - |[NO]|$ increases in the $L_2Fe(NO)_2$ complexes, ν(N–O) decreases. This is also consistent with the higher ν(N–O) values for the carbonyl-containing derivatives.

The chelate complexes $(L\text{-}L)Fe(NO)_2$ can now be considered. In the iron(0) carbonyl complexes where L-L acts as either a monodentate or bridging group, its behavior is essentially the same as that of a (mono) tertiary phosphine or arsine.[11] These results imply that the "strength" of a ligand such as diphos or f$_4$fos is comparable to that of $(C_6H_5)_3P$. Similar conclusions have been drawn from a study of derivatives of $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$.[41] However, we see from Table II that the $Fe(NO)_2$ complexes of 1 show much smaller quadrupole splittings than that for $Fe((C_3H_5)_3P)_2(NO)_2$. The crystal structure of the f$_6$fos complex[27] shows a P–Fe–P angle of 87°; thus α is large and negative. Since we can safely assume that $|[f_6fos]| > |[NO]|$, we conclude at once from Table III that V_{zz} is positive for $f_6fosFe(NO)_2$. Moreover, the Δ values for the f$_4$fos and f$_8$fos complexes are essentially identical with that of the f$_6$fos compound, and we predict that not only is V_{zz} positive in these compounds as well but that all three complexes will have very similar distortions from tetrahedral symmetry.

As the magnitudes of both V_{zz} and η depend not only on α but on the values of [L], it is not possible to attempt detailed calculations on the basis of Collins equations.[36] However, the large difference in Δ and the sign change in V_{zz} between the f$_n$fos and $((C_6H_5)_3P)_2$ complexes can be rationalized simply in terms of geometrical factors, and there is no apparent inconsistency in assuming $|[f_nfos]| \sim |[(C_6H_5)_3P]|$.

2. **Paramagnetic LFe(NO)$_2$X Complexes.**—In these compounds, paramagnetism arises from a single hole in the iron 3d shell which leaves an unpaired electron in the t$_2$ level. We can therefore formally classify these derivatives as Fe(–I) complexes.

One might expect that removal of an electron from the iron 3d shell would decrease the shielding of the 3s and 4s electrons and lead to an isomer shift smaller than that observed in Fe(–II) compounds. However the opposite is in fact observed. These results can be explained in terms of the halide bonding characteristics. Both Br and I are expected to exhibit comparatively little covalent character in their bonding to Fe, so that there will be far less augmentation of the s-electron density at Fe. The lesser shielding of the nuclear charge by the s electrons will cause the metal 3d orbitals to contract, which will in turn increase their shielding of the 3s and 4s electrons. These effects are synergetically related, and both will tend to raise the isomer shift. Further, both Br and I are poor π acceptors, and this will also lead to an increase in δ.

The quadrupole splittings for these d^9 Fe(–I) complexes arise not only from differences in strength and disposition of the ligands but also from the hole in the iron 3d shell. This will lead to a larger $|q_{\text{valence}}|$ term, but there seems no way at present to separate unambiguously the two contributions to the quadrupole splitting or to predict signs of V_{zz}. As expected, the Δ values are larger than for the d^{10} complexes, but the very pronounced increase in going from triphenylphosphine to the corresponding arsine and stibine derivatives was not anticipated. Although part of this effect is probably due to differences in the π-acceptor properties of these ligands, it is unlikely that this is the sole cause, especially since the N–O stretching frequencies are nearly constant. The most attractive explanation seems to be that the quadrupole splittings in these compounds are also very sensitive to distortions from tetrahedral symmetry and that the observed variations are largely due to changes in the bond angles about iron.

3. **[Fe(NO)$_2$X]$_2$ Compounds.**—The crystal structure of $[Fe(NO)_2I]_2$ has recently been reported.[42] The two iron and two bridging iodine atoms form a planar rhombus, the dimer being formed by the fusion of two identical tetrahedral-like $Fe(NO)_2I_2$ units along the common iodine–iodine edge. Despite the exceptionally long iron–iron distance of 3.05 Å, Dahl, *et al.*,[42] presented cogent arguments in favor of the presence of an electron-

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[40] S. L. Ruby and P. A. Flinn, *Rev. Mod. Phys.*, **36**, 351 (1964).

[41] W. R. Cullen, J. A. J. Thompson, and J. R. Sams, *Inorg. Chem.*, in press.

[42] L. F. Dahl, E. R. de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969).

pair Fe–Fe bond. We shall assume, with Dahl,[42] the presence of an Fe–Fe bond and adopt a spin-paired $3d^8$ description for both halide dimers.

The isomer shifts observed here are considerably larger than those of most other simple Fe(0) complexes (*e.g.*, $Fe(CO)_5$ and related molecules, for which $\delta \approx 0.2$ mm sec^{-1}). Since both the nitrosyl groups in $[Fe(NO)_2X]_2$ and the carbonyl groups in $Fe(CO)_5$ are strong π acceptors, we must again attribute the high isomer shifts in the nitrosyl halide dimers to the very weak σ-donor and π-acceptor properties of Br and I.

The fairly large quadrupole splittings observed are undoubtedly due to the asymmetry of the iron 3d shell as well as to bonding effects. The very different Fe–N (1.67 Å) and Fe–I (2.58 Å) distances suggest a strong anisotropy in the bonding. There is also the question of the Fe–Fe bond, which if present would be expected to increase Δ as compared with the tetrahedral compounds. It is interesting to note that the red Roussin salt $K_2[Fe(NO)_2S]_2$ shows a splitting[43] of only 0.67 mm sec^{-1}. A more detailed discussion of the quadrupole splittings must await a knowledge of the sign of V_{zz} for these interesting compounds.

Electron Paramagnetic Resonance Studies.—The epr spectra of $Fe(NO)_2BrP(C_6H_5)_3$ and $Fe(NO)_2BrAs(C_6H_5)_3$ in carbon tetrachloride solution at 20° are shown in Figures 2 and 3. The former complex exhibits a seven-line epr spectrum with intensity ratios 1:1:1:2:1:1:1 which can be attributed to the hyperfine interaction of a phosphorus and a bromine nucleus. This particular intensity pattern arises from the fortuitous overlap of the innermost bromine hyperfine lines. It will also be observed from Figure 2 that the ^{79}Br, ^{81}Br splitting is just apparent. The "extra" intensity observed in the outermost lines is probably due to incomplete averaging of the molecular motion by the anisotropic spin-Hamiltonian parameters. The spectrum of the arsine complex shows the expected 16-line trace due to the interaction of two spin $^3/_2$ nuclei. The spin-Hamiltonian parameters for these complexes are given in Table IV, together with some of the results of Burlamacchi, *et al.*[9]

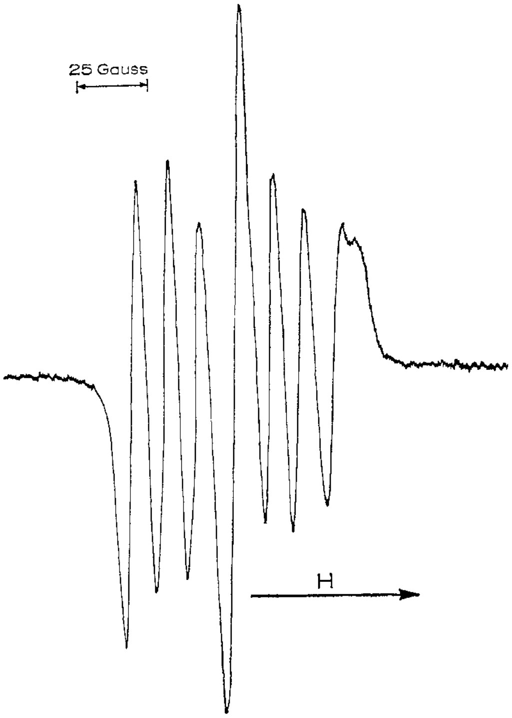


Figure 2.—The epr spectrum of $(C_6H_5)_3PFe(NO)_2Br$ in CCl_4 solution at 20°.

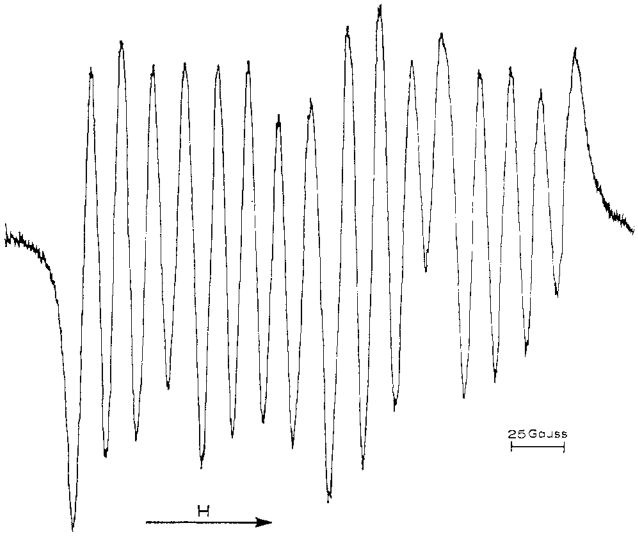


Figure 3.—The epr spectrum of $(C_6H_5)_3AsFe(NO)_2Br$ in CCl_4 solution at 20°.

A comparison of the results in Table IV shows that the tensor components for the present complexes are of the same character as those previously obtained.[9] The spin density distributions in $Fe(NO)_2Br_2^-$ and $Fe(NO)_2BrP(C_6H_5)_3$ are somewhat different. The spin density on the Br atom in the former is 0.0024 whereas in the latter it is 0.0017 on the bromine and the P atom has a spin density of 0.017. Consequently the spin density on the phosphine complex is shifted toward the iron atom, presumably reflecting the overall electron-donating character of the phosphine group relative to a more electronegative Br^- anion. A similar situation obtains in the arsine complex (*cf.* Mössbauer discussion above).

TABLE IV

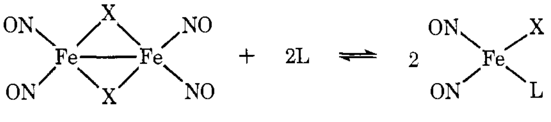
ISOTROPIC *g*-TENSOR COMPONENTS AND HYPERFINE TENSOR COMPONENTS

Complex	g_{iso}	a_{Br}, G	a_I, G	a_L, G
$Fe(NO)_2Br_2^{-}$ [a]	2.045	19.5	...	...
$Fe(NO)_2Br(H_2O)$[a]	2.039	19.5	...	...
$Fe(NO)_2I_2^{-}$ [a]	2.070	...	20.2	...
$Fe(NO_2)I(H_2O)$[a]	2.055	...	20.2	...
$Fe(NO)_2BrP(C_6H_5)_3$	2.052	14.5	...	62.9
$Fe(NO)_2BrAs(C_6H_5)_3$	2.058	14.7	...	62.1

[a] Taken from ref 9.

We have also studied the spectra of frozen solutions of the phosphine and arsine complexes, in the hope of obtaining the anisotropic components of the hyperfine tensors but so far the complexities of three noncoincident nonisotropic tensors has defied analysis.

It is thought that in solutions of the dimeric compounds $[Fe(NO)_2Br]_2$ and $[Fe(NO)_2I]_2$ the following equilibria may take place[22]



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[43] W. Kerler, W. Neuwirth, E. Fluck, P. Kuhn, and B. Zimmermann, *Z. Phys.*, **173**, 321 (1963)

When $[Fe(NO)_2Br]_2$ is dissolved in carbon tetrachloride, a very weak seven-line trace is obtained whose isotropic g value is 2.060 and hyperfine splitting is 23.3 G. The origin of this signal is not clear. The septet presumably indicates either two equivalent bromine or chlorine atoms. The former could occur if the dimer were not sufficiently strongly exchange coupled and a small population of a low-lying triplet state occurs. To test this idea we examined the epr spectra of the solid dimer. This produced a single line at $g \approx 2$; however raising or lowering the temperature did not change the signal intensity so that a thermally populated triplet can be ruled out. The presence of a small amount of impurity is possible, but since the sample was purified by sublimation, it is difficult to envisage what this could be.

On adding a complexing agent such as acetone or dimethyl sulfoxide to the solution of the bromide dimer, the seven-line pattern disappeared and an intense single broad line was obtained. This signal is no doubt due to a complex of the form $Fe(NO)_2Br(CH_3COCH_3)$ in which the spin density on the bromine atom has been reduced.

The iodide dimer, however, behaves differently, on dissolving in carbon tetrachloride. In this case the epr spectrum, shown in Figure 4, consists of a six-line pattern with an isotropic g value of 2.063 and a hyperfine splitting of 18.2 G. This spectrum may be attributed to the species $Fe(NO)_2I(CCl_4)$ since its spectral parameters are quite similar to those of $Fe(NO)_2I(H_2O)$. Again the addition of a complexing agent leads to the formation of a single intense line. The behavior of both dimers in solution in the presence of coordinating ligands is at present being investigated.

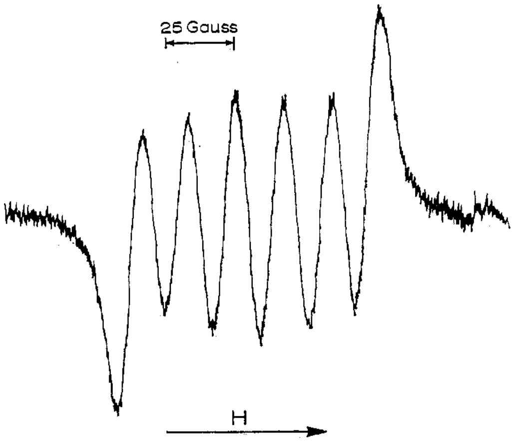

Figure 4.—The epr spectrum of $[Fe(NO)_2I]_2$ in CCl_4 solution at 20°. The species present is probably $Fe(NO)_2I(CCl_4)$.

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The Thermal Decomposition of Potassium Tris(oxalato)ferrate(III)

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The thermal decomposition of potassium tris(oxalato)ferrate(III) has been studied in the temperature range of 233–262°. The stoichiometry of the reaction may be represented by the equation $2K_3Fe(C_2O_4)_3 \rightarrow 2CO_2 + 2FeC_2O_4 + 3K_2C_2O_4$. This reaction follows a pattern that is characteristic of a number of solids. The rate of thermal decomposition at a given temperature is low, initially, then increases passing through a maximum, and finally decreases. During a major portion of the decomposition the rate follows the relationship $d\alpha/dt = k\alpha(1 - \alpha)$, where α is the fraction decomposed, t the time in seconds, and k the rate constant in reciprocal seconds. The addition of 1% iron(II) oxalate decreased the time required to attain 50% decomposition but it did not alter the rate constant. Data from two different samples and a sample containing iron(II) oxalate fell on a single Arrhenius plot from which an activation energy of 46 kcal mol^{-1} was estimated. A mechanism that is consistent with the kinetic data and the acceleratory effect of iron(II) oxalate has been suggested. A new apparatus and new techniques for the study of solids which decompose to form volatile products have been described.

Introduction

The thermal decompositions of solids and the rate laws which apply to these decompositions have been studied by many investigators.[1]

A new apparatus and new techniques have been applied to the study of the decomposition of potassium tris(oxalato)ferrate(III). The thermal and the photolytic decompositions of this compound have been extensively investigated.[2–7]

In the temperature range of 233–262° potassium tris(oxalato)ferrate(III) decomposes to form carbon dioxide and solid decomposition products. The reaction exhibits an induction period, an acceleratory period, and a decay period. Reactions which exhibit these characteristics have often been associated with models requiring the formation of growth nuclei on the surface which enlarge as the reaction proceeds.[1] A simpler

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[6] N. Tanaka and M. Nanjo, *Bull. Chem. Soc. Jap.*, **40**, 330 (1967).

[7] G. M. Bancroft, K. G. Dharmawardena, and A. G. Maddock, *Inorg. Chem.*, **9**, 223 (1970).