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Gas-Phase Ion Chemistry of Iron Pentacarbonyl by Ion Cyclotron Resonance Spectroscopy. New Insights into the Properties and Reactions of Transition Metal Complexes in the Absence of Complicating Solvation Phenomena

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Abstract: The gas-phase ion chemistry of iron pentacarbonyl is characterized using the techniques of ion cyclotron resonance spectroscopy. The ion–molecule reactions of iron pentacarbonyl alone result in the formation of polynuclear clusters containing up to four iron atoms. In mixtures of iron pentacarbonyl with other species, substitution reactions are observed in which carbon monoxide is replaced by a wide variety of σ- and π-bonding ligands. Many of these reactions result in the formation of unusual σ- and π-bonded organometallic complexes. The basicity of $Fe(CO)_5$ in the gas phase is determined by examining proton transfer reactions in mixtures with species of known proton affinity. It is found that $PA[Fe(CO)_5] = 204 \pm 3$ kcal/mol, making iron pentacarbonyl only slightly less basic than ammonia. Since the reported experiments are performed at low pressure in the gas phase, they provide information relating to the intrinsic reactivity of transition metal complexes in the absence of complicating solvation phenomena.

Metal carbonyls and their derivatives occupy a prominent position in organometallic chemistry. As a result of their unusual structures and industrial catalytic importance, there has been a revival of interest in the metal carbonyls during recent years, which has stimulated the synthesis of new compounds with novel geometries and bonding schemes.[2] The present paper, however, describes the application of a modern, highly versatile mass spectrometric method, ion cyclotron resonance spectroscopy, to one of the progenitors of carbonyl chemistry, $Fe(CO)_5$.

Ion cyclotron resonance (ICR) has proven to be a powerful technique for studying the gas-phase ion–molecule reactions of many chemically interesting molecules.[3] Applied with particular success to organic species, ICR is also appearing in investigations of inorganic[3a,4] and organometallic compounds. Since our preliminary report on iron pentacarbonyl,[5] accounts by Dunbar[6] and Kevan,[7] and their coworkers, have further emphasized the utility of ICR for studies of organometallics. In addition, the high-pressure mass spectrometry results of Müller[8] and Schildcrout[9] suggest that further experiments in this area will prove extremely fruitful. The present paper describes in detail some ion chemistry of iron pentacarbonyl, substantially expanding the results reported previously.[5] Recently developed ICR trapped-ion techniques, unavailable at the time of the earlier work, have proven extremely useful in this application. Processes described which are of particular interest include: (1) formation of polynuclear complexes containing up to four iron atoms, (2) extensive ligand substitution reactions involving both σ- and π-bonding ligands, (3) an accurate determination of the basicity of $Fe(CO)_5$, and (4) generation of unusual iron complexes in the gas phase. These experiments are performed in the absence of complicating solvation phenomena and pertain directly to the intrinsic properties and reactivity of the species considered.

Experimental Section

The theory and general instrumentation of ICR have been described previously.[3,10] The earlier experiments[5] were performed on a modified Varian V-5900 spectrometer. The more recent work employed an instrument built in these laboratories and equipped with a 15 in. electromagnet capable of a maximum field of 23.4 kG. Standard marginal oscillator detection[3a] was employed. The resolution deteriorates at the high masses encountered in this work (FWHM ≃ 3 amu at *m/e* 600), but it was easily capable of resolving peaks 28 mass units apart, which is all that was required above *m/e* ~ 200. A "flat" ICR cell was used throughout.

Iron pentacarbonyl was obtained from Alfa Inorganics and used without further purification except for degassing with several freeze-pump-thaw cycles. Other chemicals were obtained from standard commercial sources and used as supplied.

Except as noted in the text, the only experimental difficulty encountered was the gradual formation of a conducting path between the filament and adjacent trapping plate. This was controlled by machining a groove in the filament support block so that iron shadowed from the filament could not form a complete conducting pathway. The amount of carbon monoxide appearing in the mass spectrum was not inordinate, suggesting that sample decomposition in the inlet system was not a problem.

Results

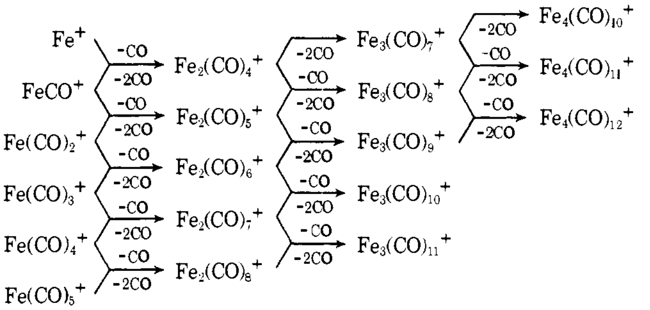
Mass Spectrum of Iron Pentacarbonyl. The 70 eV, positive ion ICR spectrum of $Fe(CO)_5$ at 5×10^{-7} Torr agrees well with previous mass spectrometry results.[11] The spectrum shows approximately equal abundances of Fe^+ and $FeCO^+$, which together comprise 70% of the total metal-containing ions, and lesser amounts of $Fe(CO)_n^+$ (n = 2-5). At 20 eV, the amount of Fe^+ is greatly reduced and the $Fe(CO)_n^+$ (n = 2-5) ions increase in abundance relative to $FeCO^+$. This electron energy was employed for the investigations of ligand displacement reactions, described below.

As expected,[12] the most prominent negative ion occurring at all electron energies is $Fe(CO)_4^-$, which is accompanied by about 10% as much $Fe(CO)_3^-$. At low electron energy (~2 eV), a small amount of $Fe(CO)_2^-$ is also observed.

Ion-Molecule Reactions in Iron Pentacarbonyl. As the pressure of $Fe(CO)_5$ is raised, ion-molecule reaction products appear at *m/e* 224, 252, and 280. The ion at *m/e* 224 might reasonably be formulated as either $Fe(CO)_6^+$ or $Fe_2(CO)_4^+$; its unequivocal identification as the latter species was established from the ^{54}Fe, ^{56}Fe isotope pattern. The ions at *m/e* 252 and 280 are $Fe_2(CO)_5^+$ and $Fe_2(CO)_6^+$, respectively. As the $Fe(CO)_5$ pressure increases, severe pyrolysis problems become evident. The ions CO^+, Fe^+, and $FeCO^+$ increase dramatically at higher pressures, and above about 5×10^{-5} Torr completely obscure the remainder of the spectrum. Thus, the presence of reaction products above *m/e* 280, if any, is difficult to discern at high $Fe(CO)_5$ pressure.

To obviate this problem, recently developed ICR trapped-ion techniques[10] were employed in this study. These techniques allow observation of bimolecular reaction sequences at relatively low pressure and are extremely advantageous in this application. Figure 1 presents the variation with time of the ions observed in 2×10^{-6} Torr of $Fe(CO)_5$ following a 6 msec, 70 eV electron beam pulse. A host of high-mass reaction products are apparent, occurring every 28 mass units above $Fe(CO)_5^+$ to *m/e* 560, beyond which observations were not attempted. Double-resonance experiments at fixed trapping times (100 msec for the secondary ions and 180 msec for the tertiary and quaternary ions) establish Scheme I as the sequence of positive ion-molecule reactions in iron pentacarbonyl (the neutral reactant in each case is understood to be $Fe(CO)_5$). Either one or two CO groups are lost in each step as the various ions condense with the parent neutral. The identity of any particular product is easily determined from its precursors. For example, the ion at *m/e* 336 is derived exclusively from $Fe(CO)_4^+$ and $Fe(CO)_5^+$, and thus must be formulated as $Fe_2(CO)_8^+$ rather than as $Fe_3(CO)_6^+$. The product of highest mass, *m/e* 560, is identified as $Fe_4(CO)_{12}^+$. Due to the difficulty in pressure measurement and the complex reaction scheme, absolute rate constants can only be estimated for the primary ions, and range from 6.8×10^{-10} cm^3 molecule^{-1} sec^{-1} for CO^+ to 1.5×10^{-10} cm^3 molecule^{-1} sec^{-1} for $Fe(CO)_2^+$. $Fe(CO)_5^+$ reacts very slowly with the parent neutral ($k < 10^{-11}$ cm^3 molecule^{-1} sec^{-1}).

Scheme I



Charge exchange reactions involving Fe^+ and CO^+ are observed to produce the $Fe(CO)_n^+$ (n = 1-5) ions, thus accounting for their initial rise in the ion intensity curves of Figure 1. Although the ionization potential of iron (IP[Fe] = 7.90 ± 0.01 eV)[13] is slightly below that of iron pentacarbonyl (IP[$Fe(CO)_5$] = 7.98 ± 0.01 eV),[11] double-resonance results indicate that $Fe(CO)_5^+$ and $Fe(CO)_4^+$ are products of a charge exchange reaction from Fe^+. This suggests that some excited Fe^+ is formed by electron impact at 70 eV. The ionization potential of carbon monoxide (IP[CO] = 14.013 ± 0.004 eV)[13] is much higher, and charge exchange of CO^+ with $Fe(CO)_5$ is sufficiently exothermic to rupture four of the five Fe-CO bonds in $Fe(CO)_5^+$ (see Table I). Double-resonance results show that CO^+ reacts to produce significant amounts of $FeCO^+$ and $Fe(CO)_2^+$, smaller amounts of $Fe(CO)_3^+$ and $Fe(CO)_4^+$, and very little $Fe(CO)_5^+$. The majority of the energy released during charge exchange evidently remains in the $(Fe(CO)_5^+)^*$ species, causing successive fragmentations of this ion.

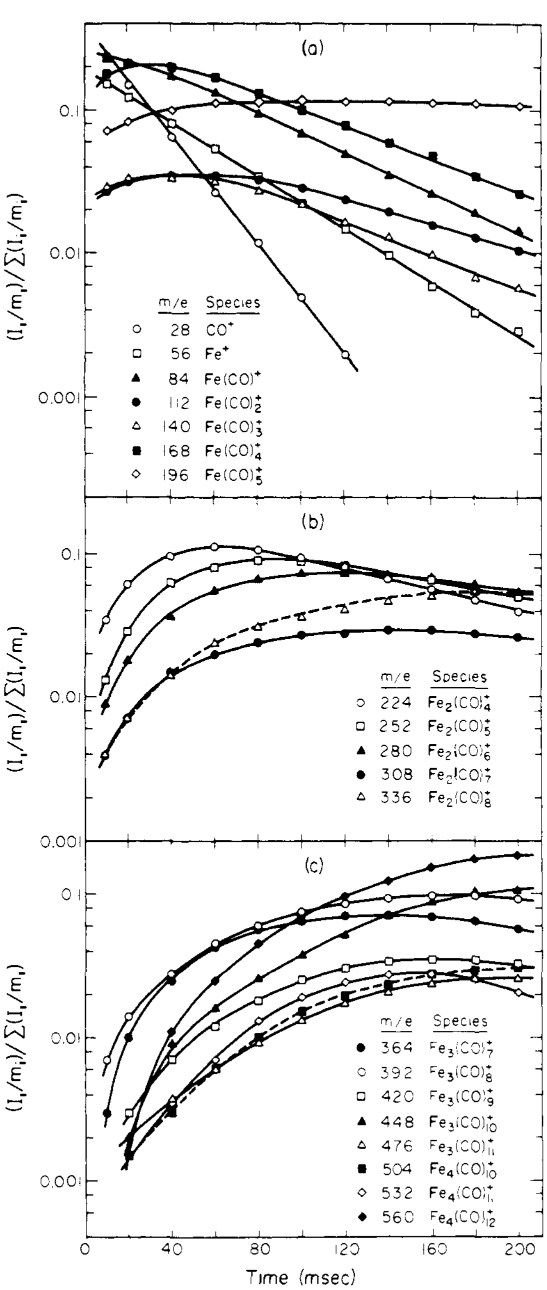


Figure 1. Variation with time of ion abundances observed in 2×10^{-6} Torr of $Fe(CO)_5$ following a 6 msec, 70 eV electron beam pulse.

In agreement with the report of Dunbar and coworkers,[6] the only negative ion-molecule reaction observed in $Fe(CO)_5$ is process 1, resulting in formation of $Fe_2(CO)_6^-$.

$$\mathrm{Fe(CO)_3^- + Fe(CO)_5 \longrightarrow Fe_2(CO)_6^- + 2CO} \qquad (1)$$

Neither pressure variation nor trapped-ion experiments revealed any other reaction products up to *m/e* 420.

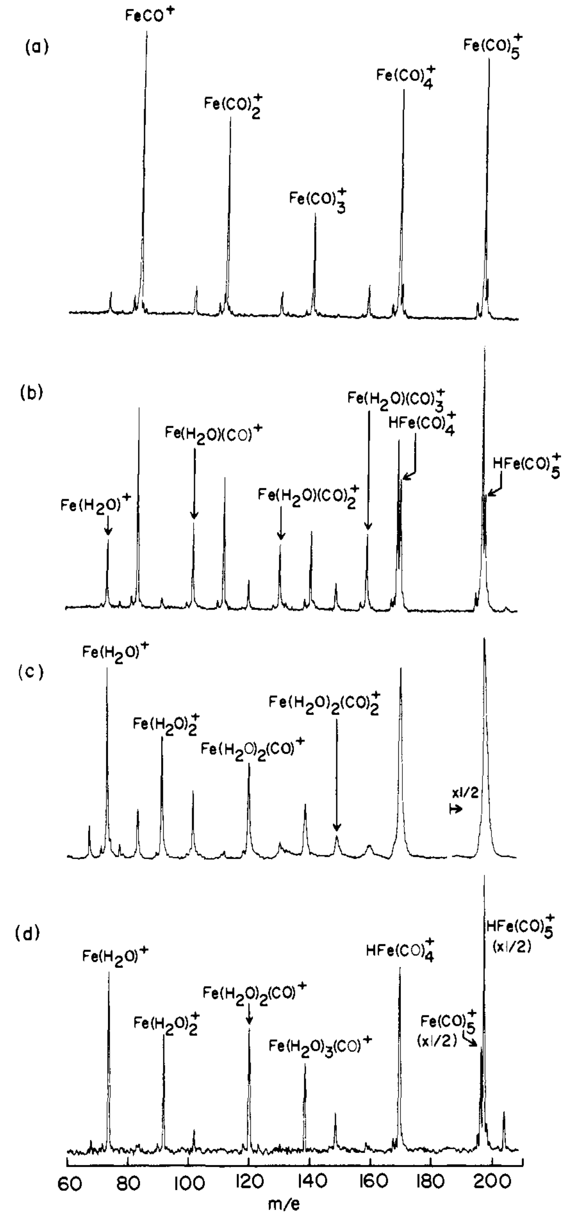


Figure 2. Single resonance mass spectra at 20 eV of ions occurring in 2 × 10^{-6} Torr of $Fe(CO)_5$ plus (a) 1 × 10^{-6} Torr of H_2O, (b) 5 × 10^{-6} Torr of H_2O, (c) 3 × 10^{-5} Torr of H_2O. Reaction time approximately 1 msec. (d) Trapped-ion mass spectrum at 20 eV of a 1:2 mixture of $Fe(CO)_5$ and H_2O at 4 × 10^{-6} Torr total pressure. Trapping time = 55 msec.

Table I. Ligand Displacement Reactions and Bond Energies in $Fe(CO)_n^+$

		Maximum number of CO groups replaced				
Ligand (L)	PA(L)[a]	$FeCO^+$	$Fe(CO)_2^+$	$Fe(CO)_3^+$	$Fe(CO)_4^+$	$Fe(CO)_5^+$
HCl	141[b]	0	0	0	0	0
CO	143[c]					
CH_3F	151[d]	1	1	1	1	0
CH_3Cl	160[d]	1	1	2	2	0
H_2O	165[b]	1	2	2	3	0
HCN	170[b]	1	2	3	3	1
CH_3OCH_3	191[e]	1	2	2	3	2
NH_3	207[b]	1	2	2	3	2
NO	~127[c]	1	2	3	3	1
C_2D_4	160[f]	1	2	2	2	0
$D[Fe(CO)_{n-1}^+-CO]$[g]		63	20	19	24	22

[a] Proton affinity, as defined in text, in kcal/mol at 298°K. [b] M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969). [c] A. E. Roche, M. M. Sutton, D. K. Bohme, and H. I. Schiff, *J. Chem. Phys.*, 55, 5480 (1971). [d] J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, 94, 2798 (1972). [e] R. H. Staley and J. L. Beauchamp, unpublished results. [f] Reference 3a. [g] Bond energies in kcal/mol at 298°K from ref 11.

Ligand Displacement Reactions. Binary mixtures of $Fe(CO)_5$ with a variety of molecules were examined principally to delineate the occurrence of ligand displacement reactions. The various species considered include σ bonding, unidentate ligands (CH_3F, CH_3Cl, H_2O, HCN, $(CH_3)_2O$, NH_3, and HCl), a σ-bonding, bidentate ligand (2,4-pentanedione), and π-bonding ligands (NO, C_2D_4, and C_6H_6). All of these experiments were performed at an electron energy of 20 V, where each of the $Fe(CO)_n^+$ (n = 1-5) ions is reasonably abundant.

Methyl Fluoride. Mixtures of $Fe(CO)_5$ and CH_3F exhibit four prominent reaction products corresponding to the general formula $Fe(CH_3F)(CO)_{n-1}^+$ (n = 1-4). Double-resonance experiments indicate that these products are derived from the $Fe(CO)_n^+$ ions according to the generalized reaction 2, which is characterized as a ligand substitution process.

$$Fe(CO)_n^+ + CH_3F \longrightarrow Fe(CH_3F)(CO)_{n-1}^+ + CO \quad (2)$$
$$n = 1\text{–}4$$

At the highest CH_3F pressures employed, 2 × 10^{-4} Torr, only one CO group is replaced in any of the $Fe(CO)_n^+$ (n = 1-4) ions, and $Fe(CO)_5^+$ remains inert toward substitution. The products of eq 2 condense with $Fe(CO)_5$ to give ions of the type $Fe_2(CH_3F)(CO)_x^+$. These processes, and any subsequent reactions, were not examined in detail.

Additional reaction products observed in this system are $CH_3Fe(CO)_4^+$ and $CH_3Fe(CO)_5^+$, both derived from the dimethylfluoronium ion,[14] $CH_3FCH_3^+$, in reactions 3 and 4. The product of eq 3, isoelectronic with $CH_3Mn(CO)_5$,

$$CH_3FCH_3^+ + Fe(CO)_5 \begin{cases} \longrightarrow CH_3Fe(CO)_5^+ + CH_3F & (3) \\ \longrightarrow CH_3Fe(CO)_4^+ + CO + CH_3F & (4) \end{cases}$$

may be formulated as originating from an oxidative-addition reaction of a d^8 metal complex.[15,16]

Methyl Chloride. In a manner analogous to that of CH_3F, methyl chloride reacts with the $Fe(CO)_n^+$ ions to give ligand displacement products according to eq 5. In this

$$Fe(CO)_n^+ + CH_3Cl \longrightarrow Fe(CH_3Cl)(CO)_{n-1}^+ + CO \quad (5)$$
$$n = 1\text{–}4$$

case, however, substitution does not stop after the first step, but proceeds a second time to give doubly-substituted products, process 6, which do not react further. Again,

$$Fe(CH_3Cl)(CO)_{n-1}^+ + CH_3Cl \longrightarrow Fe(CH_3Cl)_2(CO)_{n-2}^+ + CO \quad (6)$$
$$n = 3,4$$

$Fe(CO)_5^+$ remains inert. Substitution reactions in the binuclear and higher order complexes were not investigated for CH_3Cl or any of the other ligands discussed below.

Water. The results of adding increasing amounts of H_2O to 2 × 10^{-6} Torr of $Fe(CO)_5$ are shown in Figure 2. A large number of reaction products are observed, which correspond to sequential, multiple replacement of CO ligands by H_2O. Reactions 7-9, confirmed by double resonance, ac-

$$Fe(CO)_n^+ + H_2O \longrightarrow Fe(H_2O)(CO)_{n-1}^+ + CO \quad (7)$$
$$n = 1\text{–}4$$

$$Fe(H_2O)(CO)_{n-1}^+ + H_2O \longrightarrow Fe(H_2O)_2(CO)_{n-2}^+ + CO \quad (8)$$
$$n = 2\text{–}4$$

$$Fe(H_2O)_2(CO)_{n-2}^+ + H_2O \longrightarrow Fe(H_2O)_3(CO)_{n-3}^+ + CO \quad (9)$$
$$n = 4$$

count for these products. At the highest pressure of H_2O employed, the last CO group could not be displaced from $Fe(CO)_3^+$ or $Fe(CO)_4^+$. As with CH_3F and CH_3Cl, $Fe(CO)_5^+$ remains unreactive toward ligand substitution by H_2O.

Figure 2c exhibits clearly the serious degradation of resolution (peak broadening) suffered at high pressure in the normal, drift-mode ICR experiment. Trapped-ion techniques eliminate this difficulty by permitting operation at much lower pressure. Figure 2d is a mass spectrum of a 1:2 mixture of $Fe(CO)_5$ and H_2O at 4×10^{-6} Torr total pressure and at a fixed ion-trapping time of 55 msec. The ions which are the final ligand substitution products in the $Fe(CO)_5$-H_2O system and which appear at high pressure in Figure 2c are the same ones appearing in Figure 2d. However, the resolution is greatly enhanced, the spectrum is cleaner, and problems such as pyrolysis and termolecular reactions are avoided. No additional products are noted at longer trapping times.

The species $HFe(CO)_5^+$ and $HFe(CO)_4^+$, observed prominently in Figure 2, are derived by proton transfer from H_3O^+. These reactions pertain to the gas-phase basicity of iron pentacarbonyl and are discussed in detail below.

Hydrogen Cyanide. Similar, but still more extensive, ligand substitution reactions are observed in mixtures of $Fe(CO)_5$ and HCN. Processes 10-12 are responsible for

$$Fe(CO)_n^+ + HCN \longrightarrow Fe(HCN)(CO)_{n-1}^+ + CO \quad (10)$$
$$n = 1\text{–}5$$

$$Fe(HCN)(CO)_{n-1}^+ + HCN \longrightarrow Fe(HCN)_2(CO)_{n-2}^+ + CO$$
$$n = 2\text{–}4 \quad (11)$$

$$Fe(HCN)_2(CO)_{n-2}^+ + HCN \longrightarrow Fe(HCN)_3(CO)_{n-3}^+ + CO$$
$$n = 3, 4 \quad (12)$$

producing the observed products. Unlike the ligands encountered previously, HCN effects single substitution in $Fe(CO)_5^+$. Proton transfer from H_2CN^+ results in formation of $HFe(CO)_5^+$ and $HFe(CO)_4^+$.

Dimethyl Ether. Extensive ligand displacement processes also occur with CH_3OCH_3. Reactions 13-15 produce the

$$Fe(CO)_n^+ + CH_3OCH_3 \longrightarrow Fe(CH_3OCH_3)(CO)_{n-1}^+ + CO$$
$$n = 1\text{–}5 \quad (13)$$

$$Fe(CH_3OCH_3)(CO)_{n-1}^+ + CH_3OCH_3 \longrightarrow Fe(CH_3OCH_3)_2(CO)_{n-2}^+ + CO \quad (14)$$
$$n = 2\text{–}5$$

$$Fe(CH_3OCH_3)_2(CO)_{n-2}^+ + CH_3OCH_3 \longrightarrow Fe(CH_3OCH_3)_3(CO)_{n-3}^+ + CO \quad (15)$$
$$n = 4$$

substitution products observed. In this case, $Fe(CO)_5^+$ exchanges two of its carbonyl groups. $HFe(CO)_5^+$ is derived by proton transfer from the protonated ether, but $HFe(CO)_4^+$ is apparently not produced.

Ammonia. Addition of NH_3 to $Fe(CO)_5$ produces the same pattern of ligand substitution observed with CH_3OCH_3. The $Fe(CO)_n^+$ (n = 2-5) ions exchange twice and $Fe(CO)_4^+$ exchanges three times. Significantly, neither $HFe(CO)_5^+$ nor $HFe(CO)_4^+$ is produced in this mixture.

Hydrogen Chloride. No ligand substitution reactions were observed in a 40:1 mixture of HCl and $Fe(CO)_5$ at 10^{-4} Torr. The major reaction products are $HFe(CO)_5^+$ and $HFe(CO)_4^+$, derived from H_2Cl^+ by proton transfer.

2,4-Pentanedione. Since 2,4-pentanedione (acetylacetone, or Hacac) has two n-donor sites, it might be expected to displace two CO groups upon coordinating to the metal atom in $Fe(CO)_n^+$. Indeed, this is the dominant mode of reaction observed (process 16). $FeCO^+$ and $Fe(CO)_2^+$ also form

$$Fe(CO)_n^+ + Hacac \longrightarrow Fe(Hacac)(CO)_{n-2}^+ + 2CO \quad (16)$$
$$n = 2\text{–}5$$

complexes while losing only one CO ligand (eq 17), but the

$$Fe(CO)_n^+ + Hacac \longrightarrow Fe(Hacac)(CO)_{n-1}^+ + CO \quad (17)$$
$$n = 1, 2$$

more highly coordinated species $Fe(CO)_n^+$ (n = 3-5) do not. The subsequent coordination of two molecules of acetylacetone proceeds in a similar manner, reaction 18.

$$Fe(Hacac)(CO)_m^+ + Hacac \longrightarrow Fe(Hacac)_2^+ + CO, 2CO$$
$$m = 1, 2 \quad (18)$$

Nitric Oxide. Mixtures of $Fe(CO)_5$ with the strongly π-accepting ligand NO were also examined for the occurrence of ligand substitution processes. Facile, sequential replacement of the CO groups in $Fe(CO)_n^+$ was observed according to reactions 19-21. Significantly, the species $Fe(NO)(CO)_4^+$ and $Fe(NO)_3(CO)^+$ were not observed to exchange further at high pressure or long trapping times, a result discussed in more detail below.

$$Fe(CO)_n^+ + NO \longrightarrow Fe(NO)(CO)_{n-1}^+ + CO \quad (19)$$
$$n = 1\text{–}5$$

$$Fe(NO)(CO)_{n-1}^+ + NO \longrightarrow Fe(NO)_2(CO)_{n-2}^+ + CO \quad (20)$$
$$n = 2\text{–}4$$

$$Fe(NO)_2(CO)_{n-2}^+ + NO \longrightarrow Fe(NO)_3(CO)_{n-3}^+ + CO \quad (21)$$
$$n = 3, 4$$

Ethylene-d_4. Ethylene functions as a unidentate ligand in many organometallic π complexes. Addition of C_2D_4 to $Fe(CO)_5$ affords the single-substitution processes of eq 22

$$Fe(CO)_n^+ + C_2D_4 \longrightarrow Fe(C_2D_4)(CO)_{n-1}^+ + CO \quad (22)$$
$$n = 1\text{–}4$$

$$Fe(C_2D_4)(CO)_{n-1}^+ + C_2D_4 \longrightarrow Fe(C_2D_4)_2(CO)_{n-2}^+ + CO$$
$$n = 2\text{–}4 \quad (23)$$

and the double-substitution processes of eq 23. No further ligand replacement was observed, and $Fe(CO)_5^+$ remained inert toward C_2D_4.

Benzene. Mixtures of benzene with $Fe(CO)_5$ exhibit a number of ion-molecule reaction products containing C_6H_6 bound to the iron atom. Figure 3 presents the variation with time of the ions in a 1:1 mixture of C_6H_6 and $Fe(CO)_5$ following a 6 msec, 20 eV electron beam pulse. The final products in the system are seen to be $Fe(CO)_5^+$, $Fe(C_6H_6)(CO)_2^+$, and $Fe(C_6H_6)_2^+$. Double-resonance results indicate that reactions 24-29 are responsible for the various

$$C_6H_6^+ + Fe(CO)_5 \longrightarrow Fe(CO)_5^+ + C_6H_6 \quad (24)$$
$$C_6H_6^+ + Fe(CO)_5 \longrightarrow Fe(CO)_4^+ + CO + C_6H_6 \quad (25)$$

$$Fe(CO)_n^+ + C_6H_6 \longrightarrow Fe(C_6H_6)(CO)_{n-1}^+ + CO \quad (26)$$
$$n = 1, 2$$

$$Fe(CO)_n^+ + C_6H_6 \longrightarrow Fe(C_6H_6)(CO)_{n-2}^+ + 2CO \quad (27)$$
$$n = 2\text{–}4$$

$$Fe(C_6H_6)^+ + C_6H_6 \longrightarrow Fe(C_6H_6)_2^+ \quad (28)$$

$$Fe(C_6H_6)(CO)^+ + C_6H_6 \longrightarrow Fe(C_6H_6)_2^+ + CO \quad (29)$$

product ions. The charge-exchange reactions, eq 24 and 25, produce large quantities of $Fe(CO)_5^+$ and $Fe(CO)_4^+$ and account for the initial upward curvature of the intensity curves for these ions in Figure 3. The former species is unreactive, but $Fe(CO)_4^+$ reacts according to eq 27 to pro-

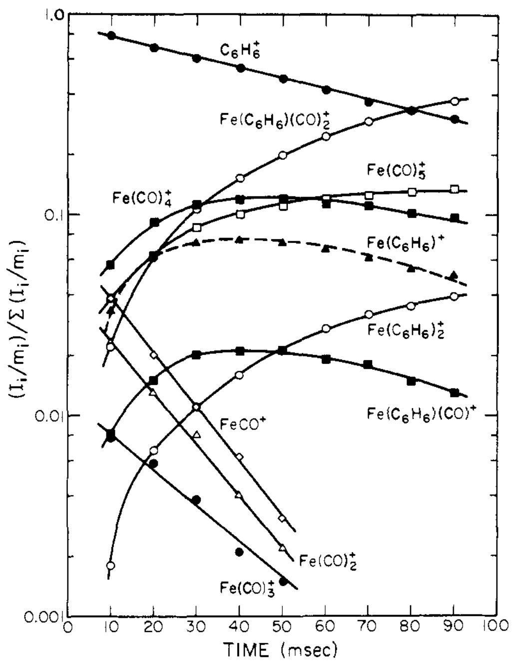
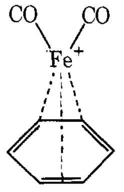


Figure 3. Variation with time of ion abundances in a 1:1 mixture of $Fe(CO)_5$ and C_6H_6 following a 6 msec, 20 eV electron beam pulse.

duce $Fe(C_6H_6)(CO)_2^+$, which is the dominant ion at long times. The remaining ions all end up as $Fe(C_6H_6)_2^+$. The species $Fe(C_6H_6)(CO)_2^+$ and $Fe(C_6H_6)_2^+$ are evidently quite stable in this system. The former can be reasonably formulated as having structure I.



I

Reactions of Anions. A number of anionic species were generated in the presence of $Fe(CO)_5$ to investigate the occurrence of nucleophilic attack on the metal complex. These included F^-, $C_2H_5O^-$, Cl^-, and CN^-, which are produced by dissociative electron capture in NF_3, C_2H_5ONO, CCl_4, and HCN, respectively. Reactions 30 and 31 were observed

$$F^- + Fe(CO)_5 \longrightarrow Fe(F)(CO)_3^- + 2CO \tag{30}$$

$$C_2H_5O^- + Fe(CO)_5 \longrightarrow Fe(C_2H_5O)(CO)_3^- + 2CO \tag{31}$$

to result in the formation of four-coordinate, 16-electron products. Neither Cl^- nor CN^- were observed to react with $Fe(CO)_5$. This unexpected result may reflect the fact that Cl^- and CN^- are much weaker bases in the gas phase than F^- and $C_2H_5O^-$.

Basicity of Iron Pentacarbonyl. Many of the mixtures investigated for ligand substitution processes also demonstrated the formation of large amounts of protonated iron pentacarbonyl (see Figure 2, for example). Proton transfer reactions from H_2Cl^+, H_3O^+, H_2CN^+, $(CH_3)_2OH^+$, and protonated dimethyl carbonate were confirmed by double resonance to produce $HFe(CO)_5^+$. The rates of these reactions are fast. On the other hand, addition of $Fe(CO)_5$ to NH_3 and CH_3NH_2 showed no evidence for formation of $HFe(CO)_5^+$ from NH_4^+ or $CH_3NH_3^+$, both of which were present in great abundance in their respective mixtures. In view of the fast rate of proton transfer observed in the other systems, this result is taken to indicate the proton transfer from NH_4^+ and $CH_3NH_3^+$ to $Fe(CO)_5$ is endothermic.

Discussion

Reactions in Iron Pentacarbonyl. The extensive condensation reactions which characterize the positive ion-molecule chemistry of iron pentacarbonyl are an intriguing result. The facile formation of the various polynuclear complexes in Scheme I must be rationalized on the basis of a strong proclivity by iron to form bonds with one or more additional iron atoms. While metal-metal bonds in carbonyl systems are rather common, the relatively nonselective nature of the reactions observed here remains surprising. That is, within the mass range studied, all of the ions condense with $Fe(CO)_5$, regardless of the number of iron atoms or CO groups already present. There seems to be no reason, in fact, to doubt that even higher order polynuclear clusters are formed.

Mass spectral investigations of polynuclear metal carbonyls generally show that the more metal atoms a fragment ion contains the higher is its mass spectral abundance.[17] This result is interpreted as evidence for the highly favorable nature of metal-metal bonds in these species and is consistent with the ICR results obtained here. The only exception to this generalization, interestingly enough, is that the mass spectra of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ show a high abundance of fragment ions containing a single iron atom and a very low abundance for those containing two iron atoms,[17] which is suggested as implying a low stability for the Fe-Fe nucleus.[18] In view of the rapid formation of $Fe_2(CO)_n^+$ (n = 4-8) by ion-molecule reactions, however, such a conclusion does not appear justified.

A simple MO approach to the various product ions in Scheme I suggests that all of them can be formulated as containing Fe-Fe multiple bonding. This is especially attractive for the symmetrical species $Fe_2(CO)_8^+$ and $Fe_4(CO)_{12}^+$, in which double-bonded iron atoms leave each metal group one electron short of the 18-electron rule.[18] The latter ion in particular is quite abundant at long times in Figure 1, suggesting that it may be significantly more stable than the other products observed. Species which would be formulated as having only Fe-Fe single bonding, such as $Fe_2(CO)_9^+$ and $Fe_3(CO)_{12}^+$, are apparently not formed by ion-molecule reactions.

In contrast to the extensive positive ion chemistry, the negative ion chemistry of $Fe(CO)_5$ is limited to reaction 1. This is probably due at least in part to the reduced number of primary anions which can be produced in reasonable abundance from $Fe(CO)_5$ (only $Fe(CO)_3^-$ and $Fe(CO)_4^-$ in this study). Nevertheless, the nonreactivity of $Fe(CO)_4^-$ suggests a basic aversion to forming polynuclear anions in the metal carbonyls. A similar conclusion can be drawn from the work of Dunbar[6] on $Ni(CO)_4$ and $Cr(CO)_6$, which show an analogous paucity of anionic reactions.

Ligand Substitution Processes. Ligand substitution reactions in the metal carbonyls and their derivatives have been studied for many years and are probably the most thoroughly investigated aspect of their chemistry.[2,20] Combined with various spectroscopic efforts,[20] this work has provided several general principles important to understanding the behavior of metal carbonyls. (1) The existence of strong bonds between a metal atom and a carbonyl group hinges upon metal-CO π bonding.[2,20] (2) The presence of a positive charge on a metal atom decreases metal-CO π bonding and concomitantly increases metal-CO σ bonding.[2,21] (3) Substitution of non- or poorly-π-bonding ligands into a metal carbonyl enhances π bonding to the remaining CO groups.[2,20] (4) Organometallic complexes and reaction intermediates show a strong aversion to exceeding 18 valence electrons around the metal atom.[19,20] These four generalities are applicable to the ligand substitution reactions observed in the iron pentacarbonyl system.

In Table I is summarized the maximum extent of carbon monoxide replacement observed in each of the $Fe(CO)_n^+$ ions for each of the unidentate ligands considered. Also included in the table are the proton affinities (gas-phase basicities) of each of the ligands, which are defined according to eq 32. Several observations are warranted by the data in the first eight lines of Table I (HCl through NH_3). (1) The one molecule, HCl, which is less basic than carbon monoxide is singularly ineffective in producing any ligand substitution. (2) The higher the basicity of the ligand L, the greater the degree of substitution it can effect. (3) While all the CO groups in $FeCO^+$ and $Fe(CO)_2^+$ are readily replaced, a maximum of three are substituted in $Fe(CO)_4^+$ and only two in $Fe(CO)_3^+$, except for the case of L = HCN. (4) $Fe(CO)_5^+$ is much less susceptible to ligand substitution than are the other four ions. An explanation for these observations resides in a consideration of the four general principles delineated above.

$$MH^+(g) \longrightarrow M(g) + H^+(g), \qquad \Delta H = PA(M) \quad (32)$$

Effect of Ligand Basicity. With the possible exception of HCN (and of CO, of course) none of the ligands listed in the upper part of Table I has any recognized π-bonding ability.[22] The strength of metal–ligand bonds for such species will depend, therefore, solely on σ bonding. On this basis the inability of HCl to displace CO is expected because of its lower basicity (poorer n-donor ability). On the other hand, each of the ligands more basic that CO is observed to displace at least one carbonyl from $Fe(CO)_n^+$ ($n = 1$-4).

That methyl fluoride can effect substitution at all suggests that the π bonding between the iron atom and the CO groups in $Fe(CO)_n^+$ ($n = 1$-4) is minimal, which is explicable on the basis of the positive charge on the iron atom. The slightly enhanced n-donor capacity of CH_3F relative to CO (as evidenced by its greater basicity) is thus sufficient to force replacement of one CO group despite the inability of CH_3F to participate in π bonding.

Each successive replacement of CO by a non-π-bonding ligand, however, increases the π bonding to the remaining carbonyl groups. Thus, each step in a sequential substitution is of higher energy than the one preceding. This must be compensated for by increased σ bonding and explains why the extent of CO substitution is directly correlated with the basicity of the entering ligand (see Table I). The enhanced π bonding to the remaining CO group in $Fe(L)_2(CO)^+$ and $Fe(L)_3(CO)^+$ evidently makes additional substitution unfavorable. The *only* exception to this pattern is observed in the case of HCN, which can effect triple substitution in $Fe(CO)_3^+$. This anomaly may result from slight π-bonding ability of HCN, such as recognized for the nitriles, RCN.[22b]

The relative inertness of $Fe(CO)_5^+$ toward ligand substitution is not unexpected. The ion is coordinatively saturated, and the bimolecular substitution process would be forced to proceed through an unfavorable,[19] 6-coordinate, 19-electron intermediate. Alternatively, the carbonyl carbon atom may be susceptible to attack, but only by a sufficiently strong nucleophile (HCN, CH_3OCH_3, or NH_3). Such a situation has precedent in the substitution reactions of six-coordinate, cationic carbonyls.[23,24]

π-Bonding Ligands. The π-bonding ability of nitric oxide in metal complexes is generally recognized to be even greater than that of carbon monoxide.[25] This must account for the extensive CO substitution effected by NO in $Fe(CO)_n^+$ (see Table I). All the CO groups are readily displaced in $FeCO^+$, $Fe(CO)_2^+$, and $Fe(CO)_3^+$, but only three in $Fe(CO)_4^+$ and one in $Fe(CO)_5^+$. Since NO is formally a three-electron donor,[2,20] the products which result in the latter two cases, $Fe(NO)_3(CO)^+$ and $Fe(NO)(CO)_4^+$, are 18-electron ions, isoelectronic with $Ni(CO)_4$ and $Fe(CO)_5$. This should endow these ions with great stability against further reaction. Most of the ionic species encountered previously have had 17 or fewer electrons in the valence shell of the metal.

Ethylene also has well-recognized π-bonding ability and forms a large number of organometallic complexes (μ complexes).[2,20] Inspection of Table I, however, shows that C_2D_4 is not significantly more effective in producing ligand substitution than is CH_3Cl, which has the same proton affinity. Thus, the π-bonding ability of C_2D_4 does not appear to play a significant role in its CO displacement reactions. This may result from ethylene's having only one π^* orbital available for back-bonding to the metal, whereas carbon monoxide and nitric oxide each have two.

As a ligand, benzene is usually considered to be a six-electron donor, occupying three coordination sites around a metal atom. The species $Fe(C_6H_6)(CO)_2^+$, observed prominently in Figure 3, is thus a 17-electron, 5-coordinate ion. Following this reasoning, $Fe(C_6H_6)_2^+$ is a 19-electron, 6-coordinate species, the only such ion encountered in this work. It appears as a final reaction product (Figure 3) and thus evidences greater stability than its precursors, which are 13- and 15-electron species (reactions 28 and 29). The 17-electron product, $Fe(C_6H_6)(CO)_2^+$, is evidently more stable, however, since reaction 33 is not observed to occur.

$$Fe(C_6H_6)(CO)_2^+ + C_6H_6 \longrightarrow Fe(C_6H_6)_2^+ + 2CO \quad (33)$$

It is possible to avoid the 19-electron interpretation of $Fe(C_6H_6)_2^+$ by ascribing to it a structure of the type $Fe(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)^+$, in which one of the benzene rings is presumably located asymmetrically with respect to the iron.

Rates of Ligand Substitution. Charge exchange reactions, such as described in detail for pure $Fe(CO)_5$ and $Fe(CO)_5$–benzene, were found to be a general feature of virtually all the systems investigated. Along with the sheer complexity of the chemistry, this makes a quantitative determination of reaction rate constants for ligand substitution difficult since the primary ions are being simultaneously formed and destroyed. Nevertheless, an inspection of the data indicates that the order of relative rates for single substitution is $Fe(CO)_3^+ > Fe(CO)_2^+ > FeCO^+ > Fe(CO)_4^+ > Fe(CO)_5^+$ with rate constants in the range 10^{-10}–10^{-9} cm^3 molecule^{-1} sec^{-1}. This order appears to hold for each of the unidentate ligands in Table I (except HCl and CO). An examination of the thermochemical data in Table I reveals that there is no correlation between $[Fe(CO)_{n-1}{}^+\text{-}CO]$ bond energies and rates of single substitution. Furthermore, only an ill-defined correlation exists between coordination number and rate of substitution; the more highly coordinated ions $Fe(CO)_4^+$ and $Fe(CO)_5^+$, particularly the latter, are considerably less reactive than the other three species.

Basicity of Iron Pentacarbonyl. The concept of transition metal basicity seems to be a useful one for systematizing the chemistry of many metal complexes.[26,27] In the case of iron pentacarbonyl, the greatly enhanced lability of the CO groups in acid solution has been rationalized on the basis of participation by the protonated complex.[28] Stable $HFe(CO)_5^+$ is formed only in strong acid solutions, indicating a low basicity, and contains a metal-proton bond.[29]

The proton transfer reactions described above serve to bracket the proton affinity of $Fe(CO)_5$, which is defined according to eq 32, within relatively narrow limits. Proton transfer from protonated dimethyl carbonate to $Fe(CO)_5$ is readily observed, but no proton transfer is seen from NH_4^+. This is interpreted to mean that $PA[(CH_3O)_2CO] \leq PA[Fe(CO)_5] \leq PA[NH_3]$. Recent results from our laboratory indicate that $PA[(CH_3O)_2CO] = 203 \pm 2$ kcal/mol,[30] and thus $PA[Fe(CO)_5]$ is assigned as 204 ± 3 kcal/mol. Iron pentacarbonyl is thus actually quite a strong base in the gas phase. The difference in gas phase and solution behavior is attributable to the understandably poor solvation of $HFe(CO)_5^+$.

The decomposition of $HFe(CO)_5^+$ by loss of CO is observed when it is formed in a sufficiently exothermic proton transfer reaction. This reaction is observed with all proton donors less basic than dimethyl ether. These results indicate that $D[HFe(CO)_4^+\text{-}CO] = 23 \pm 10$ kcal/mol, which is not significantly different from the CO binding energy in the parent ion (22 kcal/mol).

Conclusions

The results described above indicate that ICR has tremendous potential for illuminating certain aspects of organometallic chemistry. It is to be stressed that such experiments are performed at low pressure in the gas phase and provide information relating to the intrinsic reactivity of the molecules studied in the absence of solvent effects. The results above suggest that aspects of particular interest may be: (1) formation of polynuclear metal clusters containing varying numbers and types of ligands, (2) ligand substitution processes, (3) determination of relative ligand binding energies, (4) accurate determination of transition metal basicity, (5) characterization of processes involving both electrophilic and nucleophilic attack on neutral metal complexes, (6) generation and study of unusual σ- and π-bonded organometallic complexes, and (7) photochemistry of gaseous organometallic ions.[31]

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Ion–Molecule Reactions and Gas-Phase Basicity of Ferrocene

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Abstract: The gas-phase ion chemistry of ferrocene is investigated using the techniques of ion cyclotron resonance spectroscopy. Product distributions and rate constants for the principal primary ions are determined using trapped ion methods. Proton transfer reactions in mixtures of ferrocene with other molecules place fairly accurate limits on the gas-phase basicity of the molecule, leading to a proton affinity (213 ± 4 kcal/mol) which is slightly less than methylamine. The gas-phase measurements are free from complicating solvent effects which have previously led to some unwarranted conclusions about transition-metal basicity.

The unusual structures and bonding of dicyclopentadienyl metal complexes (metallocenes) have stimulated many mass spectral investigations of these molecules.[2,3] Of particular interest is the recent high-pressure study of ferrocene by Schildcrout,[4] who demonstrated the occurrence of several ion-molecule reactions. The present paper describes an ion cyclotron resonance (ICR) study of the ion chemistry of ferrocene, both alone and in mixtures with several other