Photochemistry of the Group 6 Hexacarbonyls in Low-Temperature Matrices. V.[1] Two Routes to Square Pyramidal Matrix Isolated Chromium Pentacarbonyl

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Abstract: Uv photolysis of $Cr(CO)_6$ in argon matrices doped with CO provides uv and ir evidence for the formation of weakly interacting $Cr(CO)_5 \cdots Ar$ and $Cr(CO)_5 \cdots CO$ molecules. Spectra obtained by reacting Cr atoms with CO in argon matrices are shown to be due to a mixture of these two C_{4v} species, together with $Cr(CO)_6$ and $Cr(CO)_4$. Photolysis experiments in concentrated matrices ($Cr(CO)_6$-Ar, 1:150) indicate that interaction can also occur between carbonyl fragments. The implications of these results for the interpretation of metal atom cocondensation experiments are discussed.

Sometime ago we reported[3,4] the changes in uv and ir spectra which occur during the photolysis of $M(CO)_6$ (M = Cr, Mo, and W) in inert gas matrices. It was concluded that the primary product was $M(CO)_5$ with a C_{4v} structure. More recently we have confirmed this structure using ^{13}CO substitution and have shown that the spectra are incompatible with a D_{3h} geometry.[5] Further photolysis produces ir bands which can be assigned to different lower carbonyl fragments[1,3b,6] on the basis of relative intensity ratios. In particular, Figure 1 shows the growth of bands due to $Cr(CO)_4$, in an argon matrix. The fragment is definitely not tetrahedral and the spectrum is very similar to that of $Mo(CO)_4$ which has been shown to have a C_{2v} structure in a CH_4 matrix.[1]

The fragment $M(CO)_5$ has a visible absorption band, the position of which is strongly dependent on the matrix material because of $M(CO)_5 \cdots$ matrix interactions.[4,7] Irradiation with light of wavelength corresponding to this absorption[3] causes regeneration of $M(CO)_6$. Evidence has been presented by us[3b] and independently by Braterman,[8] suggesting that this regeneration is a thermal process, which results from the local annealing caused by the nonradiative decay of the excited state of $M(CO)_5$ [but see ref 16]. Very surprisingly no purely thermal regeneration of $M(CO)_6$ occurred when an argon matrix was warmed to 40°K, but with as little as 1% CO added to the matrix, thermal reversal was observed.[3b]

Recently Kündig and Ozin have reported the results of cocondensing Cr atoms and CO or CO-argon mixtures at 4–10°K.[9] In a pure CO matrix they observed a band due to $Cr(CO)_6$ and three other bands [2020 (vw), 1962 (3), 1933 (1) cm^{-1}] which they assigned to C_{4v} $Cr(CO)_5$. Since annealing the matrix produced no further $Cr(CO)_6$, they proposed that the CO was interacting with $Cr(CO)_5$ through its vacant coordination site to form either an isocarbonyl or sideways bonded CO group, and tentatively assigned the weak 2020 cm^{-1} band to this interacting group. They suggested that the absence of thermal regeneration of $Cr(CO)_6$ following photolytic generation of $Cr(CO)_5$[3b] showed that $Cr(CO)_5$ was interacting with the photoejected CO group and was the same $Cr(CO)_5 \cdots CO$ complex as was observed by them in pure CO matrices. When they cocondensed Cr atoms with dilute CO-Ar mixtures (CO-Ar 1:20–1:100) and the matrix was subsequently annealed to 30–35°K two new bands (1964 and 1937 cm^{-1}) were observed with constant relative intensities 2:3. These bands were assigned to a single new compound D_{3h} $Cr(CO)_5$ which was proposed to

be "the most stable configuration of truly pentacoordinate $Cr(CO)_5$."[10] Using isotopic CO ($^{12}C^{16}O$–$^{13}C^{16}O$–Ar, 1:1:40) a spectrum was obtained which appeared consistent with this assignment. On annealing the matrix to 40–45°K thermal regeneration of $Cr(CO)_6$ was observed (cf. ref 3), and there was evidence for formation of C_{4v} $Cr(CO)_5$, supposedly stabilized by interaction with CO.

In this paper we present *positive* spectroscopic evidence (uv and ir) for the stereospecific interaction of $Cr(CO)_5$ and CO in matrices containing added CO. We show how results from photochemical experiments can aid the assignment of bands obtained by metal atom cocondensation, and explain how our spectra can be interpreted on the basis of $Cr(CO)_5$ C_{4v} and $Cr(CO)_4$, without recourse to a D_{3h} structure. Black and Braterman[11] have independently reached similar conclusions.

Experimental Section

Low-temperature apparatus has been described elsewhere.[12,13] Spectra were recorded using a Perkin-Elmer 356 (uv)[13] and a modified Grubb-Parsons Spectromajor (ir) spectrometer.[7] Uv spectra were calibrated using holmium oxide glass and ir spectra using DCl and DBr gas. Cr atoms were deposited by resistive heating of tungsten wire coated with metallic chromium.[12] All matrix gases were British Oxygen Company "Grade X", and were used without further purification. The photolysis source was a Phillips HPK 125W medium pressure Hg arc with a 4 cm water filter. Balzer interference filters were used to select different Hg lines.

Interaction of $Cr(CO)_5$ with CO. In an argon matrix, $Cr(CO)_5$ has a visible absorption at 533 nm and in xenon at 490 nm.[7] Such a shift in band position could be caused either by a general solvent effect or a stereospecific interaction with the vacant site of the $Cr(CO)_5$ molecule. Using argon matrices doped with 2% xenon, Perutz and Turner[7] have observed changes in the uv and ir spectra which confirm that the interaction is stereospecific, and have shown that such interactions occur in all the matrices that they have studied.

When $Cr(CO)_5$ was generated photochemically from $\cdot Cr(CO)_6$ in a pure CO matrix, the strong ir bands were within 1 cm^{-1} of those reported by Kündig and Ozin[9] for their Cr atom pure CO experiment. The visible absorption band of $Cr(CO)_5$ was at 462 nm. The shift from pure argon (533 nm) can be shown to be due to a stereospecific interaction by the experiment illustrated in Figure 2a. Spectrum 1 shows the absorption obtained after uv photolysis of $Cr(CO)_6$ in an argon matrix containing 1% added CO. There is a peak at 527 nm and a shoulder at ~460 nm. After 11 min photolysis using the filtered Hg arc (λ 586 nm) the peak at 527 nm was greatly reduced in intensity while the shoulder became a resolved peak at 457 nm, almost the same wavelength as the absorption of $Cr(CO)_5$ in pure CO (spectrum 2). Irradiation at λ 432 nm (2
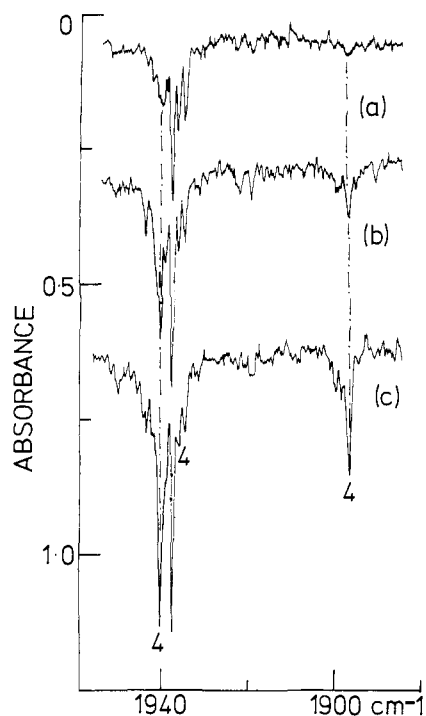
Figure 1. Ir spectra in the region 1960-1880 cm^{-1} produced during photolysis with an unfiltered Hg arc of Cr(CO)$_6$ in an Ar matrix (Cr(CO)$_6$-Ar 1:50,000, 20°K): (a) after 5 min irradiation; (b) 30 min irradiation; (c) 63 min irradiation. Bands labeled 4 are due to Cr(CO)$_4$, other bands are due to Cr(CO)$_5$. Note the small separation between the bands of Cr(CO)$_4$ and Cr(CO)$_5$ in the region of 1940 cm^{-1}.
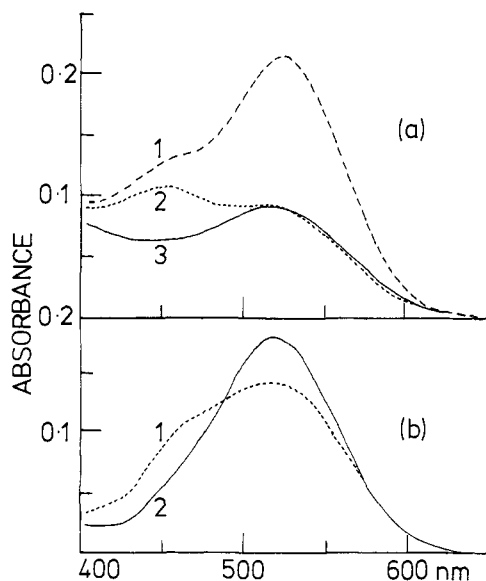
Figure 2. (a) Visible spectra of Cr(CO)$_5$ in Ar + 1% CO (Cr(CO)$_6$-Ar 1:3000). Trace 1: deposition of Cr(CO)$_6$ followed by 2 min photolysis with Hg arc + CoSO$_4$-NiSO$_4$ filter (230 < λ < 340 nm). Trace 2: 11 min with Hg arc + λ 586 nm filter. Trace 3: 2 min with Hg arc + λ 432 nm filter. (b) Visible spectra of Cr(CO)$_5$ in Ar (Cr(CO)$_6$-Ar 1:150). Trace 1: 30 min photolysis with Hg arc + monochromator (λ 300 nm), then 30 min with Hg arc + λ 586 nm filter. Trace 2: 35 min with Hg arc + λ 432 nm filter.

min) caused the total disappearance of the 457 nm band and left a single band at 527 nm very close to the wavelength observed for Cr(CO)$_5$ in pure Ar (spectrum 3). Thus it would appear that in the matrix there are two distinct species Cr(CO)$_5$···CO and Cr(CO)$_5$···Ar. Further experiments showed that annealing the matrix to 40°K caused a decrease in the band at 527 nm and no change in the other band. Thus, in the presence of excess CO,
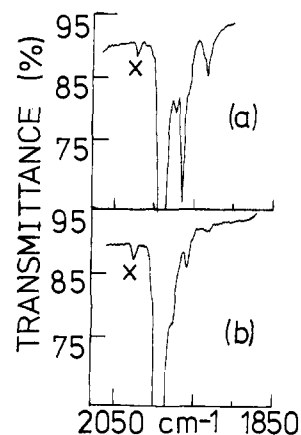

Figure 3. (a) Ir spectrum produced on cocondensing Cr atoms with pure CO (most intense band is due to Cr(CO)$_6$). (b) After 5 min photolysis with Hg arc + Pyrex filter (λ >285 nm).
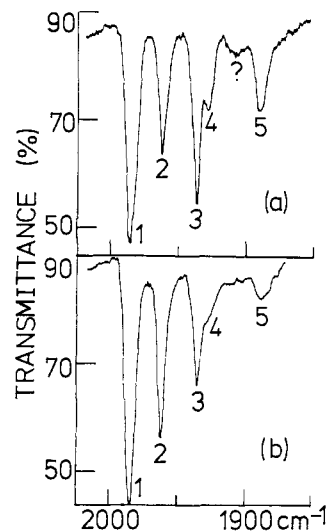

Figure 4. (a) Ir spectrum produced on cocondensing Cr atoms with a CO-Ar mixture (CO-Ar 1:100) at 19°K. (b) After warming to 45°K and recooling to 19°K. For assignment of bands see Table I.

Cr(CO)$_6$ can be regenerated thermally from Cr(CO)$_5$···Ar but *not* from Cr(CO)$_5$···CO.

Careful studies of the corresponding ir spectra showed that the two molecules had bands which were overlapping but which could be resolved in the region 1940-1930 cm^{-1}. The bands are assigned as follows:[14] Cr(CO)$_5$···Ar, E 1963 and A$_1$ 1932 cm^{-1}; Cr(CO)$_5$···CO, E 1963 and A$_1$ 1938 cm^{-1}.

Cocondensation of Cr Atoms with CO. In this laboratory we have carried out atom condensation experiments, which were briefly reported some time ago[3b,12] and which are similar to those of Kündig and Ozin.[9] In pure CO matrices, we observed the three bands (2020, 1962, 1933 cm^{-1}), which they reported to belong to a *single* molecule, Cr(CO)$_5$···CO (Figure 3a). Annealing the matrix produced no changes. However, we found that brief photolysis with a Pyrex filtered Hg lamp totally removed the two stronger bands, leaving the intensity of the 2020 band (marked X, Figure 3) unchanged. This band cannot therefore be due to the interacting CO group, as previously suggested.[9]

Using dilute CO-argon mixtures (CO-Ar 1:100-1:2500) we obtained more complicated spectra. Figure 4 shows the results of cocondensing Cr atoms and CO-Ar (1:100) at 19°K. This experiment used a CO dilution similar to the photochemical experiment described above (Figure 2a). In these circumstances one would expect to find Cr(CO)$_6$, Cr(CO)$_5$···CO, and Cr(CO)$_5$···Ar in the matrix. Furthermore, since the concentration of CO is low there should also be some Cr(CO)$_4$ present. Unfortunately, it is not possible to produce Cr(CO)$_4$ photochemically in significant quantities in an argon matrix containing 1% CO. However, it would seem reasonable to expect the same shift, about 3 cm^{-1}, from the bands

Table I. Assignment of Ir Bands Obtained by Cocondensation of Cr Atoms and CO in an Argon Matrix (Figure 4a) (CO–Ar, 1:100)[a]
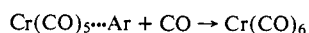
Band	cm^{-1}	Assignment
1	1987	$Cr(CO)_6$ (T_{1u})
2	1963	$Cr(CO)_5 \cdots CO$ (E) + $Cr(CO)_5 \cdots Ar$ (E)
3	1938	$Cr(CO)_5 \cdots CO$ (A_1) + $Cr(CO)_4$ (B_1)
4	1932	$Cr(CO)_5 \cdots Ar$ (A_1) + $Cr(CO)_4$ (A_1)
5	1891	$Cr(CO)_4$ (B_2)

[a] Assignment is based on the following structures: $Cr(CO)_6$ O_h, $Cr(CO)_5 \cdots CO$–Ar C_{4v}, $Cr(CO)_4$ C_{2v}.

of $Cr(CO)_4$ in pure argon[1] (1939 s, 1935 w, 1896 m cm^{-1}, Figure 1) as that observed for $Cr(CO)_6$ and $Cr(CO)_5 \cdots Ar$.[15]

We can now assign all the bands in the atom spectrum (Figure 4a) apart from a very weak band at 1915 cm^{-1} (Table I). This spectrum differs from that of Kündig and Ozin[9] in that their band at 1936 cm^{-1} has been resolved into a doublet.

Note that the 1938 cm^{-1} band is assigned to an overlap between the strongest band of $Cr(CO)_4$ and the A_1 band of $Cr(CO)_5 \cdots CO$. Also the intensity ratios of the 1963 and 1938 cm^{-1} bands changed considerably in our experiments as the CO–Ar ratio changed. On annealing the matrix which contains excess CO one would expect the following reactions to occur, not necessarily to completion.

$$Cr(CO)_4 + CO \rightarrow Cr(CO)_5 \cdots Ar + Cr(CO)_5 \cdots CO$$

$$Cr(CO)_5 \cdots Ar + CO \rightarrow Cr(CO)_6$$

$$Cr(CO)_5 \cdots CO \not\rightarrow Cr(CO)_6$$

The changes observed in the spectrum on annealing the matrix to 46°K are in agreement with our assignment and the predicted reactions (Figure 4b). [If it is assumed that these are the only species present in Kündig and Ozin's experiments, then their isotopic data can be reassigned: 1953 cm^{-1}, $Cr(CO)_{6-x}(^{13}CO)_x$ (overlap of several bands);[5] 1921 cm^{-1}, $Cr(^{13}CO)_5 \cdots CO$–Ar E mode;[5] 1902 cm^{-1}, $Cr(^{12}CO)_{4-x}(^{13}CO)_x$ (overlap of several bands);[1] 1892 cm^{-1}, $Cr(^{12}CO)_4$ B_2, $Cr(^{13}CO)_4$ B_1,[5] and overlapping $Cr(^{12}CO)_{5-x}(^{13}CO)_x$ A_1.[1]] Bands 1 $(Cr(CO)_6)$ and 2 $(Cr(CO)_5 \cdots CO$ and $Cr(CO)_5 \cdots Ar)$ have grown; bands 3 $(Cr(CO)_5 \cdots CO$ and intense $Cr(CO)_4)$ and 4 and 5 $(Cr(CO)_5 \cdots Ar$ and $Cr(CO)_4)$ have all decreased. The detailed mechanism of both thermal and photochemical regeneration of $M(CO)_6$ will be discussed in a later paper.[16]

Thus it can be seen that by treating the molecules present in a mixed CO–argon matrix as a mixture of the compounds produced in pure CO and argon matrices, we have assigned all the bands in our experiments without resort to a D_{3h} pentacarbonyl molecule, or any other new species.

Ozin[17] has commented that the 2:3 intensity ratio[9] can be obtained under conditions where our $Cr(CO)_4$ is absent; he believes that if D_{3h} $Cr(CO)_5$ is present it is *kinetically* stable and on annealing converts to the *thermodynamically* stable C_{4v} structure. That the thermodynamically stable form is C_{4v} of course agrees with our evidence both previously and in this paper.

Concentrated Matrices. (a) Photochemical. We have already reported ir evidence for formation of polynuclear $Mo_a(CO)_b$ species during the photolysis of $Mo(CO)_6$ in concentrated matrices,[3] and similar results have been obtained in hydrocarbon glasses.[8] There is no change in the position of the visible absorption of $Cr(CO)_5$ in an argon matrix in the range 1:2000 to 1:50,000. However, it is important to establish the effect of dimerization on the visible spectrum. If $Cr(CO)_5$ in a CO matrix is indeed the isocarbonyl $(OC)_5CrOC$ then the spectrum of $(OC)_5Cr \cdots OCCr(CO)_x$ $(x = 4$ or 5) should be similar.

Uv photolysis (λ 200 nm) of $Cr(CO)_6$ in an argon matrix at low dilution (1:150) produces a visible absorption band (λ_{max} 533 nm) with a distinct shoulder on the short wavelength side ($\sim$460 nm). Irradiation with λ 586 nm reduces the band of $Cr(CO)_5 \cdots Ar$ and makes the shoulder more pronounced (Figure 2b, spectrum 1). This suggests that, in a concentrated matrix, there are two species present $(Cr(CO)_5 \cdots Ar$ and $Cr(CO)_5 \cdots X)$. There are three possibilities for the identity of X: the photoejected CO group from another molecule, $Cr(CO)_6$, or $Cr(CO)_5$. After photolysis with λ 432 nm the shoulder totally disappeared and the intensity of the Cr-

$(CO)_5 \cdots Ar$ *increased* (spectrum 2). This is in contrast to a CO–Ar (1:100) matrix where λ 432 nm removed the $Cr(CO)_5 \cdots CO$ *without any increase* in $Cr(CO)_5 \cdots Ar$ (Figure 2a). Thus in a concentrated matrix the reaction

$$Cr(CO)_5 \cdots X \xrightarrow{h\nu} Cr(CO)_5 \cdots Ar$$
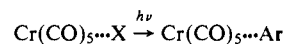
appears to occur and it seems probable that X must be some $Cr(CO)_x$ species. Although the high concentration made the ir bands too broad to make specific assignments to the dimeric species, the high-frequency A_1 band was a doublet. This experiment emphasizes the need to use high dilutions to prevent interaction between reactive fragments and shows that the position of the visible absorption bands of the dimeric species and $Cr(CO)_5$ in a CO matrix appear to be almost identical.

In a different experiment, a pure argon matrix (initially $Cr(CO)_6$–Ar 1:2000) containing $Cr(CO)_5$ was annealed until most of the argon had boiled off ($T > 50°K$). During the annealing λ_{max} of the visible absorption moved from 533 to 460 nm, exactly the same wavelength as in a concentrated argon or pure CO matrix. The same results were obtained when a methane matrix was boiled off. Thus polynuclear carbonyl aggregates can apparently be generated both photochemically and thermally.

(b) Metal Atom Cocondensation. In experiments where a high flux of Cr atoms was deposited or very high dilutions of CO were used, we observed several new bands assigned to polynuclear $Cr_x(CO)_y$ fragments. In particular a strong band was produced at 1896 cm^{-1} which could without care be confused with one of the bands of $Cr(CO)_4$, 1891 cm^{-1}.

Darling and Ogden[18] and Ozin and co-workers[19] have also obtained evidence for several such polynuclear species, including both bridged and unbridged CO groups. Thus, reducing the concentration of CO or increasing the concentration of Cr atoms in an attempt to generate lower carbonyl fragments will greatly increase the chances of forming polynuclear fragments. On the other hand, this metal atom polymerization can be turned to advantage and enables dinuclear carbonyls which are photochemically unaccessible to be characterized.[19,20]

Conclusion

This discussion shows some of the difficulties of the metal atom CO cocondensation method. All the matrices used contain a considerable excess of CO; consequently they must be treated as mixed matrices unless there is a very low concentration of CO. As a result weak interactions with either the inert species or with CO must be expected and a complete analysis may be very complicated. Interpretation is rendered more difficult by the breadth of the bands and the blocking of part of the high-frequency region by free CO. Ideally, the photolysis method and atom cocondensation should be used together.

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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 ± 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 inorganic³ᵃ,⁴ and organometallic compounds. Since our preliminary report on iron pentacarbonyl,⁵ accounts by Dunbar⁶ and Kevan,⁷ and their co-workers, have further emphasized the utility of ICR for studies of organometallics. In addition, the high-pressure mass spectrometry results of Müller⁸ and Schildcrout⁹ 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 experiments⁵ 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 detection³ᵃ 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 $m/e \sim 200$. 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