M^+/M_2^+ ratio is 3.7. The collision-induced dissociation data are interpreted as evidence that the Cr–Cr bond strength is directly influenced by the M/L ratio. That is, the metal–metal bond strength follows the order $Cr_2(CO)_6^+ < Cr_2(CO)_5^+ < Cr_2(CO)_4^+$. The CID data have also been obtained for the $Cr_3(CO)_y^+$ (y = 6, 7) ionic cluster fragments and the M^+/M_3^+ ratio is 1/12 for y = 6 and 1/10 for y = 7; whereas the M_2^+/M_3^+ ratio is 1/6 for y = 6 and 1/5 for y = 7, suggesting a very strong metal–metal interaction for the chromium trimer center. The general utility of the collision-induced dissociation experiment for probing the metal–metal bond order is now being examined on larger Cr-containing clusters as well as clusters containing Fe, Co, and Ni.

Conclusions

The reactivities of $Cr_2(CO)_y^+$ (y = 4, 5, 6) with small neutral molecules do not parallel that observed for reactions with $Cr(CO)_6$. That is, reaction rates for $Cr_2(CO)_y^+$ ions with $Cr(CO)_6$ differ considerably and the reactivity can be explained by an electron deficiency argument, but the variations in reaction rate for the $Cr_2(CO)_y^+$ ions with the small neutral molecules are rather small, e.g., 10–40%. In each case the ion–molecule reaction efficiency (determined by comparing theoretical collision frequency with the experimental reaction rate) is quite high and approaches unity.

The CO ligands of $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ are quite labile and readily undergo thermoneutral ligand exchange with ^{13}CO, whereas the CO ligands of $Cr_2(CO)_6^+$ are nonlabile and do not undergo exchange reactions with ^{13}CO. Ligand-exchange reactions of $Cr_2(CO)_6^+$ with other ligands (e.g., CH_3OH and NH_3) further illustrate the nonlability of this system. For example, both CH_3OH and NH_3 react to displace one CO ligand to form $Cr_2(CO)_5L^+$ (L = CH_3OH or NH_3), but this ion does not react further by ligand exchange.

A very interesting aspect of the observed ion–molecule reactions of the $Cr_2(CO)_y^+$ ions is the variation in the ratio of cleavage of the Cr- - -CO bond versus Cr- - -Cr bond upon addition of neutral ligand as the metal-to-ligand ratio decreases. The strong preference for metal–metal bond cleavage for $Cr_2(CO)_6^+$ suggests that the Cr- - -Cr bond in this ion is relatively labile. In addition, similar conclusions can be made on the basis of the abundance of Cr_2^+ (relative to Cr^+) in the collision-induced dissociation spectrum of $Cr_2(CO)_y^+$ (y = 4–7) ions. That is, the ratio Cr^+/Cr_2^+ varies from 0.25 for y = 4 to 3.7 for y = 6. It is surprising, therefore, that the Cr^+/Cr_2^+ ratio for $Cr_2(CO)_7^+$ is also low, e.g., 1.75, suggesting that the metal–metal bond orders for $Cr_2(CO)_7^+$ and $Cr_2(CO)_6^+$ are quite different. Our current objectives in this area are to obtain accurate metal–metal and metal–ligand bond energies for the $Cr_2(CO)_y^+$ (y = 4–7) ionic cluster fragments.

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Ligand Fluxionality and the Formation of Cationic Iron Carbonyl Clusters

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Abstract: The clustering gas-phase reactions of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ to form $Fe_x(^{13}CO)_r(CO)_s^+$ (x = 1–3; r = 0, 1; s = 4–8) are studied by Fourier transform ion cyclotron resonance mass spectrometry. It was found that the binary cluster cations formed by these reactions have a strong tendency to lose the ^{13}CO ligand during cluster formation. Label preference ratios varied only slightly from 0.56 ± 0.06 to 0.7 ± 0.1 indicating a clear preference for loss of the labeled carbonyl ligand. This preferential loss is indicative of the nonfluxional nature of these systems. Nonfluxionality in the cationic iron carbonyl clusters results from a decrease in back-bonding to the 2π orbital of the carbonyl ligands.

Introduction

Ligand fluxionality is commonly observed for coordinatively and electronically saturated iron carbonyl compounds.[1] For example, $Fe_3(CO)_{12}$ exists in solution as a continuum of structures ranging from the symmetrically bridged C_{2v} to the nonbridged D_{3h} structure. The activation energy for going from one structure to the other is estimated at <5 kcal mol^{-1}, giving rise to the observation of only a single ^{13}C NMR resonance at −150 °C.[2] The concept of ligand fluxionality has been successfully employed for prediction of structures of binary carbonyl clusters.[3,4] In this procedure, carbonyl ligands are assumed to be equivalent such that the repulsions between ligands ultimately determine their arrangement around a bare metal cluster. The solid-state C_{2v} structure of $Fe_3(CO)_{12}$ can be rationalized by this method if one considers the 12 carbonyl ligands to form an icosahedron with an Fe_3 triangle placed inside. Further, the D_{3h} structure of the isovalent $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ species can be explained by realizing that the interstice of the icosahedral carbonyl arrangement cannot support these larger homologues, causing the icosahedron to expand to an anticuboctahedron.

The amphoteric nature of the carbonyl ligand gives rise to the fluxional behavior observed for iron carbonyl compounds. Ligands with occupied σ orbitals and unoccupied π orbitals can act as both Lewis bases (σ donors) and Lewis acids (π acids). A number of transition metal atoms (especially those in groups 6–8) display a complementary amphoterism. The d orbitals of iron lie intermediate in energy between the 5σ and the 2π orbitals of CO, maximizing overlap for both the σ-donating and π-back-bonding bonding modes. If the sum of the σ- and π-bonding components remains constant as a carbonyl ligand moves from terminal to bridging for a given cluster nucleus, then CO fluxionality should occur. As the coordinative saturation or electronic charge (electronic saturation) of a cluster is changed, the tendency for

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[1] Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1-28.

[2] Cotton, F. A.; Hunter, D. L. *Inorg. Chim. Acta* **1974**, *11*, L9-110.

[3] Benfield, R. E.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1978**, 1554-1568.

[4] Benfield, R. E.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1743-1767.

0002-7863/90/1512-5959$02.50/0

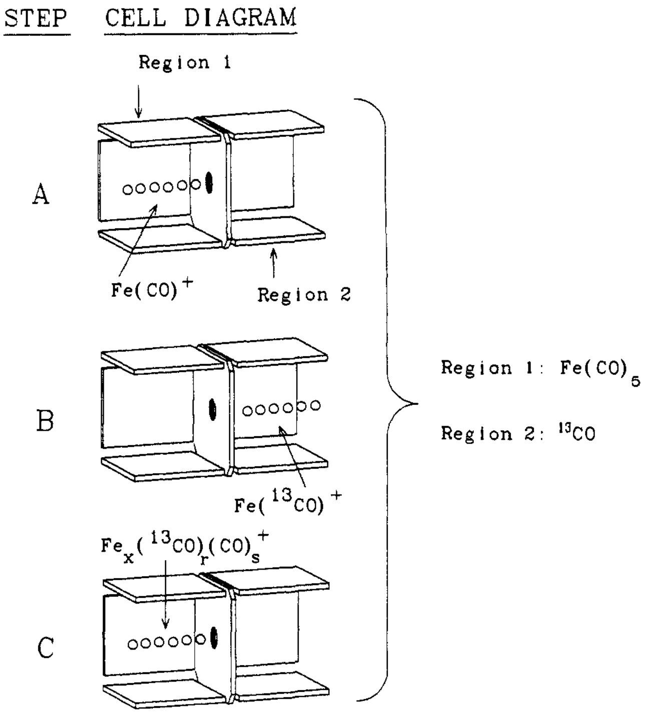

Figure 1. Schematic representation of the experiment employed here for the study of the clustering reactions of $Fe(^{13}CO)^+$ with $Fe(CO)_5$: (A) formation and isolation of $Fe(CO)^+$; (B) following ion transfer of $Fe(CO)^+$, $Fe(^{13}CO)^+$ is formed by ligand exchange in an environment of ^{13}CO; (C) $Fe(^{13}CO)^+$ is transferred back to the other region of the ion cell in order that the clustering reactions with $Fe(CO)_5$ might be monitored.

carbonyl fluxionality changes as well. This can be illustrated by noting that CO stretching frequencies decrease by about 30 cm^{-1} on loss of a single CO ligand from $Fe(CO)_5$ indicating increased back-bonding.[5] For the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$, the CO stretching frequency increases by about 100 cm^{-1} per step, indicating decreased back-bonding as well as concomitant increased σ bonding across the series.[6,7] Enhanced back-bonding in electron-rich clusters appears to support ligand fluxionality as evidenced by the number of anionic transition metal clusters which contain fluxional carbonyls.[1] Little evidence has been presented for fluxional carbonyl ligands on a cationic cluster center.[10]

This paper presents a study of the gas-phase clustering reactions of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR). The gas-phase clustering reactions of $Fe(CO)^+$ with $Fe(CO)_5$ have been studied previously from the standpoint of coordinative saturation and reaction rate.[8,9] The focus of this study is on carbonyl fluxionality in small binary iron carbonyl cationic clusters. Specifically, *are the ligands of such clusters fluxional*? Kinetic studies of the clustering reactions are employed to determine the efficiency of the ligand scrambling process during cluster formation. From these measurements and thermodynamic arguments, the fluxional nature of these species is deduced.

The generation of specific $M(CO)_n^{+/-}$ species (M is a transition-metal atom) is of seminal importance to systematic and fundamental studies of the reactivity of such fragments. Reactions of interest for these species include (i) clustering of $M(CO)_n^{+/-}$ with saturated metal containing neutrals,[8,10-12] (ii) ligand exchange,[13] and (iii) reactions of $M(CO)_n^{+/-}$ with neutral organics.[14] $M(CO)_n^{+/-}$ species can be formed in situ in an ion cyclotron resonance cell by ligand exchange on $Fe(CO)_n^{+/-}$ formed by ionization of a volatile iron carbonyl. In addition, bare metal ions formed by laser ablation often react with neutral ligand molecules to give the desired $ML_n^{+/-}$ fragment.[15,16] Both methods normally require the use of a pulsed valve for introduction of the neutral ligand to the vacuum system.[17] In this paper, we also present an alternative method for the selective formation of $ML^{+/-}$ fragments in a two-section cell FT-ICR under static pressure conditions.

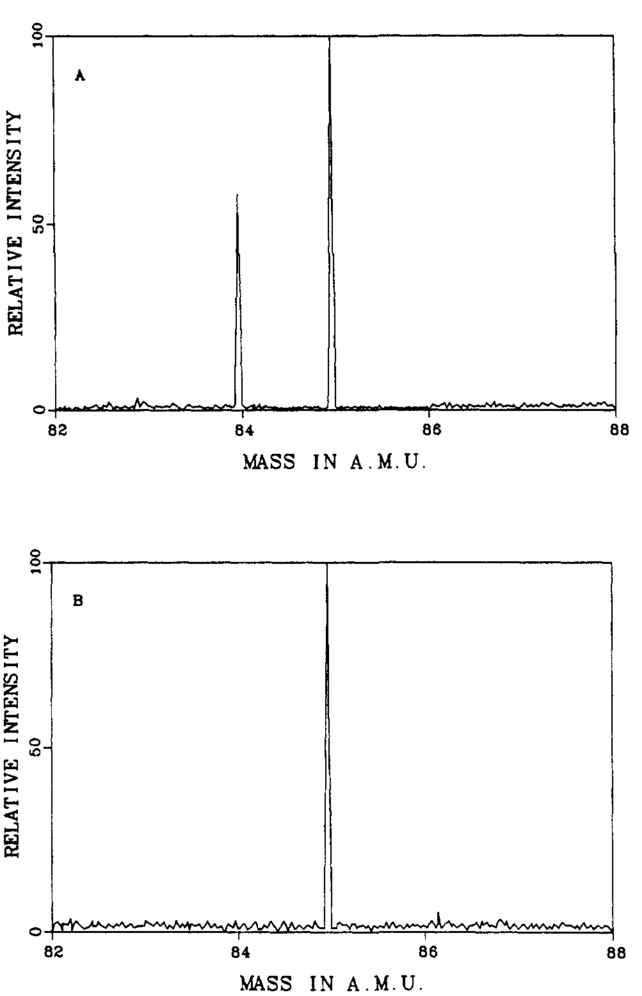

Figure 2. (A) $Fe(CO)^+$ and $Fe(^{13}CO)^+$ formed in region 2 of the ion cell (see Figure 1) by ligand exchange with ^{13}CO; (B) final isolation of $Fe(^{13}CO)$ in region 1 of the ion cell.

Experimental Section

Fourier Transform Ion Cyclotron Resonance Spectrometer. All experiments reported here were performed on a Fourier transform ion cyclotron resonance mass spectrometer constructed at TAMU. The system is centered around a Nicolet 1280 computer system and is equipped with an Oxford 3-tesla large-bore superconducting magnet as described previously.[18] The vacuum system and electronics have been modified to accommodate a two-section cell. The two-section cell consists of two cubic cells (3.8 cm) mounted collinearly along the central axis of the magnetic field.[19] The two cells share a common trap plate that also

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[5] Poliakoff, M.; Weitz, E. *Acc. Chem. Res.* **1987**, *20*, 408-414.

[6] Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, *7*, 1273-1284.

[7] Bursten, B. E.; Frier, D. G.; Fenske, R. F. *Inorg. Chem.* **1980**, *19*, 1810-1811.

[8] Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 3762-3768.

[9] Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4808-4814.

[10] Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67-71.

[11] Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 1860-1867.

[12] Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 3903-3909.

[13] Hann, L. S.; Russell, D. H. Unpublished data.

[14] Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 825-826.

[15] Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5690-5698.

[16] Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 1120-1126.

[17] Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571-574.

[18] Kerley, E. L.; Russell, D. H. *Anal. Chem.* **1989**, *61*, 53-57.

serves as a conductance limit for the differential pumping system. The vacuum is maintained by two 200 L s^{-1} oil diffusion pumps. Background pressures for both sections of the vacuum system were 1 × 10^{-8} Torr or less. Ionization was performed by electron impact (50-eV electrons), and the trapping potential was maintained at 4 V. Excitation of the ions in either the source or the analyzer region of the cell was performed by electronically switching the rf excite pulses between the cell regions.

Synthesis of $Fe(^{13}CO)^+$. The two-section ion cell can be used to maintain two different neutral reagents in the two differentially pumped regions of the cell. This allows one to compartmentalize reactions performed in the FT-ICR instrument by selecting the *location* at which a reaction is allowed to occur. For example, $Fe(^{13}CO)^+$ (m/z 85) was synthesized by the procedure outlined in Figure 1. $Fe(CO)_5$ was admitted (ca. 2 × 10^{-7} Torr, static) to one region of the cell and ionized to form $Fe(CO)^+$ (m/z 84) (Figure 1A). Unwanted ions were ejected from the cell at this point by rf sweeps[20,21] such that only $Fe(CO)^+$ remained. The $Fe(CO)^+$ ions were transferred to the second region of the cell (Figure 1B) which contained ^{13}CO (ca. 5 × 10^{-7} Torr, static). The isolated $Fe(CO)^+$ ions were then allowed to ligand exchange with ^{13}CO to give $Fe(^{13}CO)^+$ (Figure 1B). Figure 2A contains the mass spectrum of the ions contained in region 2 of the two-section cell after allowing the ligand-exchange reaction to proceed for 300 ms (see Figure 1B). Finally, the newly formed $Fe(^{13}CO)^+$ ions were moved to region 1 of the cell where subsequent reaction studies were performed without complication from ligand exchange with ^{13}CO (Figure 1C). The transfer of $Fe(^{13}CO)^+$ from region 2 to region 1 was performed under conditions such that residual $Fe(CO)^+$ cannot transfer.[18] Figure 2B contains a spectrum of the ions found in region 1 of the cell after moving the $Fe(^{13}CO)^+$ ions to this region. Such selective isolation of $ML_n{}^+$ species allows studies of gas-phase reactions of specific $ML_n{}^{+/-}$ species without the complication of interfering ions.

An additional advantage for forming unsaturated ligated metal fragments in this manner is the thermalization of the fragments by thermoneutral ligand-exchange reactions. For example, $Fe(CO)_n{}^+$ ions formed by electron impact could possess significant excess internal energy. This energy can is dissipated by ligand exchange with thermal, neutral CO molecules. Such experimental control can be tedious in single-cell experiments owing to complicating reactions and the requirement of pulsed valves.

Kinetic Studies. All ion abundances measurements are based on integrated peak areas.[22,23] Kinetic studies were performed by taking the complete mass spectrum for each reaction period interval across a given reaction period window. Because all ion abundances are measured simultaneously in FT-ICR, relative abundances for a given spectrum are considered to be accurate. If all product ions react to form observable products, the sum of the ion abundances for all reactant and product ions should remain constant for all spectra. This is generally true in practice except for ions lost from detection (and presumably from the cell) by Z-axis (magnetic field axis) ejection[24] and changes in measured ion abundance due to Z-axis relaxation.[25] These effects can be minimized by (i) operating at trap potentials in excess of 1 V and (ii) producing low numbers of ions. In the experiments reported here, the electron emission current during the ionization event was maintained at 200 nA for <10 ms in order to produce low quantities of ions in the cell. As a trade-off for the low ion abundance, trap potentials were maintained at 4 V in order to increase ion partitioning efficiency.

Ion abundances for all products and reactants were first corrected for isotopic abundances of ^{54}Fe, ^{57}Fe, and ^{13}C. The corrected data were summed for each spectrum and normalized to the total abundance at $t_{react} = 0$. The normalized data were then scaled to the most intense signal for the entire run, i.e., the abundance of $Fe(^{13}CO)^+$ at $t_{react} = 0$. Kinetic schemes were derived for the observed reactions, and the associated rate laws were solved to give mathematical representations of the abundance of a given ion with respect to time[26] according to the method used by Reents et al.[27,28]

Table I. Rate Equations for the $Fe_x(^{13}CO)_r(CO)_s{}^+/Fe(CO)_5$ System ($x = 1-3$; $r = 0, 1$; $s = 3-8$)

pseudo 1st order rate equation,[a] nonlinear	solution of rate equation[b]	rate constants fitted by least squares[c,d]
$A' = -k_A A$	$A_t = A_0 e^{(-k_A t)}$ ($A_0 = 1$)	k_A
$C' = k_{AC}A - k_C C$	$C_t = k_{AC}(k_C - k_A)^{-1}[e^{(-k_A t)} - e^{(-k_C t)}]$ $+ C_0 e^{(-k_C t)}$	k_{AC}, k_C
$D' = k_{AD}A - k_D D$	$D_t = k_{AD}(k_D - k_A)^{-1}[e^{(-k_A t)} - e^{(-k_D t)}]$ $+ D_0 e^{(-k_D t)}$	k_{AD}, k_D
$E' = k_{AE}A - k_E E$	$E_t = k_{AE}(k_E - k_A)^{-1}[e^{(-k_A t)} - e^{(-k_E t)}]$ $+ E_0 e^{(-k_E t)}$	k_{AE}, k_E
$F' = k_{AF}A - k_F F$	$F_t = k_{AF}(k_F - k_A)^{-1}[e^{(-k_A t)} - e^{(-k_D t)}]$ $+ F_0 e^{(-k_F t)}$	k_{AF}, k_F
$G' = k_{CG}C - k_G G$	$G_t = k_{AC}k_{CG}[(k_G - k_A) \times (k_C - k_A)]^{-1}[e^{(-k_A t)} - e^{(-k_G t)}]$ $+ k_{AC}k_{CG}[(k_G - k_C) \times (k_C - k_A)]^{-1}[e^{(-k_G t)} - e^{(-k_G t)}]$ $+ C_0 k_{CG}(k_G - k_C)^{-1}[e^{(-k_C t)} - e^{(-k_G t)}]$	k_{CG}, k_G
$H' = k_{CH}C + k_{DH}D$ $-k_H H$	$H_t = k_{AC}k_{CH}[(k_H + k_A) \times (k_C - k_A)]^{-1}[e^{(-k_A t)} - e^{(-k_H t)}]$ $+ k_{AC}k_{CH}[(k_H - k_C) \times (k_C - k_A)]^{-1}[e^{(-k_H t)} - e^{(-k_C t)}]$ $+ k_{AD}k_{DH}[(k_H - k_A) \times (k_D - k_A)]^{-1}[e^{(-k_A t)} - e^{(-k_H t)}]$ $+ k_{AD}k_{DH}[(k_H - k_D) \times (k_D - k_A)]^{-1}[e^{(-k_H t)} - e^{(-k_D t)}]$ $+ C_0 k_{CH}(k_H - k_C)^{-1}[e^{(-k_C t)} - e^{(-k_H t)}]$ $+ D_0 k_{DH}(k_H - k_D)^{-1}[e^{(-k_D t)} - e^{(-k_H t)}]$	k_{CH}, k_{DH}, k_H

[a] The pressure of $Fe(CO)_5$ was maintained constant throughout the experiment. Absolute rate constants = $k_\alpha p(Fe(CO)_5)$. [b] The solution for products C–H required the substitution of other numerical solutions (such as $e^{(-k_A t)}$ for A_t. Rate constants once determined were not allow to vary when substituted in this manner. [c] See ref 26. [d] Only the rate constants listed were allowed to vary during the fitting procedure.

Errors for the rate constants were estimated by varying one rate constant while leaving the other constants at the converged value until R doubled.[28] This method overestimates errors on fits of more than one constant because it assumes the error is due to one parameter alone, and, therefore, it is assumed (not rigorously proven) that the error in the pseudo-first-order rate constants is accurate at the 95% confidence level. The number density (hard sphere) for $Fe(CO)_5$ was calculated to be 6.4 ± 1.3 × 10^9 molecules cm^{-3} based on a pressure of 2.0 ± 0.4 × 10^{-7} Torr for $Fe(CO)_5$. Pressure readings were not corrected for gauge sensitivity. The precision reported for the pressure measurement of $Fe(CO)_5$ is supported by repetitive measurement of the cluster formation reaction of Fe^+ with $Fe(CO)_5$ and by published values for precision of ion gauge readings.[29]

Results

$Fe(^{13}CO)^+$ reacts with thermal $Fe(CO)_5$ in the gas phase according to eq 1–7. The product ions $Fe_4(^{13}CO)(CO)_{11}{}^+$ and

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(19) Ghaderi, S.; Littlejohn, D. *Proceedings of the 33rd Annual Conference on Mass Spectrometry and Allied Topics, San Diego*, 1985; p 727.

(20) Beauchamp, J. L.; Armstrong, T. J. *Rev. Sci. Instrum.* **1969**, *40*, 123-128.

(21) Goode, G. C.; Ferrer-Correia, A. J.; Jennings, K. R. *Int. J. Mass Spectrom. Ion Proc.* **1970**, *5*, 229-240.

(22) Shockley, W. J. *J. Appl. Phys.* **1938**, *9*, 635-636.

(23) McIver, R. T.; Hunter, R. L.; Ledford, E. B.; Locke, M. J.; Francl, T. J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65-84.

(24) Huang, S. K.; Rempel, D. L.; Gross, M. L. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *72*, 15-31.

(25) Rempel, D. L.; Huang, S. K.; Gross, M. L. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *70*, 163-184.

(26) Noggle, J. H. *Physical Chemistry on a Microcomputer*; Little, Brown: Boston, 1985; p 148.

(27) Reents, W. D., Jr.; Strobel, F.; Freas, R. B., III; Wronka, J.; Ridge, D. P. *J. Phys. Chem.* **1985**, *89*, 5666-5670.

(28) In addition to convergence, the goodness-of-fit for the nonlinear, least-squares fitting routine is given by $R = [SS/(M - 1)]^{0.5}$. SS refers to the sum of the squares of the difference between fit calculated points and corresponding data points, and M is the number of data points. The fit is considered to be "good" if R for the fit is on the order of the absolute error for the data points. The absolute error (95% confidence) is estimated to be ±0.008 abundance unit. R values ranged from 4.5 × 10^{-3} ($Fe(^{13}CO)^+$) to 2.0 × 10^{-3} ($Fe_2(CO)_4{}^+$).

(29) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149-153.

$$\underset{A}{Fe(^{13}CO)^+} + \underset{B}{Fe(CO)_5} \xrightarrow{k_{AC}} \underset{C}{Fe_2(^{13}CO)(CO)_4^+} + CO \tag{1}$$

$$\xrightarrow{k_{AD}} \underset{D}{Fe_2(CO)_5^+} + {}^{13}CO \tag{2}$$

$$\xrightarrow{k_{AE}} \underset{E}{Fe_2(^{13}CO)(CO)_3^+} + 2CO \tag{3}$$

$$\xrightarrow{k_{AF}} \underset{F}{Fe_2(CO)_4^+} + {}^{13}CO + CO \tag{4}$$

$$\underset{C}{Fe_2(^{13}CO)(CO)_4^+} + \underset{B}{Fe(CO)_5} \xrightarrow{k_{CG}} \underset{G}{Fe_3(^{13}CO)(CO)_7^+} + 2(CO) \tag{5}$$

$$\xrightarrow{k_{CH}} \underset{H}{Fe_3(CO)_8^+} + {}^{13}CO + CO \tag{6}$$

$$\underset{D}{Fe_2(CO)_5^+} + \underset{B}{Fe(CO)_5} \xrightarrow{k_{DH}} \underset{H}{Fe_3(CO)_8^+} + 2(CO) \tag{7}$$

$Fe_4(CO)_{12}^+$ are also formed, but the very low abundance of these ions make accurate kinetic measurements difficult. The reaction scheme shown is in qualitative agreement with previous studies.[8,9]

The equations for the temporal abundances of each species of the $Fe_x(^{13}CO)_r(CO)_s^+/Fe(CO)_5$ system (x = 1–3; r = 0, 1; s = 3–8) are found in Table I. These equations correlate to solutions of the predicted rate laws according to the reactions in eq 1–7. Equation 1–7 are assumed to proceed only via bimolecular collisions as the pressure of $Fe(CO)_5$ was maintained at 2×10^{-7} Torr throughout these studies. Solutions of the temporal equations for reaction products rely on the solution of the equation of the temporal abundance of the reactants. The solutions to the equations in Table I were obtained by fitting these equations to the normalized, scaled, temporal data for each ion (see Experimental Section). The numerical solutions of the temporal equations are done in sequence from initial reactant ($Fe(^{13}CO)^+$) to final products (the isotopomers of $Fe_3(CO)_8^+$). Rate constants, once determined, are not allowed to vary in subsequent fits for finding other rate constants. For example, k_A is determined by fitting the measured A_t values to the expression for A_t in Table I. This value of k_A is taken as a constant for all subsequent fits.

A plot of reaction velocity versus concentration yields a line (for simple rate laws) having the reaction order as the slope.[30] For $Fe(^{13}CO)^+$, the slope of this plot (95% confidence[30]) is 1.0001 ± 0.0004 (r = 1), indicating first-order disappearance and ruling out significant reverse reaction from cluster products. The rate law and associated temporal abundance relation describing reaction of $Fe_2(^{13}CO)(CO)_3^+$ in addition to $Fe_2(^{13}CO)(CO)_4^+$ with $Fe(CO)_5$ to form $Fe_3(^{13}CO)(CO)_7^+$ would not converge. The rate law assuming that only $Fe_2(^{13}CO)(CO)_4^+$ reacts to form $Fe_3(^{13}CO)(CO)_7^+$ converges and is reported as the correct rate law in Table I. This indicates that $Fe_2(^{13}CO)(CO)_3^+$ does not participate in the formation of $Fe_3(^{13}CO)(CO)_7^+$. $Fe_2(^{13}CO)(CO)_3^+$ instead most likely forms only the labeled and unlabeled $Fe_3(CO)_7^+$.[9] This product was most likely not detected in these studies owing to the fact that only a very small amount of the $Fe_2(CO)_4^+$ isotopomers were formed while the $Fe_3(CO)_7^+$ isotopomers would be expected to be more reactive than the $Fe_3(CO)_8^+$ homologues.[8] The disappearance rates reported for the $Fe_2(CO)_4^+$ isotopomers (k_E, k_F) represent mathematical solutions to the proposed rate laws (see Table I) and are not confirmed by monitoring the products they represent. These products, however, have been observed in earlier studies.[8,9]

Figures 3–6 depict the temporal abundances for each of the ions studied. Each of these plots show the measured ion abundances as symbols with appropriate error bars. The curves in the plots are defined by the fitted data.[31]

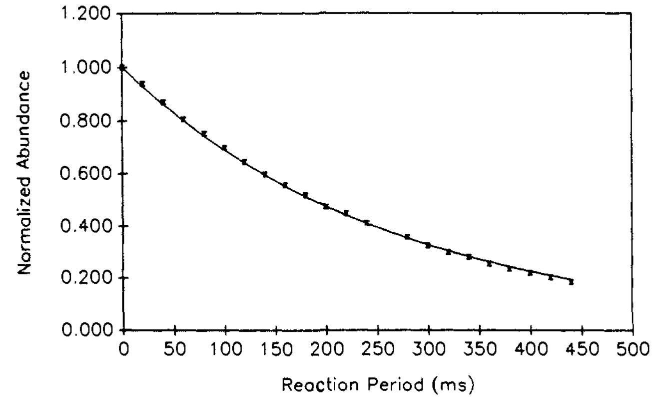

Figure 3. Disappearance of $Fe(^{13}CO)^+$ (I) in the formation of cationic iron carbonyl clusters.

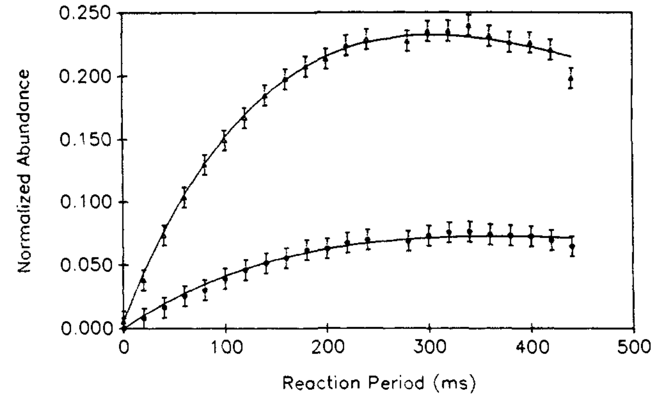

Figure 4. Formation of the isotopomers of $Fe_2(CO)_5^+$; ● = $Fe_2(^{13}CO)(CO)_4^+$ (II); Δ = $Fe_2(CO)_5^+$ (III).

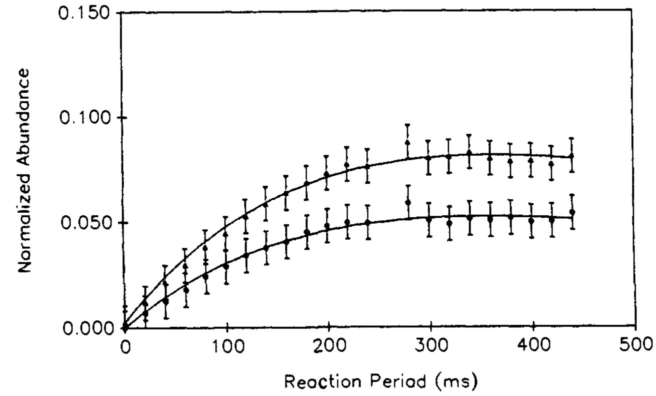

Figure 5. Formation of the isotopomers of $Fe_2(CO)_4^+$: Δ = $Fe_2(^{13}CO)(CO)_3^+$ (IV); ● = $Fe_2(CO)_4^+$ (V).

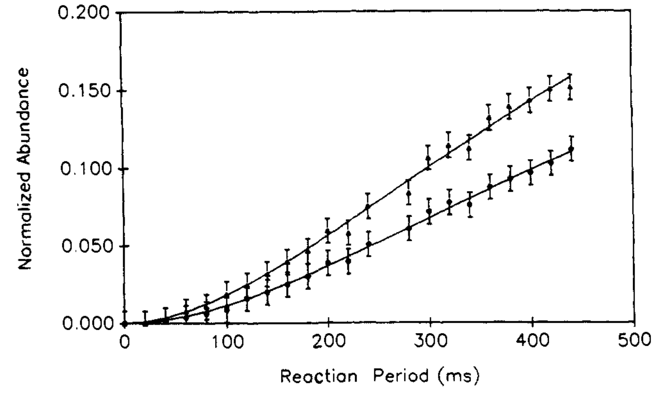

Figure 6. Formation of the isotopomers of $Fe_3(CO)_8^+$: Δ = $Fe_3(^{13}CO)(CO)_7^+$; ● = $Fe_3(CO)_8^+$.

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[30] Noggle, J. H. *Physical Chemistry*; Little, Brown: Boston, 1985; pp 476–477, 905–907.

Table II. Rate Equations for the $Fe_x(^{13}CO)_r(CO)_s^+/Fe(CO)_5$ System (x = 1–3; r = 0, 1; s = 3–8)

rate constant descriptor[a]	pseudo 1st order, s^{-1}	absolute, $\times 10^{10}$ cm^3 $molecules^{-1}$ s^{-1}	ADO, 10^{10} cm^3 $molecules^{-1}$ s^{-1}	product
k_A[b]	4.0 ± 0.1	6.2 ± 1.4	11.8	*c*
k_{AC}	1.88 ± 0.08	2.9 ± 0.7	*d*	$Fe_2(^{13}CO)(CO)_4^+$
k_C[b]	3.0 ± 0.3	4.7 ± 1.4	8.7	*c*
k_{AD}	0.67 ± 0.05	1.0 ± 0.3	*d*	$Fe_2(CO)_5^+$
k_D[b]	2.2 ± 0.4	3.4 ± 1.3	8.7	*c*
k_{AE}	0.56 ± 0.04	0.88 ± 0.24	*d*	$Fe_2(^{13}CO)(CO)_3^+$
k_E	2.1 ± 0.4	3.3 ± 1.3	8.9	*c*
k_{AF}	0.43 ± 0.4	0.67 ± 0.20	*d*	$Fe_2(CO)_4^+$
k_F	2.2 ± 0.6	3.4 ± 1.6	8.9	*c*
k_{CG}	2.2 ± 0.2	3.4 ± 1.0	*d*	$Fe_3(^{13}CO)(CO)_7^+$
k_G	0.7 ± 0.5	1.1 ± 0.9	8.0	*c*
k_{CH}	0.86 ± 0.09	1.3 ± 0.4	*d*	$Fe_3CO)_8^+$
k_{DH}	1.9 ± 0.2	3.0 ± 0.9	*d*	$Fe_3(CO)_8^+$
k_H	0.4 ± 0.4	0.6 ± 0.7	8.0	*c*

[a] See Table I. [b] k_A, k_C, and k_D correspond to the rates of disappearance of $Fe(^{13}CO)^+$, $Fe_2(^{13}CO)(CO)_4^+$, and $Fe_2(CO)_5^+$, respectively. [c] The rate constant measured is for rate of disappearance of the reactant ion; thus the product ion is not unambiguously determined. [d] ADO theory applies only to the ion–neutral collision frequency and is not unique for formation of a single product ion.

Discussion

The pseudo-first-order rate constants obtained for eq 1–7 are listed in Table II. The absolute rate constants (based on the number density of $Fe(CO)_5$) are included in Table II. Also included in Table II are the calculated average dipole orientation (ADO)[32,33] collision frequencies assumes the ion is a point charge approaching a point neutral.

Four observations emerge from comparison of the experimental and theoretical rate constants: (i) the reactions are inefficient with respect to the calculated ADO collision rates (k_i), (ii) the reaction inefficiency increases with mass/complexity, (iii) the rate constants are internally consistent, and (iv) the rate constants for the formation of the labeled products are in all cases larger than for their nonlabeled counterparts.

The overall inefficiency for the disappearance reactions is most likely due to the fact that the reaction has high demands on required orientation. The marked decrease in efficiency (from ca. 50% to 5%) on going to higher nuclearity clusters can be explained by (i) increasing steric/orientational requirement for reaction and (ii) breakdown of the point charge ion assumption for the dimer and cluster ions. Steric effects on reaction velocity for the transition metal clusters are directly related to arguments based on electron deficiency.[10] In most cases, ions of high electron deficiency will have low steric pressure.

Internal consistency for the proposed kinetic scheme is apparent in comparing reactant disappearance rate constants and corresponding product rate constants in Table II. $Fe(^{13}CO)^+$ reacts with $Fe(CO)_5$ to give four major products. Therefore, k_A (4.0 ± 0.1 s^{-1}) should equal $k_{AC} + k_{AD} + k_{AE} + k_{AF}$ (3.6 ± 0.2 s^{-1}). The discrepancy here is presumably due to (i) reaction of $Fe(^{13}CO)^+$ with residual CO (from $Fe(CO)_5$) to re-form $Fe(CO)^+$ [a small amount (maximum 5%) of $Fe(CO)^+$ is observed at moderate reaction periods] and (ii) charge exchange of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ to form $Fe(CO)_5^+$. The ionization potential for formation of $Fe(CO)_5^+$ from $Fe(CO)_5$ is 8 eV, whereas the ionization potential of Fe(CO) is calculated to be approximately 8 eV [from the sum of (1) $Fe(CO) + 4(CO) \rightarrow Fe(CO)_5$[5] and (2) $Fe(CO)_5 \rightarrow Fe(CO)^+ + 4(CO)$[34]]. Only rate constants for reactions with $Fe(CO)_5$ above ca. 1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} are detectable in this experiment. $Fe_2(^{13}CO)(CO)_4^+$ reacts to form two products in a self-consistent manner ($k_C = k_{CG} + k_{CH}$; 3.0 ± 0.3 s^{-1} = 3.1 ± 0.3 s^{-1}). Finally, $Fe_2(CO)_5^+$ reacts with $Fe(CO)_5$ to form $Fe_3(CO)_8^+$ self-consistently within error ($k_D = k_{DH}$; 2.2 ± 0.4 s^{-1} = 1.9 ± 0.2 s^{-1}).

Table III. Preference for Lable Retention for the $Fe_x(^{13}CO)_r(CO)_s^+/Fe(CO)_5$ System (x = 1–3; r = 0, 1; s = 3–8)

rate constant ratio[a]	k_l/k_l	abundance factor	label preference
k_{AC}/k_{AD}	2.8 ± 0.3	5	0.56 ± 0.06
k_{AE}/k_{AF}	1.3 ± 0.2	2	0.7 ± 0.1
k_{CG}/k_{CH}	2.6 ± 0.5	4	0.7 ± 0.1

[a] See Table I for definition of rate constants. [b] The abundance factor corrects for the fractional abundance of ^{13}CO in a completely statistical intermediate (see text).

The degree of label retention in each clustering reaction is curious. Table III summarizes the ratios of the rate constants for the formation of the labeled to the unlabeled products (k_l/k_u). The abundance factor is based on assumption of a collision complex/intermediate of the form $[Fe_x(^{13}CO)_r(CO)_s \cdots Fe(CO)_5]^+$ with equivalent carbonyls. For example, the reaction of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ would have six carbonyl ligands in the collision complex. If the carbonyls in this complex are equivalent, the probability that ^{13}CO would be retained in the formation of $Fe_2(CO)_5^+$ is 5:1. Thus, dividing (k_l/k_u) by the abundance factor corrects for statistical bias. The corrected ratios are quoted as "label preference" ratios in Table III. A preference ratio of unity implies ligand equivalence. Ratios less than unity indicate preferential loss of label, and ratios greater than one indicate preferential loss of unlabeled ligands. From Table III, one notices that the label preference ratios statistically indicate a preference for label loss of 0.6 to 0.7. The range in these values is surprisingly small given the possible range of ion structures. Stated succinctly, is label preference an indicator of the measure of overall ligand fluxionality in the collision complex?

The preference ratios listed in Table III are a measure of the degree to which fluxionality competes with ligand loss. By definition, ligand fluxionality is a low activation energy process. That is, a complex will be very fluxional if the difference in energy between terminal and bridged sites is small, a few kilocalories or less. For "cold" rapidly fluxional molecules (like $Fe_3(CO)_{12}$) it is easily realized that ligand fluxionality far outpaces ligand loss given the molecule has sufficient energy for both to occur, and both reactions have comparable frequency factors. It is certain that the metal–ligand bonding in small iron carbonyl clusters varies widely with stoichiometry.[35,36] That is, particular sites on a given cluster are more labile than others, so that the ability of a ligand to "step-in" to a labile site will be reflected in the ligand preference ratio. Ligand preference ratios of other than unity cannot result from distinct weak bonding sites alone. A cluster with equivalent ligands lost regiospecifically would display a ligand preference ratio of unity. Therefore, *nonunity ligand preference ratios must indicate decreased ligand fluxionality prior to ligand loss.*

Clearly, $[Fe_x(^{13}CO)_r(CO)_s \cdots Fe(CO)_5]^+$ corresponds to a "chemically activated" species in the gas phase with excess internal energy up to the ligand dissociation threshold. If the activation energy (versus ground state) for fluxionality is increased and enough energy is deposited into the cluster (by bond formation in the gas phase where energy must be accommodated within the collision complex), then the possibility of fluxionality remains. The dynamics of ligands on the clusters formed in this study cannot be probed directly, but insight can be gained from previous work. The photodissociation of the $Fe_x(CO)_y^+$ (x = 1–3, y = 0–6) ions

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(31) It is apparent from Table II and Figures 3–6 that the data at 260 ms have been deleted. This point was discontinuous from the remainder of the data in each plot and in some cases (e.g., $Fe_2(^{13}CO)(CO)_3^+$) by almost 1.5 times the error margin.

(32) Su, T.; Bowers, M. T. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 2.

(33) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347–356. The *c* values for parameterized ADO calculations were determined from nonlinear least-squares fit (see text ref 26) of data presented in the reference. $c = (0.8597{*}Z)^{0.2704} - 0.3063{*} \ln (4.0808{*}(Z + 1))$, where $Z = \mu_d/(\alpha{*}10^{24})^{1/2}$.

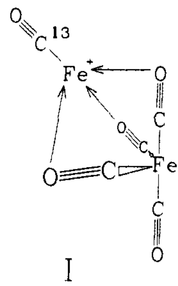
(34) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6(1)*, I-519.

(35) Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569–5573.

(36) Tecklenberg, R. E., Jr.; Bricker, D. L.; Russell, D. H. *Organometallics* **1988**, *7*, 2506–2514.

formed by electron impact on $Fe_3(CO)_{12}$ have been reported.[36] In general, the $D°(Fe_x^+(CO)_{y-1}–CO)$ is at least 20 kcal mol^{-1} per bond for $x/y < 1$.[37] Assuming that similar bond energy estimates are valid for systems such as $[Fe_x(^{13}CO)_r(CO)_5\text{---}Fe(CO)_5]^+$, it appears that fluxionality does not compete with ligand loss for ions having internal energies of tens of kcal mol^{-1}. It is clear that the relationship of ligand loss and ligand fluxionality is reversed on going from "cold" neutral clusters to "hot" cationc clusters. This observation can be rationalized by a combination of two possible phenomenon: (i) a loose transition state from which ligand expulsion proceeds and/or (ii) a reversal of the observed solution-phase activation energies (or frequency factors) for ligand loss and ligand fluxionality.

If one assumes that CO expulsion precedes relaxation of the collision complex (i.e., metal–metal bond formation and cluster orbital organization[38]), then the collision complex is better represented by $[(^{13}CO)_r(CO)_sFe_x^+\text{---}Fe\text{---}(CO)_5]^*$. This activated complex corresponds to a loosely bound transition state where intimate communication between the metal centers (such as ligand fluxionality) is not possible. After ligand loss and cluster reorganization, ligand fluxionality could occur, but this result cannot always be observed by the kinetic studies reported here. The inefficiency of these reactions (eq 1–4) (as compared to theoretical rates) possibly supports the contention of a loose transition state. A loose transition state would probably display little correlation between ligand preference ratios and reaction efficiency as is observed. Ligand preference ratios for similar reactants proceeding through a loose transition state would be expected to be similar as the weakest metal–ligand bond would remain unperturbed, whereas reaction efficiency is dramatically affected by the overall physical nature of the incoming ion or neutral, which normally varies widely. The loose transition-state argument is weakened by considering the process of formation of the $Fe_2(CO)_5^+$ isotopomers (eq 1 and 2) versus the $Fe_2(CO)_4^+$ isotopomers (eq 3 and 4). The formation of the $Fe_2(CO)_5^+$ requires the loss of a single CO from the collision complex. If the collision complex is loose, then the ratio of the energy required to remove a single CO from $Fe(CO)^+$ to the energy required to remove a single CO from $Fe(CO)_5$ should be a predictor for the ligand retention preference ratio. $D°(Fe^+–CO)$ is >39 kcal mol^{-1} [36] and ca. 55 kcal mol^{-1} for $Fe(CO)_5$.[35] The ligand preference ratio in this case should be less than 1, as is observed. However, in the formation of $Fe_2(CO)_4^+$, two CO's must be lost from the collision complex (I).



I

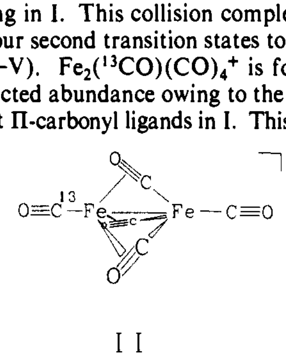
If I is indeed loose, loss of two CO's occurs by one of two processes: (i) loss of one CO each from a $Fe(CO)^+$ and a $Fe(CO)_5$ moiety or (ii) loss of two CO's from the $Fe(CO)_5$ moiety. The former should require at least 94 kcal mol^{-1} (55 kcal mol^{-1} [35] + 39 kcal mol^{-1} [36]). The latter requires only 60 kcal mol^{-1}.[35] This should result in a dramatic preference for label retention for this reaction (eq 3 and 4), yet this reaction has a label retention preference ratio of 0.7 indicating preferential *loss* of ^{13}CO.

A preliminary interpretation of the data indicates that a fundamental property of the ion–molecule reaction controls the ligand preference ratios. The ^{13}CO–Fe bond must remain weak with respect to other Fe–CO bonds in the complex and fairly constant for these reactions. It is apparent that significant communication (bonding) must exist in the transition state because of the lack of correlation of the ligand preference ratios with thermodynamic data.

As discussed earlier, the low-energy barrier to ligand fluxionality for many neutral binary carbonyls is the result of favorable energy matching between the CO 5σ and 2π orbitals and the metal d block. For these same fluxional molecules, the d block generally lies between the CO bonding orbitals maximizing overlap in both modes. The case for the cationic iron center is far different. The d orbital block drops by about 8 eV on the loss of one electron from Fe^0, virtually eliminating the possibility for Fe–CO 3d–2π back-bonding.[39] For Fe^+, the 5σ as well as a 1π–3d forward donation (resulting in Π-carbonyls[40]) is dramatically enhanced. Π-Carbonyls are frequently encountered in electrophilic transition metal compounds.[40] The actual bonding situation in the cationic binary clusters would not be as skewed as for Fe^+ ion owing to charge delocalization. Nonetheless, substantially decreased back-bonding and enhanced 1π to 3d donation should result in a "freezing out" of ligand fluxionality by significantly increasing the energetic requirement for ligand walking. It is likely that even if the activation energy for ligand walking (via a terminal-bridged-terminal mechanism) is competitive with that for ligand expulsion, the frequency factors for ligand walking will be far smaller because of the reduced energy match for the required bonding modes. Therefore, *ligand fluxionality plays a dramatically reduced role* (*with respect to neutral clusters*) *in cationic iron carbonyl clustering reactions*.

Reduced ligand fluxionality for cationic iron carbonyl clusters results in the creation of unique ligand bonding sites or regions on the cluster. Such regions could result from islands of electronic/coordinative saturation or charge localization at the metal center. The ligand preference ratio most likely reflects site specificity in the clustering reactions and the ability of the ligands at reactive sites to remain distinct. The ligand preference ratios of 0.6–0.7 measured here indicate that the $Fe–^{13}CO^+$ bond is among the weakest in each of the $Fe_x(^{13}CO)(CO)_s^+$ (x = 1–3; s = 0, 4, 5) clusters. The magnitude of the ligand preference ratios further indicates that there exists a significant tendency for either (i) nonlabeled CO ligands to walk into the reactive bonding mode (i.e., moderate fluxionality) or (ii) loss of unlabeled ligands at distinct sites with bond enthalpies nearly equal to the $Fe–^{13}CO$ bond. Evidence for site specificity (and, hence, the loss of ligand fluxionality) on transition metal carbonyl cluster cations has been reported. $Co_2(CO)^+$ is proposed to be highly nonsymmetrical with the carbonyl ligand associated with a single cobalt atom.[10] $Fe_2(CO)_3^+$ is observed to exchange only two CO's in the thermoneutral ligand exchange reaction with ^{13}CO.[13] These two observations indicate that some fully formed binary transition metal carbonyl cluster fragments (as opposed to fragments undergoing formation in a collision complex) are not fluxional.

A proposed reaction mechanism for the scheme in eq 1–7 begins by the electrophilic, Lewis acid attack of the iron of $Fe(^{13}CO)^+$ on the basic 1π orbitals of three carbonyl ligands on a face of $Fe(CO)_5$ resulting in I. This collision complex then dissociates through one of four second transition states to yield the observed product ions (II–V). $Fe_2(^{13}CO)(CO)_4^+$ is formed in less than statistically predicted abundance owing to the labilizing effect of the three incipient Π-carbonyl ligands in I. This inclination toward



II

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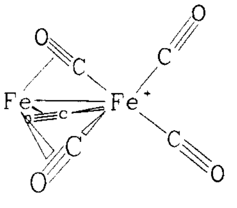
(37) This value assumes that an excited electronic state resides near in energy to the dissociation threshold such that the reported bond strength is roughly equivalent to the activation energy for the dissociation process.

(38) Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305–5315.

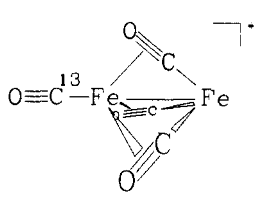
(39) Mandich, M. L.; Steigerwald, M. L.; Reents, W. D., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 197–6202. The covalence of $FeCl^+$ indicates that the valence orbitals of Fe^+ have dropped by at least 5 eV from Fe^0.

(40) Horowitz, C. P.; Shriver, D. P. *Adv. Organomet. Chem.* **1984**, *23*, 219–305.

^{13}CO loss is supported thermodynamically under the loose transition-state model as discussed above. The charge of II is probably delocalized between the iron atoms, rendering the metal–metal bond more dative in character. Assuming that charge localization in II is minimized, then each center has a formal electron count of 16.5 electrons. The loss of ^{13}CO from I to form $Fe_2(CO)_5^+$ (III) results in greater than 18 electrons on the initially neutral iron atom for a single Fe–Fe bond and equal charge distribution between the centers. Therefore, III is stabilized by localizing the charge on the iron atom with five terminal carbonyls.

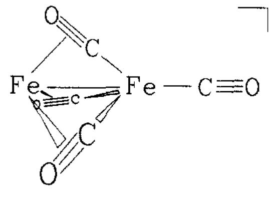


III



IV

Formation of $Fe_2(^{13}CO)(CO)_3^+$ (IV) proceeds from I by loss of two of the nonlabeled, terminal carbonyls of the collision complex (I). The loss of these terminal carbonyls formally results in a pyramidal $Fe(CO)_3$ bound to $Fe(^{13}CO)^+$. The proposed reaction mechanism is consistent with what is known about the structure of $Fe(CO)_3$ and the thermodynamics of its formation. $Fe(CO)_3$ formed in a matrix at 20 K is known to be pyramidal[41] (C_{3v}), requiring about 60 kcal mol^{-1} for formation from $Fe(CO)_5$ according to the reaction: $Fe(CO)_5 \rightarrow Fe(CO)_3 + 2CO$.[35] The Fe–Fe bond energy in Fe_2^+ is reported to be >62 kcal mol^{-1};[36] therefore, formation of the Fe–Fe bond in I is sufficiently exoergic to cause the expulsion of two carbonyls to form IV. Formation of $Fe_2(CO)_4^+$ (V) would result from loss of a terminal carbonyl ligand from each iron center in I. This loss would be assisted by the incipient stabilization of charge on the iron atoms by 5σ donation as for $Fe_2(^{13}CO)(CO)_4^+$ above. Site specificity on the cluster coupled with very similar energies for the second transition states result in a better description of the observed product ion distribution between IV and V. The formation of $Fe(CO)_3$ and $Fe(CO)_4$ requires similar energy[35] such that the formation of IV over V could result from subtle differences in the energies of the Fe–^{13}CO bond and the nonlabeled, terminal Fe–CO bonds in I. The ligand preference ratio of 0.7 indicates that the 1π–3d donation is effective in labilizing ^{13}CO.



V

The labeled and unlabeled versions of $Fe_2(CO)_5^+$ react with $Fe(CO)_5$ at statistically different rates ($Fe_2(^{13}CO)(CO)_4^+$ 3.0 ± 0.3 s^{-1} (II); $Fe_2(CO)_5^+$ 2.2 ± 0.4 s^{-1} (III)); the labeled and unlabeled isotopomers of $Fe_2(CO)_4^+$ do not. The difference in the clustering rates for the dimer pentacarbonyl ions could indicate the presence of two distinct ion structures for the labeled and nonlabeled versions. If the collision complex is nonfluxional between iron centers, the loss of a single carbonyl ligand from the collision complex (I) would result in two unique structures for the labeled (II) versus the unlabeled (III) product.

The close match between the Fe–Fe bond formation energy and the loss of two carbonyls could explain why the four dimer products are observed. That is, the internal energy remaining in $Fe(^{13}CO)^+$ could control the product distribution. If one assumes equal probability factors for going from I to II or from I to IV, the difference in reaction rate correlates to a difference in activation energy of about 1 kcal mol^{-1}. Higher internal energy for $Fe(CO)^+$ could explain why an earlier study showed that $Fe_2(CO)_4^+$ was formed considerably *faster* than $Fe_2(CO)_5^+$.[8] A higher internal energy distribution would increase the possibility of formation of $Fe_2(CO)_4^+$ especially if the frequency factor for loss of CO ligands from the collision complex favors the loss of two ligands. Similar activation energies in the formation of these products supports the hypothesis of similar transition states for the formation of the $Fe_2(CO)_x^+$ ions.

The mechanism for the formation of the $Fe_3(CO)_8^+$ isotopomers is complicated by the question of multiple distinct structures for the cluster ion reactants (II and III) and products. The kinetic treatment employed here allowed different structures for II and III, but not for the labeled and unlabeled $Fe_3(CO)_8^+$ products. The disappearance rate constants for these clusters are not very sensitive to change in the fitting procedure resulting in large error brackets (Table II). This could indicate that several structures of the $Fe_3(CO)_8^+$ isotopomers exist complicating the kinetic treatment.[42] Nonetheless, some conclusions can be drawn with respect to the formation of the $Fe_3(CO)_8^+$ species. The central core of the $Fe_3(CO)_8^+$ isotopomers could feasibly contain a highly Π-CO bonded $Fe_3(CO)_4^+$ core. This species displays unusual stability to collision-induced dissociation[36] and agrees with the idea of significant Π-CO bonding in cationic systems. Two trends can be distinguished in the trimer formation reactions. First, the ligand preference ratio indicates site specificity and preferential ^{13}CO loss. Secondly, the formation of the $Fe_3(CO)_8^+$ isotopomers by loss of two carbonyls from the $Fe(CO)_5$ moiety of $[Fe_2(CO)_5^+\cdots Fe(CO)_5]$ fits the scheme of stable $Fe(CO)_3$ centers being preferred in the rate-limiting transition state. These trends indicate that the $^{13}CO–Fe^+$ bond is still largely unperturbed in II, allowing $Fe(CO)_3$ Lewis base attack on that site in a fashion similar to that proposed for the $Fe_2(CO)_x^+$ ions. Further, the apparent uniqueness of the ^{13}CO–Fe bond in forming the $Fe_3(CO)_8^+$ ions indicates that ligand fluxionality does not ensue after ligand loss in II.

Conclusions

The gas-phase reactions for the formation of $Fe_x(^{13}CO)_r(CO)_s$ (x = 1–3; r = 0, 1; s = 4–8) from $Fe(^{13}CO)^+$ and $Fe(CO)_5$ demonstrate a marked tendency to lose the labeled carbonyl ligand. This nonequalization of ligands is contrary to the ubiquitous examples of rapid fluxionality for internally cool, saturated binary carbonyl clusters in the solution phase. One explanation for this is that the ligand scrambling reaction coordinate is not available in the collision complex before ligand loss has occurred. Alternately, ligand fluxionality is not allowed for cationic iron carbonyl clusters owing to an orbital energy mismatch between the metal d orbitals and the ligand 2π orbitals.

More detailed studies on this question are planned. For example, collision-induced dissociation or photodissociation of $Fe_x(^{13}CO)(CO)_{y-1}^+$ formed by reactions of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ could be used to probe questions concerning the lability of the ^{13}CO ligand and the issue of fluxionality. Clearly, the results of thermoneutral ^{13}CO ligand exchange reaction with $Fe_2(CO)_3^+$ suggest nonequivalency of the CO ligands. If other systems also reveal nonequivalent CO ligands, then the nonfluxionality of cationic systems can be attributed to a mismatch in orbital energies.

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(41) Poliakoff, M. J. *J. Chem. Soc., Dalton Trans.* **1974**, 210.

(42) No further refinement of the kinetic scheme was attempted.