

The activation energy associated with translational diffusion in the plastic phase of adamantane is  $E_a^d = 36.7$  kcal mol<sup>-1</sup>, much larger than either of those measured in this work. It is believed that self diffusion in molecular crystals occurs by a vacancy mechanism. If so, then one expects some reduction in the activation energy for diffusion of 2-cyclohexanonyl radicals in adamantane because of the expected decrease in the free energy of formation of vacant lattice sites of the appropriate size. Some decrease in the repulsive part of the intermolecular potential energy function might also be anticipated. However, even in the plastic phase of cyclohexane, the activation energy for self diffusion is of the order of 10 kcal mol<sup>-1</sup>. This value is still much larger than the measured activation energy for the fast decay process. Thus,

if as suggested above, the fast decay is the result of radical-radical recombination, then it would appear that the rate of this reaction is also not strongly influenced by the host. This is not unreasonable, as the time scale for diffusional motion in a system having an activation energy as high as 10 kcal mol<sup>-1</sup> is still many orders of magnitude faster than the time scale for the fast free radical decay process in adamantane.

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**Registry No.** 2-Cyclohexanonyl radical, 40528-46-9; adamantane, 281-23-2; cyclohexanone, 108-94-1.

## Double Metal-to-Metal Bonds in Metal Carbonyl Clusters Formed in the Gas-Phase Negative Ion Chemistry of Iron Pentacarbonyl

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**Abstract:** Fe(CO)<sub>4</sub><sup>-</sup> is observed to form Fe<sub>2</sub>(CO)<sub>8</sub><sup>-</sup> in a gas-phase reaction with Fe(CO)<sub>5</sub>. The rate constant for the reaction is log  $k = -12 \pm 0.5$ , fast enough to account for the Fe<sub>2</sub>(CO)<sub>8</sub><sup>-</sup> which has been reported to form in the condensed phase chemistry of Fe(CO)<sub>5</sub>. Relative rate constants for clustering reactions of Fe(CO)<sub>3</sub><sup>-</sup>, Fe<sub>2</sub>(CO)<sub>5</sub><sup>-</sup>, Fe<sub>2</sub>(CO)<sub>6</sub><sup>-</sup>, Fe<sub>3</sub>(CO)<sub>9</sub><sup>-</sup>, Fe<sub>3</sub>(CO)<sub>10</sub><sup>-</sup>, and Fe<sub>4</sub>(CO)<sub>11</sub><sup>-</sup> are reported. Other observed products include Fe<sub>4</sub>(CO)<sub>13</sub><sup>-</sup>, which is reportedly observed in the condensed phase chemistry of Fe(CO)<sub>5</sub> and Fe<sub>5</sub>(CO)<sub>14</sub><sup>-</sup>. It is concluded from reactivity patterns that Fe<sub>2</sub>(CO)<sub>5,6,7</sub><sup>-</sup> each have a double metal-metal bond.

### Introduction

It has been known for some years that cationic metal clusters are formed by gas-phase ion-molecule reactions in metal carbonyls.<sup>1-5</sup> Such processes were first reported in the ion-molecule reactions of metal complexes with both CO and cyclopentadienyl ligands.<sup>1</sup> Clustering reactions in Fe(CO)<sub>5</sub> have been studied in some detail.<sup>2</sup> Clusters containing up to four iron atoms result from a sequence of reactions beginning with reactions between Fe(CO)<sub>5</sub> and Fe(CO)<sub>n</sub><sup>+</sup> fragments formed by electron impact. Cations formed from Ni(CO)<sub>4</sub>,<sup>3</sup> Cr(CO)<sub>6</sub>,<sup>4</sup> and CoNO(CO)<sub>3</sub><sup>5</sup> have also been shown to undergo clustering reactions with their parent neutral compounds. Reactivity of this kind is probably common to all metal carbonyls.

Metal carbonyl cluster compounds have a rich chemistry in the condensed phase. They are useful as models for heterogeneous metal catalysis<sup>6</sup> and as stoichiometric reagents in a number of useful organic syntheses.<sup>7</sup> Parallels between chemistry of the clusters in the gas phase and in the condensed phase have not been extensively studied. One reason for this is that carbonyls form about electron-rich metal centers. Anionic metal carbonyl clusters are quite common in the condensed phase and have an extensive chemistry.<sup>8</sup> Unfortunately, few gas-phase anionic clustering reactions are known. One such reaction in each of Ni(CO)<sub>4</sub><sup>9</sup> and Fe(CO)<sub>5</sub>,<sup>2,9</sup> and two in Cr(CO)<sub>6</sub><sup>9</sup> have been described.

The present report describes a number of previously unobserved gas-phase anionic clustering reactions in Fe(CO)<sub>5</sub>. New ion cyclotron resonance techniques make it possible to observe these reactions, several of which have rate constants three orders of magnitude less than the collision rate. The reactions are unique and interesting in several ways. First, the products include such

species as Fe<sub>2</sub>(CO)<sub>8</sub><sup>-</sup>, and Fe<sub>4</sub>(CO)<sub>13</sub><sup>-</sup>, which occur in the condensed-phase chemistry of Fe(CO)<sub>5</sub>.<sup>10</sup> Second, the reactants include a number of highly coordinatively unsaturated species, some formed only by collision-induced decomposition of more saturated ions accelerated by irradiation at their cyclotron frequencies. Third, the kinetics of the reactions suggest that some of the clusters are double metal-metal bonds.

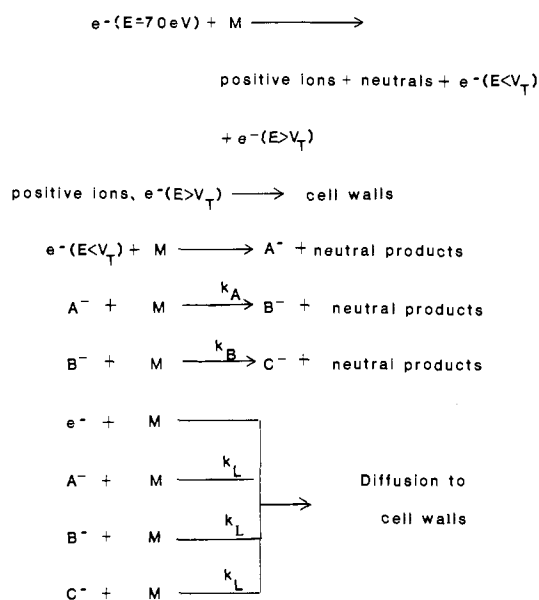
### Experimental Section

These studies were done by use of an ion cyclotron resonance spectrometer having a conventional three-region rectangular cell with a square cross section 2.54 × 2.54 cm.<sup>11</sup> The source region is 2.54 cm long

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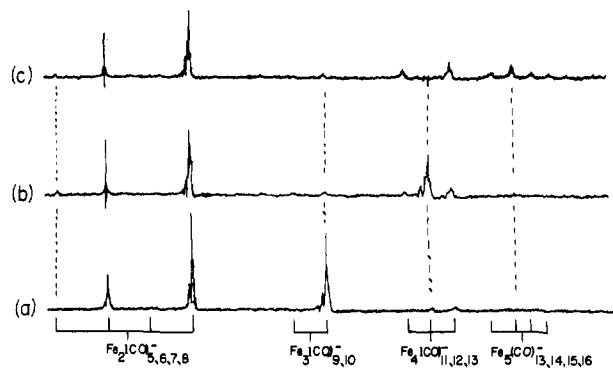
## Scheme I



with the electron beam in the middle. The analyzer is 7.62 cm long and the ion collector is 2.54 cm long. The spectrometer was operated in the continuous trap mode.<sup>12,13</sup> The drift plates in the source and analyzer are all at approximately the same voltage. There is an end plate in the source which is also at that voltage. The trapping plates are biased 2 to 3 V more positive than the drift plates. The drift plates in the ion collector are biased more positive than the other drift plates. This arrangement produced electric fields which, in combination with the magnetic field, confine the ions to the source and analyzer regions of the cell. Ions are lost from the trap as they slowly diffuse to the walls. The ions that are replaced by those formed by electron impact or electron attachment. The contents of the trap are monitored by a frequency swept bridge detector which has been previously described.<sup>14,15</sup> The detector is applied in the analyzer region of the cell, but the signals obtained appear to be representative of all the contents of the trap. The peak intensities, for example, vary with pressure as expected from the kinetic model for continuous trapping as discussed below. The detector is provided with the means to add one double resonance signal to the voltages applied to the drift plates. Additional multiple resonance signals may be applied simultaneously to the drift plates in the source. The multiple resonance experiments are discussed in more detail below. The detector can be swept rapidly enough that the mass spectrum of the contents of the trap may be observed continuously on an oscilloscope.<sup>14</sup> This makes it possible to eliminate space charge induced instabilities in the trapped ion concentrations. The electron beam current can be slowly reduced until the mass spectrum as observed on the oscilloscope is stable and the peak intensities do not oscillate. Under these circumstances steady-state kinetics apply as discussed below. Mass spectra are then recorded by scanning the bridge detector more slowly. Interpretation of these spectra is discussed below.

Pressure was measured with an ionization gauge.  $\text{Fe}(\text{CO})_5$  was obtained commercially and no impurities were detected in its mass spectrum.

**Kinetic Analysis.** Kinetic analysis of ion cyclotron resonance spectra of ions reacting in a closed electromagnetic trap has been discussed by Hunter and McIver<sup>12</sup> and by Bartmess and Caldwell.<sup>13</sup> Application to the present results may be discussed in terms of Scheme I. Secondary electrons are formed as a result of collisions between 70-eV electrons and the neutral. Positive ions and energetic secondary electrons are lost from the trap. Electrons with energy less than the trapping voltage  $V_T$  are confined in the trap. The trapped electrons are captured by M forming  $A^-$  and neutral products. For species with large electron capture cross sections this will be the source of most of the trapped ions.  $A^-$  then reacts sequentially with M forming  $B^-$  and  $C^-$ .  $A^-$ ,  $B^-$ , and  $C^-$  all diffuse toward the walls where they are neutralized and lost to system. For the purposes of this analysis the diffusive loss process is treated as a "reaction" that



**Figure 1.** Continuous trapping ion cyclotron resonance spectra of negative ions with  $m/z > 250$  in  $3.0 \times 10^{-6}$  torr  $\text{Fe}(\text{CO})_5$  obtained with frequency scanned bridge detector: (a) unperturbed spectrum. (b)  $\text{Fe}_2(\text{CO})_6^-$ , at  $m/z$  280, is irradiated in the analyzer region as spectrum is obtained; (c) in addition to irradiating  $m/z$  280 in the analyzer,  $\text{Fe}_4(\text{CO})_{12}^-$ , is irradiated in the source.

is first order in ion concentration and first order in neutral concentration. The "rate constant" for this process will depend on the electric and magnetic fields and the geometry and dimensions of the cell as well as the diffusion constant of the ion neutral pair. The fields and cell are fixed during a given experiment. Theory suggests that the diffusion constants for the ions of interest in this study will only vary over a small range.<sup>16</sup> The "rate constant" for the loss process is, therefore, taken to be the same for all the ions. At steady state eq 1 and 2 apply for Scheme I, where

$$\frac{k_A}{k_L} = \frac{[B^-] + [C^-]}{[A^-]} \quad (1)$$

$$\frac{k_B}{k_L} = \frac{[C^-]}{[B^-]} \quad (2)$$

$k_A$  is the rate constant for the reaction of  $A^-$ ,  $k_B$  is the rate constant for the reaction of  $B^-$ , and  $k_L$  is the "rate constant" for the loss process. Ion cyclotron resonance spectra of the contents of the trap are taken at steady state as indicated in the Experimental Section. Thus, the ion concentrations in eq 1 and 2 may be replaced by peak intensities from these spectra, and relative rate constants may be determined simply from peak heights in the spectra. More complex reaction schemes may be treated in the same way. In general, peak heights in the spectra are simply related to rate constants.

An interesting and important consequence of this analysis is that the neutral concentration does not appear in eq 1 and 2. If the analysis applies, the appropriate ratios of peak heights should be independent of neutral pressure. This provides a means of testing the applicability of the analysis.

**Multiple Resonance Experiments.** We have discussed the applications of multiple resonance experiments with the bridge detector in the continuous trapped mode elsewhere.<sup>15</sup> Figure 1 gives an example of the technique applied to negative ion reactions in  $\text{Fe}(\text{CO})_5$ . Trace a shows a normal spectrum. Trace b was taken while  $\text{Fe}_2(\text{CO})_6^-$  was irradiated in the source. The  $\text{Fe}_2(\text{CO})_{10}^-$  product of  $\text{Fe}_2(\text{CO})_6^-$  reaction disappears almost completely. This identifies the product-reactant relationship between the two ions. In addition, a sizable peak for the  $\text{Fe}_4(\text{CO})_{12}^-$  ion appears. This is the result of a series of rapid reactions beginning with  $\text{Fe}_2(\text{CO})_5^-$  which is produced by collision-induced decomposition when  $\text{Fe}_2(\text{CO})_6^-$  is irradiated. With this enhanced  $\text{Fe}_4(\text{CO})_{12}^-$  concentration it is possible to examine the consequences of irradiating that ion. If  $\text{Fe}_4(\text{CO})_{12}^-$  is irradiated in addition to irradiating  $\text{Fe}_2(\text{CO})_6^-$ , trace c is obtained.  $\text{Fe}_4(\text{CO})_{11}^-$  appears as a result of collision-induced decomposition of  $\text{Fe}_4(\text{CO})_{12}^-$ . Furthermore, ion-molecule reaction products of  $\text{Fe}_4(\text{CO})_{11}^-$  appear at higher mass. The major product is  $\text{Fe}_5(\text{CO})_{13}^-$ . In this way reactions of species not present or present only in low abundance in the single resonance spectrum can be examined.

## Results

The negative ions formed by thermal electron attachment to  $\text{Fe}(\text{CO})_5$  are  $\text{Fe}(\text{CO})_3^-$  and  $\text{Fe}(\text{CO})_4^-$ .<sup>2,9,17</sup> At higher electron

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(16) Simple theory of diffusive ion loss from the trap (see Sharp, T. E.; Eyley, J. R.; Li, E. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *9*, 421-439) predicts that ion loss rates should vary as the square root of the reduced mass of the ion neutral pair. The loss rates for all ions in this study should accordingly be within >20% of the average of all loss rates.

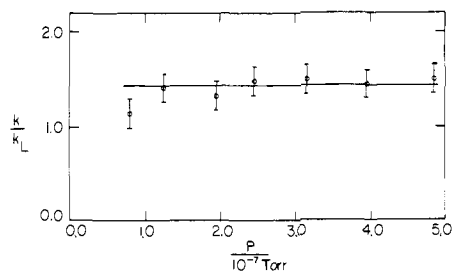
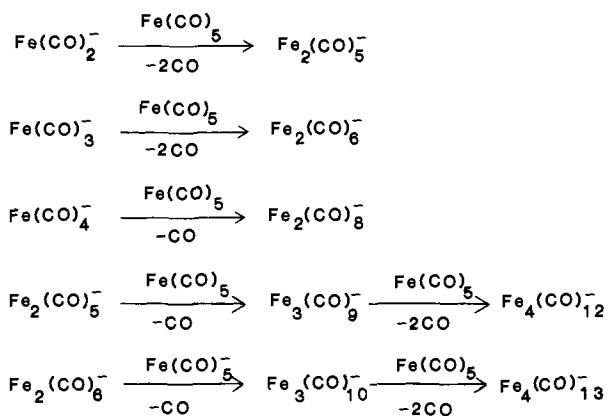


Figure 2. Relative rate constant for reaction of  $\text{Fe}_2(\text{CO})_6^-$  according to Scheme II calculated from eq 3 at various  $\text{Fe}(\text{CO})_5$  pressures.

## Scheme II



energies  $\text{Fe}(\text{CO})_2^-$  is formed.<sup>17</sup> These ions react with  $\text{Fe}(\text{CO})_5$  according to Scheme II. This sequence of reactions was determined by multiple resonance experiments analogous to the example outlined above.

The reactions of this scheme may be treated by the kinetic analysis outlined above. As discussed above, the applicability of the steady-state analysis may be tested by determining that the appropriate ratios of peak intensities are pressure independent. Consider the reaction of  $\text{Fe}_2(\text{CO})_6^-$  to produce  $\text{Fe}_3(\text{CO})_{10}^-$  which in turn reacts to form  $\text{Fe}_4(\text{CO})_{13}^-$ . Substituting into eq 1 gives eq 3, where  $k/k_L$  is the ratio of the rate constant for reaction of

$$k/k_L = ([\text{Fe}_3(\text{CO})_{10}^-] + [\text{Fe}_4(\text{CO})_{13}^-]) / [\text{Fe}_2(\text{CO})_6^-] \quad (3)$$

$\text{Fe}_2(\text{CO})_6^-$  with  $\text{Fe}(\text{CO})_5$  to the rate constant for ion loss from the trap. Taking the peak heights as proportional to the ion concentrations,  $k/k_L$  can be calculated from spectra obtained at different  $\text{Fe}(\text{CO})_5$  pressures. As seen in Figure 2,  $k/k_L$  is, indeed, independent of pressure. Table I contains relative rate constants for reactions of all the ions except  $\text{Fe}(\text{CO})_2^-$  in Scheme II as well as several others produced by collision-induced decomposition as outlined in the above discussion of multiple resonance.

The  $\text{Fe}(\text{CO})_2^-$  ion is formed by high-energy electrons in the electron beam and not by low energy electrons caught in the trap. In spectra taken at 70-eV electron energy, for example, daughters of  $\text{Fe}(\text{CO})_2^-$  are observed. The current of electrons in the high-energy beam is held constant as the  $\text{Fe}(\text{CO})_5$  pressure is increased, so the rate of formation of  $\text{Fe}(\text{CO})_2^-$  increases linearly with  $\text{Fe}(\text{CO})_5$  pressure. The  $\text{Fe}(\text{CO})_3^-$  and  $\text{Fe}(\text{CO})_4^-$  ions are formed by thermal electrons which are produced in collision between high-energy electrons and  $\text{Fe}(\text{CO})_5$ . The production of these two ions increases with the square of  $\text{Fe}(\text{CO})_5$  pressure. The ratio of the peak intensities of  $\text{Fe}(\text{CO})_2^-$  and its daughters to that of  $\text{Fe}(\text{CO})_3^-$  and its daughters, therefore, drops with pressure. The  $\text{Fe}(\text{CO})_2^-$  concentration is so small and it is so reactive that it is not normally observed directly. Only its daughters are observed. Its role in the kinetics can be deduced from the pressure and electron energy dependence of the spectra, but an estimate of its

Table I. Relative Rate Constants for Reactions of  $\text{Fe}_n(\text{CO})_m^-$  Ions with  $\text{Fe}(\text{CO})_5^a$

reactant ion	electron deficiency	rel rate const
$\text{Fe}(\text{CO})_3^-$	3	$118 \pm 50$
$\text{Fe}(\text{CO})_4^-$	1	[1]
$\text{Fe}_2(\text{CO})_5^-$	$2^{1/2}{}^b$ ( $3^{1/2}{}^c$ )	$140 \pm 60$
$\text{Fe}_2(\text{CO})_6^-$	$1^{1/2}{}^b$ ( $2^{1/2}{}^c$ )	$16 \pm 2$
$\text{Fe}_2(\text{CO})_7^-$	$1/2{}^b$ ( $1^{1/2}{}^c$ )	$< 0.2$
$\text{Fe}_2(\text{CO})_8^-$	$1/2{}^b$	$< 0.1$
$\text{Fe}_3(\text{CO})_9^-$	$1^{2/3}$	$150 \pm 60$
$\text{Fe}_3(\text{CO})_{10}^-$	1	$1.4 \pm 0.5$
$\text{Fe}_4(\text{CO})_{11}^-$	$1^{1/4}$	$6.5 \pm 3.0$
$\text{Fe}_4(\text{CO})_{12}^-$	$3/4$	$< 0.4$
$\text{Fe}_4(\text{CO})_{13}^-$	$1/4$	$< 2$

<sup>a</sup> Relative to the rate constant for reaction of  $\text{Fe}(\text{CO})_4^-$ .

<sup>b</sup> Assuming a double bond between the Fe atoms. <sup>c</sup> Assuming a single bond between the Fe atoms.

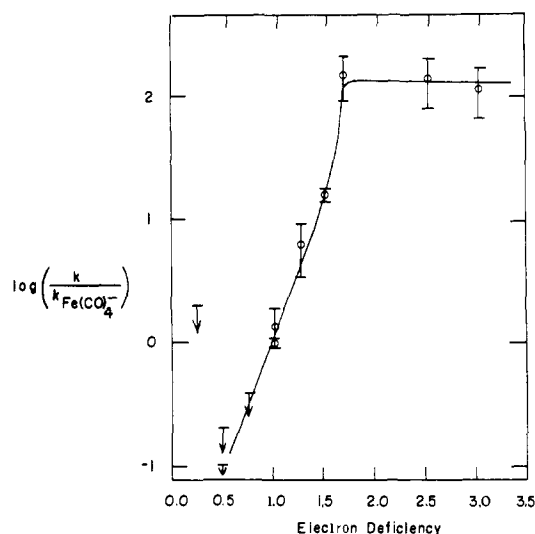


Figure 3. Relative rate constants for reaction of  $\text{Fe}_n(\text{CO})_m^-$  ions vs. electron deficiency assuming  $\text{Fe}_2(\text{CO})_6^-$  species have double metal-metal bonds where  $m = 5, 6,$  and  $7$ .

relative rate of reaction was not obtained. At nominal electron beam energies below 5 eV,  $\text{Fe}(\text{CO})_2^-$  and its daughters are not observed.

## Discussion

**Metal-to-Metal Double Bonds.** Inspection of Table I reveals that the relative rate constants tend to decrease with the number of CO ligands in the cluster. This is to be expected since the reactivity of transition metal complexes generally increases with coordinative unsaturation. The 18-electron rule provides the simplest basis for quantifying coordinative unsaturation. Listed in Table I as a measure of coordinative unsaturation are the electron deficiencies per iron atom of each reactant ion determined by the 18-electron rule. This is obtained by subtracting the total number of valence electrons from  $n \times 18$ , where  $n$  is the number of Fe atoms in the clusters, and dividing the result by  $n$ . A deficiency of two electrons per iron atom indicates that on average each iron atom in the cluster has a vacancy in its coordination shell for one 2-electron donating ligand such as CO. Clusters with deficiencies of 2 or more electrons per iron atom should, therefore, be particularly accessible to interaction with neutral reactant molecules. Indeed, it is evident from Figure 3 that rate constants are large for clusters with deficiencies above 2 and drop rapidly for smaller deficiencies.

Determination of the number of valence electrons in the clusters requires assumptions about the number of metal-metal bonds in the clusters. A metal-metal bond adds an electron to the valence shells of each of the bonded metal atoms. The assumptions that give the deficiencies in Table I are (1) clusters with four iron atoms have six metal-metal bonds as they would in a tetrahedral structure; (2) the clusters with three iron atoms have three

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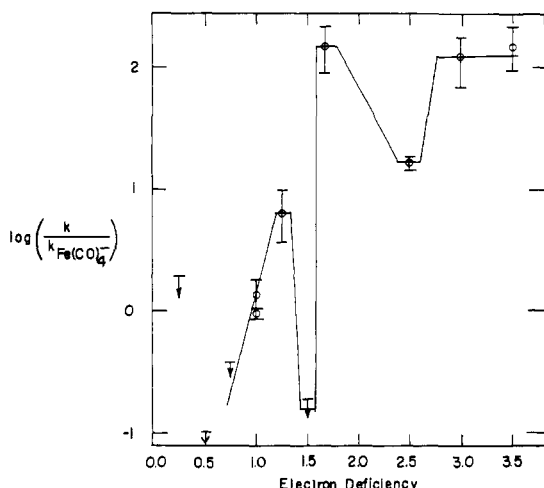


Figure 4. Relative rate constants for reaction of  $\text{Fe}_n(\text{CO})_m^-$  ions vs. electron deficiency assuming  $\text{Fe}_2(\text{CO})_m^-$  species have single metal-metal bonds.

metal-metal bonds as they would in a triangular structure; and (3) the clusters with two iron atoms have a double bond between the iron atoms except in  $\text{Fe}_2(\text{CO})_8^-$  where that is forbidden by the 18-electron rule. ESR evidence<sup>10</sup> suggests that  $\text{Fe}_3(\text{CO})_{11}^-$  is triangular with three metal-metal bonds and that  $\text{Fe}_4(\text{CO})_{13}^-$  is tetrahedral with six metal-metal bonds. If it is assumed that the clusters with two iron atoms all have only a single metal-metal bond, their electron deficiencies change from those used to plot Figure 3. Figure 4 shows the results of using these "single bond electron deficiencies" to plot the rate constants against electron deficiency. No longer does the reactivity remain large until the deficiency drops to two electrons and then decline sharply and regularly. This supports the assumption that  $\text{Fe}_2(\text{CO})_5^-$ ,  $\text{Fe}_2(\text{CO})_6^-$ , and  $\text{Fe}_2(\text{CO})_7^-$  have double metal-metal bonds. While this is tenuous evidence, previous studies have not provided any evidence on the electronic structure of gaseous ionic metal carbonyl clusters.

Several features of the relationship between electron deficiency and relative rate constants merit further comment. It is consistent with the general behavior of transition metal complexes that complexes with an electron deficiency of two per iron atom should react much more rapidly than complexes which are coordinatively saturated or nearly so (electron deficiency  $\leq 1$ ). Figure 3 shows that the present systems follow that pattern if we make the assumptions about metal-metal bonding outlined above. It also appears in Figure 3, however, the  $\log k$  for reactions of complexes with electron deficiencies between 1 and 2 drops almost linearly with electron deficiency. We are not aware of previous experimental or theoretical work which would lead us to expect this effect. It is not difficult, however, to rationalize the fact that the rate constants for these species fall in an intermediate range between the more nearly saturated complexes and those with an average electron deficiency  $\geq 2$ . The species in this category are  $\text{Fe}_2(\text{CO})_6^-$ ,  $\text{Fe}_3(\text{CO})_{10}^-$ , and  $\text{Fe}_4(\text{CO})_{11}^-$ . It is possible that in each of these species the coordinative unsaturation of one Fe atom in the cluster can be increased by moving a CO ligand. The CO could move from a terminal site on one metal atom to a bridging position to a terminal position on another metal atom, or from a bridging position to a terminal position. This would shift electron deficiency from one Fe atom to another and create one site with a deficiency of two electrons. This kind of shift should require less energy than actually removing a CO from the coordination shell of the metal atom. Thus, these complexes react at rates intermediate between the more nearly saturated species and those species with electron deficiencies  $\geq 2$ .

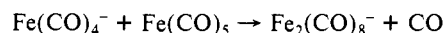
Another interesting feature of the data in Table I is that the fast rate constants seem to go to an approximately constant value for electron deficiencies  $\geq 2$ . Although there are difficulties in measuring the absolute rate constants accurately, we estimate that the rate constant for reaction of  $\text{Fe}(\text{CO})_4^-$  is given by  $\log k = 12 \pm 0.5$ .<sup>18-20</sup> This implies that the largest rate constants are within

an order of magnitude of the collision rate. This is, of course, what is expected. The highly unsaturated complexes should react at a rate limited only by the frequency of collisions and, perhaps, the inherent efficiency of those features of the reaction mechanism common to all the clustering reactions. That is, we expect highly coordinatively unsaturated clusters to react at the collision frequency or perhaps at a constant fraction of the collision frequency. The latter case would be a consequence of some entropy of activation term common to the mechanisms of all the clustering reactions. Our rough estimate of the absolute rates would imply that the fastest rate constants are about 15% of the collision rate.

Comparison of Figures 3 and 4 suggest that the conclusion concerning double metal bonds rests on just two of the rate constants, those for  $\text{Fe}_2(\text{CO})_6^-$  and  $\text{Fe}_2(\text{CO})_7^-$ . Actually, the assignment of the number of bonds in the three and four metal atom complexes are equally important. Changing the number of metal-metal bonds assigned to these species would have a dramatic effect on the coherence of any interpretation. Fortunately, the number of bonds in complexes closely related to the three and four metal atom clusters are known from condensed-phase studies.<sup>10</sup>

**Larger Clusters.** An important feature of the multiple resonance experiments is the production of clusters containing five iron atoms. These ions result when  $\text{Fe}_4(\text{CO})_{12}^-$  is excited at its cyclotron frequency and decomposes on collision to  $\text{Fe}_4(\text{CO})_{11}^-$  which reacts to form the clusters containing five iron atoms, the most abundant of which is  $\text{Fe}_5(\text{CO})_{14}^-$ . This suggests that clusters of arbitrary size can be prepared by removing ligands from smaller clusters to enhance their clustering reactivity. A similar conclusion is suggested by studies of infrared multiphoton dissociation of cationic metal carbonyl clusters.<sup>21</sup>

**Comparison with Solution.** Using electron spin resonance (ESR) spectroscopy, we observed<sup>10</sup>  $\text{Fe}_2(\text{CO})_8^-$ ,  $\text{Fe}_3(\text{CO})_{11}^-$ ,  $\text{Fe}_3(\text{CO})_{12}^-$ , and  $\text{Fe}_4(\text{CO})_{13}^-$  in the condensed phase as products of the reduction of  $\text{Fe}(\text{CO})_5$  by alkali metals in THF.  $\text{Fe}(\text{CO})_4^-$  is not observed in the condensed phase. The reactions in the gas phase indicate that  $\text{Fe}_2(\text{CO})_8^-$  in the condensed phase may be formed by



The gas-phase rate constant for this reaction is approximately  $10^{-12} \text{ cm}^3 \text{ s}^{-1}$  ( $-\log k = 12 \pm 0.5$ ).<sup>19</sup> In the lowest concentrations used in the condensed phase studies ( $10^{-3} \text{ M}$ ), this rate constant would result in a half-life of less than a 1 ms for  $\text{Fe}(\text{CO})_4^-$ . This is consistent with the absence of  $\text{Fe}(\text{CO})_4^-$  in the ESR spectra of the reduction products of  $\text{Fe}(\text{CO})_5$ . An alternative explanation of the formation of  $\text{Fe}_2(\text{CO})_8^-$  in the condensed phase postulates the dimerization of  $\text{Fe}(\text{CO})_4^-$  to form  $\text{Fe}_2(\text{CO})_8^{2-}$  which is oxidized to  $\text{Fe}_2(\text{CO})_8^-$ . Such a process cannot be the source of  $\text{Fe}_2(\text{CO})_8^-$  in the gas phase because dimerization of like-charged ions is impossible unless the coulombic repulsion is mediated by solvent. The gas-phase results thus show that direct reaction of  $\text{Fe}(\text{CO})_4^-$  with  $\text{Fe}(\text{CO})_5$  can account for formation of  $\text{Fe}_2(\text{CO})_8^-$  in the condensed phase and that it is not necessary to postulate dimerization of  $\text{Fe}(\text{CO})_4^-$ .

In addition to  $\text{Fe}_2(\text{CO})_8^-$ ,  $\text{Fe}_4(\text{CO})_{13}^-$  is also observed in both the gas phase and the condensed phase. In the gas phase  $\text{Fe}_4(\text{CO})_{13}^-$  results from a reaction sequence that begins with  $\text{Fe}(\text{CO})_3^-$  and includes  $\text{Fe}_3(\text{CO})_{10}^-$  as a reaction intermediate.  $\text{Fe}_3(\text{CO})_{11}^-$  is observed in the condensed phase and  $\text{Fe}(\text{CO})_4^-$  may

(18) Determined by estimating  $k_1$  from the time required for signal to decay to half its initial value following turning off the electron beam. This time is found to agree reasonably well with times calculated from a theoretical model of trapping described in Wronka, J., Ph.D. Dissertation, University of Delaware, 1982, and ref 20. This theoretical model determines loss resulting from the motion of the ions to the cell plates produced by the combined effects of collisions and the electrostatic potentials applied to the plates. It is based on previous treatments of ion motion in an ICR cell<sup>16,19</sup> and is the subject of a paper to be submitted.<sup>20</sup> In a typical experiment, the trapping time was 12 s and the theoretical model gave 19 s. In this case,  $k_1$  would be taken as  $1/12 \text{ s}^{-1}$ .

(19) Ridge, D. P., Beauchamp, J. L. *J. Chem. Phys.* **1976**, *64*, 2735-2746.

(20) Wronka, J.; Ridge, D. P., to be submitted for publication.

(21) Beauchamp, J. L., private communication.

have a transient existence as discussed above. The loss of a carbonyl group (CO) by either of these species would give a gas-phase precursor for  $\text{Fe}_4(\text{CO})_{13}^-$ . Were these precursor ions to react to solution with the same rate constants as they do in the gas phase, they would have lifetimes of less than a 1 ms and not be observable by ESR. If the energy required for  $\text{Fe}(\text{CO})_4^-$  and  $\text{Fe}_2(\text{CO})_{11}^-$  to lose a CO is not too large,<sup>22</sup> then it is possible that  $\text{Fe}_4(\text{CO})_{13}^-$  is formed in solution by the same mechanism as in the gas phase.

The other ions observed in condensed phase are  $\text{Fe}_3(\text{CO})_{11}^-$  and  $\text{Fe}_3(\text{CO})_{12}^-$ . These ions could also result from reaction sequences beginning with  $\text{Fe}(\text{CO})_4^-$  or  $\text{Fe}(\text{CO})_3^-$ . In the condensed phase the loss of CO ligands in the individual steps of the clustering

(22) If  $D(\text{Fe}(\text{CO})_3^- - \text{CO}) \approx 0.25$  eV, then  $\text{Fe}(\text{CO})_3^-$  might form by dissociation of  $\text{Fe}(\text{CO})_4^-$  at a sufficiently rapid rate to produce observable products in condensed phase. Appearance potential measurements (ref 17) do not give a definitive value for  $D(\text{Fe}(\text{CO})_3^- - \text{CO})$ , but do suggest that it is substantially less than 1 eV.

reaction could be moderated by the solvent medium. In the gas phase the collision complex of  $\text{Fe}_2(\text{CO})_6^-$  with  $\text{Fe}(\text{CO})_5$  can only dissipate reaction exothermicity by losing some fragment such as CO. In the condensed-phase reaction exothermicity can be dissipated to the medium without loss of CO. Thus, in the condensed phase  $\text{Fe}_2(\text{CO})_6^-$  might associate directly with  $\text{Fe}(\text{CO})_5$  to form  $\text{Fe}_3(\text{CO})_{11}^-$ .  $\text{Fe}_3(\text{CO})_{12}^-$  might similarly result from direct association of  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}_2(\text{CO})_7^-$  formed by loss of CO from  $\text{Fe}_2(\text{CO})_8^-$  or from reaction of  $\text{Fe}_2(\text{CO})_8^-$ . Although not observed to react in the gas phase,  $\text{Fe}_2(\text{CO})_8^-$  could react as a rate fast enough to produce observable product in the condensed-phase studies, but too slow to be observed in the present gas-phase studies.

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**Registry No.**  $\text{Fe}(\text{CO})_5$ , 13463-40-6;  $\text{Fe}(\text{CO})_3^-$ , 53221-56-0;  $\text{Fe}(\text{CO})_4^-$ , 51222-96-9.

## Mechanism of Carbon Monoxide Substitution in Metal Carbonyl Radicals: Vanadium Hexacarbonyl and Its Phosphine-Substituted Derivatives

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**Abstract:** Carbon monoxide substitution in the metal radical  $\text{V}(\text{CO})_6$  proceeds at or below room temperature to form monosubstitution products  $\text{V}(\text{CO})_5\text{L}$  (L = phosphine or phosphite). The substitution occurs solely by a second-order process according to a rate law that is first order in both  $\text{V}(\text{CO})_6$  and phosphorus nucleophile. The rate of reaction is strongly dependent on the basicity and size of the ligand. Activation parameters further support the associative nature of the reaction:  $\text{P}(n\text{-Bu})_3$ ,  $\Delta H^\ddagger = 7.6 \pm 0.4$  kcal/mol,  $\Delta S^\ddagger = -25.2 \pm 1.7$  cal/mol-deg;  $\text{P}(\text{OMe})_3$ ,  $\Delta H^\ddagger = 10.9 \pm 0.2$  kcal/mol,  $\Delta S^\ddagger = -22.6 \pm 0.8$  cal/mol-deg;  $\text{PPh}_3$ ,  $\Delta H^\ddagger = 10.0 \pm 0.4$  kcal/mol,  $\Delta S^\ddagger = -27.8 \pm 1.6$  cal/mol-deg. The rate of substitution of  $\text{V}(\text{CO})_6$  by  $\text{PPh}_3$  is unchanged under 1 atm of carbon monoxide or in the presence of  $[\text{V}(\text{CO})_6]^-$ . The carbon monoxide substitution reactions of  $\text{V}(\text{CO})_5\text{L}$  with additional L also proceed by an associative mechanism with the rate of substitution approximately three orders of magnitude slower than for  $\text{V}(\text{CO})_6$ . The disubstituted product adopts the cis stereochemistry with small phosphorus donor ligands or with chelating phosphines. For L =  $\text{P}(\text{OMe})_3$ , activation parameters were determined:  $\Delta H^\ddagger = 13.2 \pm 0.4$  kcal/mol,  $\Delta S^\ddagger = -27.6 \pm 1.8$  cal/mol-deg. Phosphine exchange reactions of  $\text{V}(\text{CO})_5\text{L}$  were also observed indicating that, in addition to carbon monoxide, phosphine ligands on vanadium are substitution labile. Nucleophilic attack of  $\text{P}(n\text{-Bu})_3$  at  $\text{V}(\text{CO})_5[\text{P}(n\text{-Bu})_3]$  is  $10^5$  times slower than that at  $\text{V}(\text{CO})_6$ , presumably because the increased electron density on the metal hinders nucleophilic attack. Quantitative comparisons between the 17-electron complex  $\text{V}(\text{CO})_6$  and its 18-electron analogue  $\text{Cr}(\text{CO})_6$  indicate that associative carbon monoxide substitution takes place  $10^{10}$  times faster in the vanadium system.

Metal carbonyl radicals have become increasingly prevalent in organometallic chemistry.<sup>1</sup> In addition to their postulated role as intermediates in a variety of catalytic and stoichiometric chemical transformations, several stable, paramagnetic organometallic complexes have been isolated recently.<sup>2</sup> Typically these are stabilized by phosphine or cyclopentadienyl ligands. Vanadium hexacarbonyl is unique as the only stable homoleptic metal carbonyl radical.<sup>3</sup> This has prompted a number of investigations of the physical properties of  $\text{V}(\text{CO})_6$  by X-ray crystallography,<sup>4</sup> EPR,<sup>5</sup> electrochemical techniques,<sup>6</sup> electronic spectra, and theoretical calculations.<sup>7</sup> In addition, synthetic studies resulting in phosphine substitution,<sup>8</sup> disproportionation,<sup>3,9</sup> or reduction of

$\text{V}(\text{CO})_6$  have been reported.<sup>10</sup> Indeed, substitution and electron-transfer processes are often competitive reactions in the

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