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Gas Phase Study of the Kinetics of Formation and Dissociation of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ ($L = C_2H_4$ and C_2F_4)

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The bond dissociation energy for loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$, produced by the reaction of C_2H_4 + $Fe(CO)_3(C_2H_4)$, has been determined as 21.3 ± 2.0 kcal/mol. An estimate is made for a lower limit for the bond dissociation energy of $Fe(CO)_4(C_2H_4)$, which can be formed by reaction of CO + $Fe(CO)_3(C_2H_4)$ or $Fe(CO)_4$ + C_2H_4 with rate constants of $(4.3 \pm 0.8) \times 10^{-12}$ and $(1.7 \pm 0.2) \times 10^{-13}$ cm^3/(molecule s) at 24 °C, respectively. The values for these bond dissociation energies are compared with those determined in prior studies of these systems. A new compound with infrared absorptions at 2147, 2091, and 2068 cm^{-1} is best assigned as $Fe(CO)_3(C_2F_4)_2$. A rate constant of $(5.4 \pm 1.7) \times 10^{-12}$ cm^3/(molecule s) at 24 °C is reported for the reaction of C_2F_4 with $Fe(CO)_3(C_2F_4)$ to form $Fe(CO)_3(C_2F_4)_2$. $Fe(CO)_4(C_2F_4)$ can be formed by reaction of C_2F_4 and $Fe(CO)_4$, with a rate constant of $(1.8 \pm 0.4) \times 10^{-14}$ cm^3/(molecule s) at 24 °C. Infrared absorptions observed at 2135, 2074, and 2043 cm^{-1} are assigned to this species. The relative stabilities of the mono- and bisethylene and perfluoroethylene compounds of iron are compared. Where possible, they are also compared to the corresponding chromium compounds and are discussed in the context of current concepts regarding metal−olefin bonding.

I. Introduction

Olefins have a long history as ligands in organometallic compounds, dating to Zeise's salt.[1] Olefins can participate in a variety of catalytic transformations induced by organometallic species including isomerization, hydrogenation, and hydrosilation processes.[2−4] Efforts have been made to delineate the microscopic kinetics involved in the complex kinetic mechanisms that lead to such transformations.[5−8] Recently, using time-resolved infrared spectroscopy, it has been possible to identify and demonstrate that $Fe(CO)_3(C_2H_4)_2$[5,7,8] and $H_2Fe(CO)_3(C_2H_4)$[7,8] are crucial intermediates in the gas phase catalytic hydrogenation of ethylene induced by photolysis of $Fe(CO)_5$. It has also been pointed out that a knowledge of the rates of dissociation of these species, which depend on the bond dissociation energies, is crucial to formulating a complete model of the kinetics of this system.[8]

For more than 40 years, the Dewar−Chatt−Duncanson model has provided a framework for discussing metal-olefin bonding.[9,10] As implied above, a knowledge of the magnitudes of olefin−metal bonds can be crucial to a full understanding of the reaction mechanisms involving such species. Though there has been progress in the ability to experimentally measure and to quantitatively calculate bond energies, information in this area is still limited.

This study employs time-resolved infrared spectroscopy to monitor the rates of formation and dissociation of a number of iron carbonyl−olefin species. Where possible, comparisons are made to corresponding Cr compounds. An objective is to obtain a better understanding of how the nature of the olefin, the number of olefin ligands, and the nature of the metal center influence bonding and bond dissociation energies. Systems studied include $Fe(CO)_4(C_2H_4)$, $Fe(CO)_3(C_2H_4)_2$, $Fe(CO)_4(C_2F_4)$, and an iron carbonyl compound containing multiple C_2F_4 ligands. The infrared absorptions of this latter compound are not compatible with those previously assigned to iron tetracarbonyl−cyclooctafluorotetramethylene.[11] As such, the absorptions identified in this study are best assigned to a new compound, $Fe(CO)_3(C_2F_4)_2$, an analog of the previously identified compound, iron bisethylene−tricarbonyl.

II. Experimental Section

The apparatus used to monitor CO and C_2H_4 addition to $Fe(CO)_3(C_2H_4)$ has been described previously.[12,13] Coordinatively unsaturated metal carbonyls are photogenerated by the output of either a frequency-tripled Nd:YAG laser (355 nm) or an excimer laser, operating on either XeF (351 nm) or XeCl (308 nm). In each case, the laser delivered 7−10 mJ/cm^2 at the cell window. Photolysis of $Fe(CO)_5$ at either 355 or 351 nm is expected to produce an ∼60:40 mixture of $Fe(CO)_3$ and $Fe(CO)_4$[14] while photolysis at 308 nm produces almost exclusively $Fe(CO)_3$.[15]

The infrared beam from either a home-built, line-tunable, CO laser or a diode laser was used to probe the kinetics of association reactions. The beam double passed either a 16 or a 42 cm long gas cell terminated with CaF_2 windows. Detection of the infrared laser beam was by a fast ($\tau_{1/2} \approx 70$ ns) InSb detector. The output of the detector was amplified and sent to a digital oscilloscope which averaged 20−40 wave forms. The digitized, averaged signal was sent to a computer for fitting and analysis.

Rate constants for association reactions were measured under the indicated conditions in a static cell: $Fe(CO)_3(C_2H_4)$ + C_2H_4 − 0.200−0.210 Torr of $Fe(CO)_5$, 0.49−11.42 Torr of C_2H_4, and enough He to bring the total pressure to at least 90 Torr; $Fe(CO)_3(C_2H_4)$ + CO − 0.200−0.211 Torr of $Fe(CO)_5$, 1.22−2.02 Torr of C_2H_4, 0.00−8.36 Torr of CO, and He to raise the total pressure to at least 85 Torr; $Fe(CO)_4$ + C_2H_4 − 0.030−0.037 Torr of $Fe(CO)_5$, 11.2−153.5 Torr of C_2H_4, and enough He to bring the total pressure to at least 90 Torr; $Fe(CO)_3$ + C_2F_4 − ∼0.025 Torr $Fe(CO)_5$, 0.000−1.010 Torr C_2F_4 and enough He to bring the total pressure to at least 80 Torr; $Fe(CO)_4$ + C_2F_4 − ∼0.1 Torr of $Fe(CO)_5$, 3.66−51.11 Torr of C_2F_4, and either ∼2.4 or ∼3.9 Torr of CO and He to bring the total pressure to at least 75 Torr; $Fe(CO)_3(C_2F_4)$ + C_2F_4 − ∼0.050 Torr of $Fe(CO)_5$, 1.055−9.00 Torr of C_2F_4, and enough He to bring the total pressure to at least 85 Torr. All of the experiments that involved ethylene as a ligand were performed using 351 nm photoysis pulses while those with perfluoroethylene as a ligand were performed using 308 nm photoysis pulses.

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Dissociation of Fe(CO)$_3$(C$_2$H$_4$)$_2$ was monitored with a Mattson RS1 FTIR operating at 4 cm^{-1} resolution and averaging 25 scans. A spectrum was obtained every 3 s for the first 35 s and every 5.7 s thereafter. Samples were followed out to 0.5−10 min, depending on the ratio of C$_2$H$_4$:CO and the temperature. Samples of 0.098−0.134 Torr of Fe(CO)$_5$, 19.6−200 Torr of CO, and 404−641 Torr of C$_2$H$_4$ were placed in a 42 cm long, 2 $^1/_2$ cm diameter static gas cell. The cell contents were allowed to thermally equilibrate and mix for 30 min before being photolyzed for ~20 s at 10 Hz with the output of the frequency-tripled Nd:YAG laser.

Experiments directed toward a measurement of the bond dissociation energy for Fe(CO)$_4$(C$_2$H$_4$) involved photolysis of mixtures of 0.020−0.203 Torr of Fe(CO)$_5$, 20−330 Torr of CO, and 100−565 Torr of C$_2$H$_4$ with ~200 laser pulses from a frequency-tripled Nd:YAG laser. Analogous experiments directed toward measurements of the bond dissociation energy for Fe(CO)$_4$(C$_2$F$_4$) and Fe(CO)$_3$(C$_2$F$_4$)$_2$ involved photolysis of mixtures of 0.100−0.200 Torr of Fe(CO)$_5$, 8.3−111.0 Torr of CO, and 39.5−65.6 Torr of C$_2$F$_4$ with between ~200 and 1000 pulses from the frequency-tripled Nd:YAG laser. The cells used for these experiments were covered with opaque tape to inhibit photolytic processes due to ambient light.

For experiments above room temperature, the cells were wrapped with heating tape and insulated with cotton batting. The windows of the 16 cm cell were warmed with two 60 W incandescent light bulbs to inhibit the condensation of iron carbonyls. Chromel−alumel thermocouples, attached to the outside of the cells, monitored the temperature. The temperature uncertainty for the 16 cm cell was ±1 K and ±2 K for the 42 cm cell.

Fe(CO)$_5$ was obtained from Aldrich Chemical and subjected to a series of freeze−pump−thaw cycles before use. At the beginning of each day, the iron pentacarbonyl was briefly pumped on to remove CO and any volatile polynuclear iron species that were present due to decomposition. C$_2$F$_4$ (97%) was purchased inhibited from PCR Corp. The gas was passed through a copper tube packed with activated charcoal to remove the D-limonene inhibitor. Based on a calibration with neat D-limonene, FTIR measurements of the C$_2$F$_4$, subsequent to this procedure, showed the D-limonene concentration was less than 0.07%. The following gases were obtained from Matheson, at the indicated purity, and were used as received: C$_2$H$_4$, 99.5%; CO, 99.9%; He, 99.999%.

III. Results

The kinetic scheme used to determine bond dissociation energies (BDEs), based on dissociative loss of a ligand bound to a metal carbonyl, has been previously described.[16] Conditions are set up such that the rate of loss of a weakly bound ligand is rate-limiting in the regeneration of parent or a product produced by addition of another ligand, typically CO. For the case of Fe(CO)$_3$(C$_2$H$_4$)$_2$, the relevant reactions are

$$\mathrm{Fe(CO)_3(C_2H_4)_2} \xrightarrow{k_d} \mathrm{Fe(CO)_3(C_2H_4)} + \mathrm{C_2H_4} \tag{1}$$

$$\mathrm{Fe(CO)_3(C_2H_4)} + \mathrm{C_2H_4} \xrightarrow{k_2} \mathrm{Fe(CO)_3(C_2H_4)_2} \tag{2}$$

$$\mathrm{Fe(CO)_3(C_2H_4)} + \mathrm{CO} \xrightarrow{k_3} \mathrm{Fe(CO)_4(C_2H_4)} \tag{3}$$

$$\mathrm{Fe(CO)_3(C_2H_4)} + \mathrm{Fe(CO)_5} \xrightarrow{k_4} \mathrm{Fe_2(CO)_8(C_2H_4)} \tag{4}$$

where it is assumed that the polynuclear compound formed as a result of reaction of Fe(CO)$_3$(C$_2$H$_4$) with Fe(CO)$_5$ is Fe$_2$(CO)$_8$(C$_2$H$_4$). Fe(CO)$_3$(C$_2$H$_4$)$_2$ is initially produced by sequential addition of C$_2$H$_4$ to Fe(CO)$_3$. Fe(CO)$_4$(C$_2$H$_4$), the product in reaction 3, dissociates on a much longer time scale than Fe(CO)$_3$(C$_2$H$_4$)$_2$. As a result, addition of CO to Fe(CO)$_3$(C$_2$H$_4$) is effectively an irreversible step, taking the coordinatively unsaturated species out of the formation−dissociation cycle for Fe(CO)$_3$(C$_2$H$_4$)$_2$. Under experimental conditions, as applied to the dissociation of Fe(CO)$_3$(C$_2$H$_4$)$_2$, the process in eq 4 is not expected to be significant and can be neglected. Applying the steady state approximation to Fe(CO)$_3$(C$_2$H$_4$) results in the following expression for the dissociation rate constant, k_d, for Fe(CO)$_3$(C$_2$H$_4$)$_2$:

$$k_d = k_{obs}\left(\frac{k_2[\mathrm{C_2H_4}]}{k_3[\mathrm{CO}]} + 1\right) \tag{5}$$

k_{obs} is a first-order phenomenological rate constant for the disappearance of the substituted species and the appearance of the compound resulting from CO addition, in this case Fe(CO)$_4$(C$_2$H$_4$). The temperature dependence of k$_d$ can be related to the bond dissociation energy; [12] therefore, it is necessary to measure the temperature dependence of k_2, k_3, and k_{obs} to determine a bond dissociation energy.

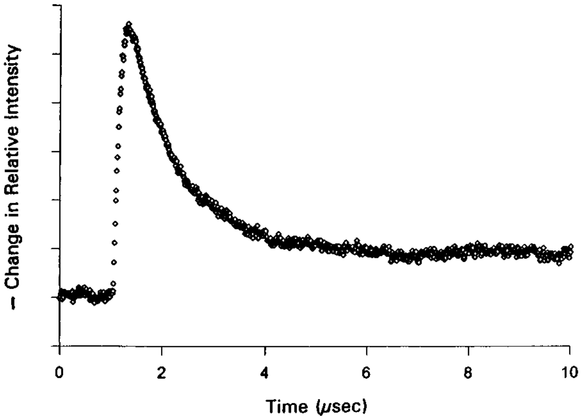

Figure 1. Plot of the negative of the change in relative intensity of the probe beam at 1966 cm^{-1} versus time following 355 nm photolysis of 0.205 Torr of Fe(CO)$_5$, 2.02 Torr of C$_2$H$_4$, 3.10 Torr of CO, and 88.8 Torr of He. The rise is due to formation of Fe(CO)$_3$(C$_2$H$_4$) which is depleted on reaction with CO or C$_2$H$_4$.

A. Addition Rate Constants. The rate constants for the various addition reactions were determined from plots of the rate of the addition process versus pressure of the appropriate ligand (under pseudo-first-order conditions), monitored at an absorption of either or both the iron carbonyl reactant or the reaction product. Experiments were performed to assure measurements on all reactions were in the high-pressure limit below the total pressure listed in section II.[13]

1. *Fe(CO)$_3$(C$_2$H$_4$) + CO.* A plot of a typical signal, monitored at the 1966 cm^{-1} absorption of Fe(CO)$_3$(C$_2$H$_4$) used to probe the reaction of Fe(CO)$_3$(C$_2$H$_4$) + CO, is shown in Figure 1. Figure 2 shows a plot of the rate for this process versus CO pressure at 35 °C, which yields a rate constant of (4.3 ± 0.8) × 10^{-12} cm^3/(molecule s). Within experimental error the rate constant is independent of temperature from 24 to 47 °C. The errors on measured rate constants are ±2σ and are based solely on precision.

2. *Fe(CO)$_3$(C$_2$H$_4$) + (C$_2$H$_4$) → Fe(CO)$_3$(C$_2$H$_4$)$_2$.* The rate constant for ethylene addition to Fe(CO)$_3$(C$_2$H$_4$), k$_2$, has been previously measured to be (10.8 ± 0.6) × 10^{-12} cm^3/(molecule s) at 23 °C.[7] In this work k_2 was measured to be (11.1 ± 0.8) × 10^{-12} cm^3/(molecule s) at 24 °C, in good agreement with the prior work, by plotting the rate of loss of Fe(CO)$_3$(C$_2$H$_4$) at

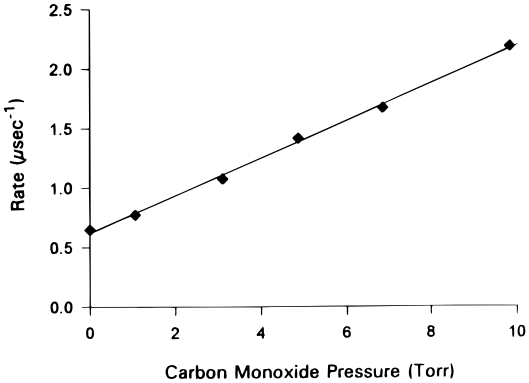

Figure 2. Rate of disappearance of $Fe(CO)_3(C_2H_4)$ probed at 1966 cm^{-1} plotted versus CO pressure.

1966 cm^{-1} versus pressure of C_2H_4. The rate constant is temperature independent from 24 to 45 °C.

3. $Fe(CO)_5 + Fe(CO)_3(C_2H_4) \rightarrow Fe_2(CO)_8(C_2H_4)$. The reaction of $Fe(CO)_5$ and $Fe(CO)_3(C_2H_4)$ is included in the kinetic scheme discussed above, as eq 4, and can potentially act as a termination step in the catalytic hydrogenation of C_2H_4.[8] The kinetic equation for the loss of $[Fe(CO)_3(C_2H_4)]$ is

$$\frac{-d[Fe(CO)_3(C_2H_4)]}{dt} = (k_3[CO] + k_2[C_2H_4] + k_4[Fe(CO)_5])[Fe(CO)_3(C_2H_4)] \quad (6)$$

Experiments to determine the rate constant for addition of C_2H_4 to $Fe(CO)_3(C_2H_4)$, at 1966 cm^{-1}, were performed at a constant pressure of $Fe(CO)_5$, in the absence of added CO, under the conditions indicated in section II. Only a small portion of the initial concentration of $Fe(CO)_5$ is photolyzed during each experiment. Thus, $[Fe(CO)_5] \gg [CO]$, where the CO is produced photolytically, and the first term on the right-hand side of eq 6 can be ignored. The intercept of a plot of reaction rate, in eq 6, versus C_2H_4 pressure gives the rate of formation of polynuclear species which on division by the $Fe(CO)_5$ concentration yields $k_4 = (4 \pm 2) \times 10^{-11}$ cm^3/(molecule s) at 24 °C.

4. $Fe(CO)_4 + C_2H_4 \rightarrow Fe(CO)_4(C_2H_4)$. The rate constant for addition of ethylene to $Fe(CO)_4$ was determined to be $(1.7 \pm 0.2) \times 10^{-13}$ cm^3/(molecule s) by plotting the rate of the rise of $Fe(CO)_4(C_2H_4)$, at 2024 cm^{-1}, versus the pressure of C_2H_4 at 24 °C. The rate constant is temperature independent up to 46 °C.

5. $Fe(CO)_3 + C_2F_4 \rightarrow Fe(CO)_3(C_2F_4)$. The rate of loss of $Fe(CO)_3$ at 1955 cm^{-1} was plotted against C_2F_4 pressure to give a rate constant of $(3.3 \pm 1.2) \times 10^{-11}$ cm^3/(molecule s) at 24 °C.

6. $Fe(CO)_4 + C_2F_4 \rightarrow Fe(CO)_4(C_2F_4)$. The rate constant for $Fe(CO)_4 + C_2F_4$ was determined by monitoring the rate of loss of $Fe(CO)_4$ and the rise of $Fe(CO)_4(C_2F_4)$. CO present in the cell can react with nascent $Fe(CO)_3$ to generate $Fe(CO)_4$ subsequent to 308 nm photolysis of $Fe(CO)_5$. A plot of the rate of loss of $Fe(CO)_4$ at 1990 cm^{-1} versus C_2F_4 pressure gives a rate constant of $(1.3 \pm 0.5) \times 10^{-14}$ cm^3/(molecule s) at 24 °C. A plot of the rate of rise of product at 2076 cm^{-1} versus C_2F_4 pressure gave a rate constant of $(2.2 \pm 0.6) \times 10^{-14}$ cm^3/(molecule s) at 24 °C. These measurements yield an error weighted average rate constant of $(1.8 \pm 0.4) \times 10^{-14}$ cm^3/(molecule s).

7. $Fe(CO)_3(C_2F_4) + C_2F_4 \rightarrow Fe(CO)_3(C_2F_4)_2$. The rate of rise of an absorption at 2092 cm^{-1}, belonging to a species assigned as $Fe(CO)_3(C_2F_4)_2$ (see section B), was plotted against C_2F_4 pressure to give a rate constant of $(5.4 \pm 1.7) \times 10^{-12}$ cm^3/(molecule s) at 24 °C.

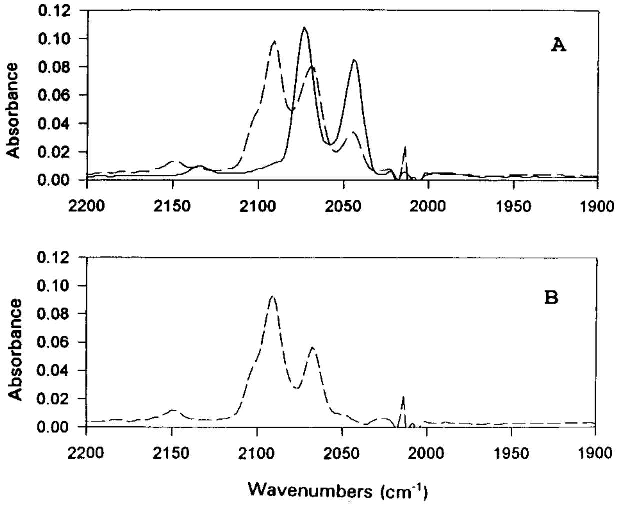

Figure 3. Spectra generated on 355 nm photolysis of $Fe(CO)_5$, C_2F_4, and CO. A prephotolysis spectrum was used as the background in both experiments. (A) The solid line spectrum was recorded after 200 laser pulses irradiated a mixture of 0.106 Torr of $Fe(CO)_5$, 41.6 Torr of C_2F_4, and 48.7 Torr of CO. The dotted line spectrum was recorded after 1000 laser pulses irradiated a mixture of 0.106 Torr of $Fe(CO)_5$, 39.6 Torr of C_2F_4, 6.4 Torr of CO, and 54.1 Torr of He. (B) The solid line in panel A, assigned as $Fe(CO)_4(C_2F_4)$, was subtracted from the dotted line spectra in (A). The resulting spectrum (dotted line) is assigned to $Fe(CO)_3(C_2F_4)_2$. In both panels a reference spectrum of $Fe(CO)_5$ has been added in to compensate for photolytic loss of $Fe(CO)_5$.

B. $Fe(CO)_3(C_2F_4)_2$ and $Fe(CO)_4(C_2F_4)$ Absorptions. The spectrum indicated by the solid line in Figure 3A was generated by photolysis of 0.106 Torr of $Fe(CO)_5$, 41.6 Torr of C_2F_4, and 48.7 Torr of CO with 200 pulses from the tripled Nd:YAG laser. The spectrum indicated by the dotted line was generated by photolysis of 0.106 Torr of $Fe(CO)_5$, 39.6 Torr of C_2F_4, 6.4 Torr of CO, and 54.1 Torr of He photolyzed with 1000 pulses. In each case a full background spectrum was taken before photolysis, and an $Fe(CO)_5$ reference spectrum has been used to compensate for photolytic loss of $Fe(CO)_5$.

Iron carbonyl compounds, containing C_2F_4 as ligands, have been previously reported.[11,17–20] $Fe(CO)_4(C_2F_4)$ has been observed and studied by electron diffraction[19] and NMR.[20] $Fe(CO)_4(C_2F_4)_2$, which is thought to have two C_2F_4 ligands arranged in a cyclic structure[17] so that its formula can be written as $Fe(CO)_4(CF_2)_4$, has absorptions at 2150, 2092, 2072, and 2056 cm^{-1} in hexane.[11] The absorptions, in the carbonyl stretch region, of $Fe(CO)_4(C_2H_4)$, have been recorded in hydrocarbon solution and in the gas phase. The average shift is ~10 cm^{-1} to lower frequency for absorptions observed in solution relative to the gas phase.[21,22] The experimentally observed peaks at 2147, 2135, 2091, 2074, and 2043 cm^{-1} do not provide a good correspondence relative to the previously reported absorptions of $Fe(CO)_4(CF_2)_4$ when the expected liquid to gas phase shifts are considered. In addition, there is no absorption reported for $Fe(CO)_4(CF_2)_4$ that corresponds to the 2043 cm^{-1} absorption observed in these experiments.

Another indication that $Fe(CO)_4(CF_2)_4$ is not observed in the present experiments is the changes in relative peak intensities as a function of conditions. As can be seen in Figure 3A, changes in photolysis conditions and C_2F_4:CO ratio result in changes in the relative intensities of the peaks at 2091 and 2074 cm^{-1}. This clearly indicates that both of these absorptions cannot belong to the same species and thus the observed absorptions are due to more than one compound. Additionally, the absorptions that best correlate with some of those that would

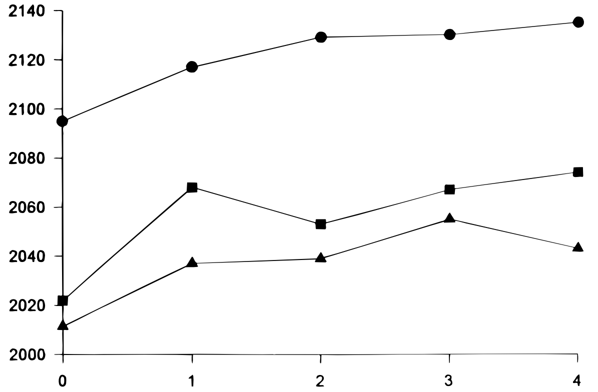

Figure 4. Frequencies of the carbonyl stretching absorptions in $Fe(CO)_4(C_2H_{4-x}F_x)$ are plotted versus X. The spectra of $Fe(CO)_4(C_2H_4)$ were obtained in the gas phase, and the positions indicated for the low-frequency A_1 and B_1 absorptions of $Fe(CO)_4(C_2H_4)$ are the average of the positions reported in refs 6 and 21. The absorptions reported in light petroleum have been shifted by $+10$ cm^{-1} to facilitate comparison with gas-phase absorptions. Symbols: ●, high-frequency A_1 absorption; ■, low frequency A_1 absorption; ▲, B_1 absorption.

be expected for $Fe(CO)_4(CF_2)_4$ are favored by lower C_2F_4 concentrations and shorter irradiation time: *opposite what would be anticipated* if these absorptions belonged to $Fe(CO)_4(CF_2)_4$.[18] Thus, we have no evidence to indicate that $Fe(CO)_4(CF_2)_4$ is produced in the present experiments. Experiments in which this compound was reported involved relatively long time scale solution phase photolysis[11] compared to the pulsed gas phase photolysis experiments described herein.

The simplest interpretation that is consistent with the data in Figure 3, and other related data generated by photolysis of $Fe(CO)_5$ in the presence of different concentrations of CO and C_2F_4, is that two different C_2F_4-containing species are produced by photolysis. The solid line spectrum in Figure 3A shows peaks at 2135 (0.04), 2074 (1.00), and 2043 cm^{-1} (0.78), which are assigned to $Fe(CO)_4(C_2F_4)$ due to their greater relative absorption with shorter photolysis times and lower C_2F_4:CO ratios. Additionally as indicated in section III.A.7, the rate of loss of $Fe(CO)_4$ in the presence of C_2F_4 and the rate of rise of the 2074 cm^{-1} absorption (monitored at 2076 cm^{-1}) assigned to $Fe(CO)_4(C_2F_4)$ agree within experimental error. The numbers in parentheses are the approximate relative peak heights. The peaks at 2147 (0.08), 2091 (1.00), and 2068 cm^{-1} (0.60) (Figure 3B), which are favored by longer photolysis times and higher C_2F_4:CO ratios, are assigned to another C_2F_4-containing iron carbonyl compound. This compound has not been previously reported, but its behavior is consistent with it being $Fe(CO)_3(C_2F_4)_2$, an analog of $Fe(CO)_3(C_2H_4)_2$. It would be expected to form, under conditions used to generate the spectra in Figure 3, by addition of a second C_2F_4 to a $Fe(CO)_3(C_2F_4)$ moiety that is generated by photolytic loss of CO from $Fe(CO)_4(C_2F_4)$ or directly by addition of two molecules of C_2F_4 to photolytically generated $Fe(CO)_3$. As indicated in section III.A.7, and consistent with this assignment, the reaction that occurs involving $Fe(CO)_3$, which is almost the exclusive photoproduct of 308 nm photolysis of $Fe(CO)_5$, and C_2F_4 was monitored at 2092 cm^{-1}. This frequency lies within the strongest absorption of the species observed in Figure 3B.

The assignment of absorptions at 2135, 2074, and 2043 cm^{-1} to $Fe(CO)_4(C_2F_4)$, which appears to be the first literature report of infrared absorptions for this compound**,** is supported by their positions relative to the IR absorptions of related compounds. Figure 4 shows the literature values for the infrared absorptions, in the CO stretching region, for $Fe(CO)_4(C_2H_{4-x}F_x)$ compounds where $x = 0-4$. $Fe(CO)_4(C_2H_3F)$, $Fe(CO)_4(C_2H_2F_2)$, and $Fe(CO)_4(C_2HF_3)$ were studied in light petroleum solutions.[23] As such, these absorptions are plotted with the aforementioned anticipated 10 cm^{-1} shift toward higher frequency to allow the positions of these absorptions to be more directly comparable to gas phase numbers. The general trend for the effect of additional fluorines on the positions of the absorption of these compounds is clear and consistent with fluorine acting as an electron-withdrawing moiety. Most likely, the B_2 modes of $Fe(CO)_4(C_2H_4)$ and $Fe(CO)_4(C_2F_4)$ are not observed because they are masked by the strong $Fe(CO)_5$ absorption. However, even if the lowest observed $Fe(CO)_4(C_2F_4)$ absorption is the B_2 mode, the overall conclusions regarding trends in the frequency of a given mode as a function of the number of fluorine atoms remains unchanged, as does the assignment of the absorptions at 2135, 2074, and 2043 cm^{-1} to $Fe(CO)_4(C_2F_4)$.

In principle, the second compound, which we have indicated is likely $Fe(CO)_3(C_2F_4)_2$, could be an $Fe(CO)_x(C_2F_4)_{5-x}$ ($x \leq 2$) species. This compound would have to form by sequential photolysis of $Fe(CO)_4(C_2F_4)$ and/or $Fe(CO)_3(C_2F_4)_2$. It would not be expected to form as a result of an initial photolytic process since 355 nm photolysis of $Fe(CO)_5$ is expected to produce significant quantities of only $Fe(CO)_4$ and $Fe(CO)_3$.[14] However, there is nothing clearly apparent in the data in Figure 3. and related experiments that would indicate the presence of more than two compounds. Thus, if one of the two compounds is $Fe(CO)_x(C_2F_4)_{5-x}$ ($x \leq 2$), then an intermediate must be photolyzed to produce this species before the concentration of the intermediate can build up to significant concentrations. The most likely intermediate for this process would be $Fe(CO)_3(C_2F_4)_2$, which would have to have a large photolysis cross section at 355 nm relative to both $Fe(CO)_4(C_2F_4)$ and the putative $Fe(CO)_x(C_2F_4)_{5-x}$ ($x \leq 2$) species. However, $Fe(CO)_x(\text{olefin})_{5-x}$ ($x \leq 2$) species are anticipated to be unstable. In fact, even $Fe(CO)_2(\text{olefin})_3$ compounds are very limited.[24-26] Though $Fe(CO)_3(C_2F_4)_2$ is clearly more stable than $Fe(CO)_3(C_2H_4)_2$, it would not be surprising based on the aforementioned data that even if $Fe(CO)_2(C_2F_4)_3$ were to form in the experiments reported in Figure 3, it would be short-lived and not observed.[25] Thus, though we cannot rule out the possible formation and observation of an $Fe(CO)_x(C_2F_4)_{5-x}$ ($x \leq 2$) species, we feel it is very likely that the simplest interpretation of this data is accurate: we are observing $Fe(CO)_4(C_2F_4)$ and $Fe(CO)_3(C_2F_4)_2$. However, if one of the species we are observing is $Fe(CO)_x(C_2F_4)_{5-x}$ ($x \leq 2$) instead of $Fe(CO)_3(C_2F_4)_2$, then, as commented on again in section IV.D, its stability is even more remarkable.

It would, in principle, be possible for C_2F_4 to oxidatively add to $Fe(CO)_3$ to produce $Fe(CO)_3(CF_2)_2$. This possibility is made more plausible because C_2F_4 has a carbon–carbon bond energy of 76.3 kcal/mol.[27] However, if oxidative addition were to take place, the rate of formation of $Fe(CO)_3(CF_2)_2$ would equal the rate of reaction of $Fe(CO)_3$ with C_2F_4. A comparison of rate constants reported in section III.A indicates this is not the case, and thus formation of $Fe(CO)_3(CF_2)_2$ by this route can be ruled out.

C. k_{obs} for $Fe(CO)_3(C_2H_4)_2 \rightarrow Fe(CO)_4(C_2H_4)$.

The FTIR was used to monitor $Fe(CO)_3(C_2H_4)_2$ absorptions at 2070 cm^{-1} and 1997 cm^{-1} and an $Fe(CO)_4(C_2H_4)$ absorption at 2095 cm^{-1}. Both species have absorptions between 2020 and 2000 cm^{-1} [6] that could not be easily resolved because they overlap with absorptions of $Fe(CO)_5$. k_{obs} was obtained from single-exponential fits of absorbance versus time for each of the three observed peaks. Figure 5 is a plot of the time evolution of the spectrum, in the 2050–2150 cm^{-1} region, which depicts the decay of the $Fe(CO)_3(C_2H_4)_2$ absorption at 2070 cm^{-1} and the

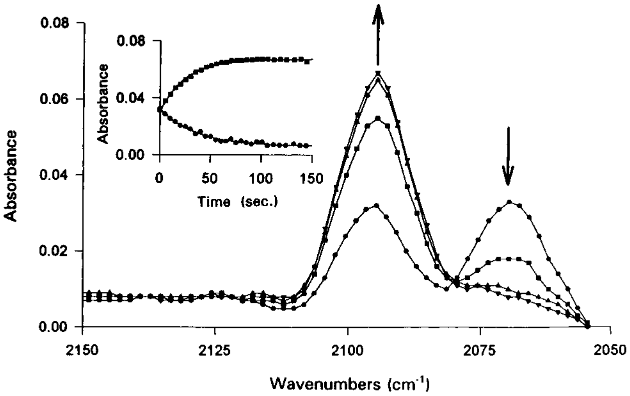

Figure 5. Time-resolved spectra generated by 355 nm photolysis of 0.101 Torr of $Fe(CO)_5$, 494 Torr of C_2H_4, and 160 Torr of CO. The four spectra are separated by 30 s intervals starting at $t = 0$. Arrows show the direction of evolution of the peaks. The inset is a plot of the absorbance versus time for the peaks at 2095 (rise) and 2070 cm^{-1} (fall).

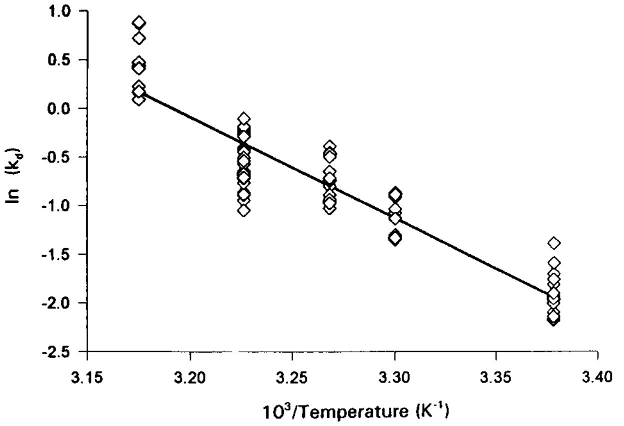

Figure 6. Arrhenius plot for the loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$. The decomposition rate constant, k_d, is plotted versus $10^3/T$.

TABLE 1: Rate Constant, k_d, for Loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$

temp (°C)	k_d (s^{-1})	temp (°C)	k_d (s^{-1})
24	0.15 ± 0.08	37	0.6 ± 0.3
30	0.34 ± 0.12	42	1.6 ± 0.9
33	0.5 ± 0.3		

growth of the $Fe(CO)_4(C_2H_4)$ absorption at 2095 cm^{-1}, at 30 s intervals. The inset in this figure shows the absorbance of the two peaks vs time over a longer time period.

D. $Fe(CO)_3(C_2H_4)-C_2H_4$ Bond Dissociation Energy. Table 1 shows the average k_d for a range of temperatures for the dissociation of $Fe(CO)_3(C_2H_4)$. For unactivated association reactions, the energy of activation for the corresponding dissociation reaction can be directly related to the change in internal energy, ΔU, and the bond dissociation energy.[12] The bond dissociation energy for loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$, based on the Arrhenius plot in Figure 6, is 21.3 ± 2.0 kcal/mol, and $\ln A = 33 \pm 3$, where A is the preexponential for k_d.

E. $Fe(CO)_4(C_2H_4)$ Dissociation. Attempts to directly measure the rate for loss of C_2H_4 from $Fe(CO)_4(C_2H_4)$, as a result of a dissociative homogeneous gas phase process, were unsuccessful. The $Fe(CO)_4(C_2H_4)$ peak at 2095 cm^{-1} was monitored for an extended period of time. Over the first few hours, the peak amplitude dropped significantly and reached a nonzero absorption with little additional change over the next few days. There was no apparent trend in the rate of the initial fall as the C_2H_4:CO ratio and temperature were varied.

A possible explanation for the decay of the $Fe(CO)_4(C_2H_4)$ signal, to a nonzero absorption value, is an equilibrium between $Fe(CO)_4(C_2H_4) + CO$ and $Fe(CO)_5 + C_2H_4$. However, there was no evidence for production of $Fe(CO)_4(C_2H_4)$ when $Fe(CO)_5$ and C_2H_4 were allowed to stand for 24 h in the dark, making this explanation unlikely. The initial fast decay of the $Fe(CO)_4(C_2H_4)$ signal, to a nonzero value, could be a result of heterogeneous decay and/or adsorption of $Fe(CO)_4(C_2H_4)$ on the cell walls and/or windows. The cell surfaces then become passivated, and since there is no significant homogeneous gas phase dissociation of $Fe(CO)_4(C_2H_4)$ taking place on the experimental time scale, the $Fe(CO)_4(C_2H_4)$ absorbance levels off. However, the rate and amplitude of the decay did not change significantly when the cell was partially filled with glass beads. Thus, it is possible that the decay process occurs preferentially on the windows of the cell. Nevertheless, whatever the initial loss mechanism, it is consistent with an initial acceleration of the rate of loss of $Fe(CO)_4(C_2H_4)$. Therefore, these observations can be used to estimate an upper limit for the gas phase dissociation rate constant for $Fe(CO)_4(C_2H_4)$.

Using the measured rate constant for addition of C_2H_4 to $Fe(CO)_4$ and the previously reported rate constant for CO addition to $Fe(CO)_4$[28] in conjunction with eq 5, an upper limit for the rate constant for $Fe(CO)_4-C_2H_4$ dissociation of 6×10^{-6} s^{-1} was estimated at 24 °C. However, the decay may be almost exclusively due to a heterogeneous reaction, and thus the actual rate constant for homogeneous gas phase dissociation could be much smaller than this limiting value.

F. $Fe(CO)_3(C_2F_4)_2$ and $Fe(CO)_4(C_2F_4)$ Dissociation. Attempts were also made to directly determine the rate constant for dissociation of $Fe(CO)_3(C_2F_4)_2$ and $Fe(CO)_4(C_2F_4)$. The time dependence of the absorptions for both of these species behaved very similarly to what was observed with $Fe(CO)_4(C_2H_4)$. They exhibited a relatively rapid partial decay, at a rate essentially independent of temperature, and C_2F_4:CO ratio, which leveled off to a nonzero value and exhibited very little subsequent change over a period of days.

The observed decay rate of $Fe(CO)_3(C_2F_4)_2$ is consistent with the perfluoroethylene being more strongly bound than ethylene in $Fe(CO)_3(C_2H_4)_2$. Under similar reaction conditions, $Fe(CO)_3(C_2H_4)_2$ completely decays away, as a result of the homogeneous gas phase processes in eqs 1−4, in a few minutes, while the $Fe(CO)_3(C_2F_4)_2$ peak does not fully disappear even after a number of days. An upper limit for k_{obs} for $Fe(CO)_3(C_2F_4)_2$ requires knowledge of the rate constant for addition of C_2F_4 to $Fe(CO)_3(C_2F_4)$, which has been measured, and the rate constant for addition of CO to $Fe(CO)_3(C_2F_4)$, which was not measured since an absorption for $Fe(CO)_3(C_2F_4)$ was not identified.

Based on the relative positions of absorptions of ethylene versus perfluoroethylene-containing iron compounds, the absorption of $Fe(CO)_3(C_2F_4)$, which corresponds to the absorption of $Fe(CO)_3(C_2H_4)$ that was used to monitor the addition rate of C_2H_4 to $Fe(CO)_3$, could be masked by the intense $Fe(CO)_5$ peak. As such, a gas kinetic rate constant, which would result in the smallest value of k_d, was assumed for addition of CO to $Fe(CO)_3(C_2F_4)$. Based on these conditions and the lack of significant long-term decay of $Fe(CO)_3(C_2F_4)_2$, eq 5 can be used to provide an estimate of an upper bound for k_d of $\sim 6 \times 10^{-6}$ s^{-1}, the same value as the estimate for $Fe(CO)_4(C_2H_4)$. Though this same limiting value was also determined for $Fe(CO)_4(C_2H_4)$, it should be emphasized that these limits may be almost exclusively for heterogeneous processes, and the homogeneous gas phase processes are likely to be slower and their rates may be different for the different compounds.

IV. Discussion

A. $Fe(CO)_3(C_2H_4)-C_2H_4$ Bond Dissociation Energy. The dissociation of $Fe(CO)_3(C_2H_4)_2$ has been previously investigated.[5,6] In ref 6, k_d and the ratio k_3/k_2 were reported as $(2.9 \pm 0.3) \times 10^{-3}$ s^{-1} and 35 ± 5, respectively, at ambient temperature. In the current work, k_d has been measured as 0.15 ± 0.08 s^{-1} at 24 °C, and the values for k_3 and k_2, measured independently, give 0.40 ± 0.08 for the ratio k_3/k_2, at 24 °C. Using the values of k_{obs} reported in ref 5 and the values of k_2 and k_3 determined in this work, a value for k_d of 0.15 ± 0.04 s^{-1} can be calculated, in good agreement with the value determined in this work. The value of 27 ± 6 kcal/mol, reported in ref 5, as an approximate activation energy for loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$, agrees, within experimental error, with the value of 20.7 ± 2.0 kcal/mol determined in this study for the activation energy.

B. $Fe(CO)_4-C_2H_4$ Bond Dissociation Energy. There are two previous reports of the ethylene−Fe bond energy in $Fe(CO)_4(C_2H_4)$.[29,30] Laser pyrolysis experiments by Lewis and co-workers give a value of 37.4 kcal/mol.[29] Earlier work by Brown et al., using data from thermal decomposition experiments, puts the BDE at 23.1 kcal/mol[30] assuming all five Fe−C bonds had the same bond dissociation energy of 28.1 kcal/mol. However, there are a number of more recent determinations which report bond energies for the $Fe(CO)_4-CO$ bond relative to either the singlet or triplet (ground state) of $Fe(CO)_4$ that are significantly greater than this average value.[29,31−33] Recent calculations conclude that the energy difference between the singlet and triplet states of $Fe(CO)_4$ is small.[34] As such, the bond energy for $Fe(CO)_4-C_2H_4$, recalculated based on a $Fe(CO)_4-CO$ bond energy of 40 kcal/mol,[29,31] is likely to be encompassed by the range 36.0 ± 2.5 kcal/mol, irrespective of whether the singlet or triplet state of $Fe(CO)_4$ is taken as a reference. Larger bond energies for $Fe(CO)_5$ will result in a larger recalculated energy for the $Fe(CO)_4-C_2H_4$ bond. Taking the value of k_d of 6×10^{-6} s^{-1} and any reasonable value for the preexponential for dissociation of $Fe(CO)_4(C_2H_4)$ leads to a lower limit for the bond dissociation energy for $Fe(CO)_4(C_2H_4)$ of less than 36 kcal/mol. Thus, our results are compatible with both the $Fe(CO)_4-C_2H_4$ bond dissociation energy reported in ref 29 and the recomputed value based on work in ref 30.

C. Carbonyl Stretching Frequencies. Table 2 contains information on the infrared absorptions of $Fe(CO)_4$ and $Fe(CO)_4(C_2H_4)$. To compare the two A_1 absorptions of $Fe(CO)_4$, which have been only observed in an SF_6 matrix, to the corresponding absorptions of $Fe(CO)_4(C_2H_4)$, the absorptions reported in the matrix for $Fe(CO)_4$ were incremented by +8 cm^{-1}, the average shift between the positions of the two $Fe(CO)_4$ absorptions which have been observed in both a matrix and the gas phase. The two lower frequency absorptions of $Fe(CO)_4$ have been reported in the gas phase and thus they can be directly compared to gas phase absorptions for $Fe(CO)_4(C_2H_4)$. Comparing the $Fe(CO)_4$ absorptions with the $Fe(CO)_4(C_2H_4)$ absorptions of Andrews et al.,[21] there is no shift of the highest frequency A_1 mode, a +13 cm^{-1} shift for the other A_1 mode, a +3 cm^{-1} shift for the B_1 mode, and a +4 cm^{-1} shift for the B_2 mode in going from $Fe(CO)_4$ to $Fe(CO)_4(C_2H_4)$. Grant et al. have also reported gas phase absorptions for $Fe(CO)_4(C_2H_4)$.[6] These absorptions indicate no shift for the highest frequency A_1 mode of $Fe(CO)_4$ relative to $Fe(CO)_4(C_2H_4)$, but shifts of +17 to +20 cm^{-1} for the three lower frequency modes $Fe(CO)_4(C_2H_4)$ relative to $Fe(CO)_4$. These shifts represent an interesting contrast to the $Cr(CO)_5$ system, where on complexation of C_2H_4 the E mode absorptions shift to lower frequency by ~10 cm^{-1}. Thus, when complexed to $Fe(CO)_4$ ethylene is a net electron-withdrawing ligand while when complexed to $Cr(CO)_5$ it is a net donator of electron density.

TABLE 2: Some IR Absorptions of $Fe(CO)_5$, $Fe(CO)_4$, and $Fe(CO)_4(C_2H_4)$

compound	point group	CO stretch (cm^{-1})	mode symmetry[j]	
$Fe(CO)_5$[a] (vapor)	D_{3h}	2118[b]	A_1'	A_1
		2045[b]	A_1'	A_1
		2034	A_2''	B_1
		2013	E'	$A_1 + B_2$
$Fe(CO)_4$[c] (SF_6 matrix)	C_{2v}	2087	A_1	
		1999	A_1	
		1994	B_1	
		1974	B_2	
$Fe(CO)_4$[d] (vapor)	C_{2v}	2000	B_1(o)[e]	
		1984	B_2(o)	
$Fe(CO)_4(C_2H_4)$[f] (vapor)	C_{2v}	2095 (s)	A_1	
		2020 (vs)	A_1	
		2003 (vs)	B_1	
		1988 (vs)	B_2	
$Fe(CO)_4(C_2H_4)$[g] (vapor)	C_{2v}	2095 (0.11)	A_1	
		2024 (0.74)	A_1	
		2020 (1.00)	B_1	
		2007 (0.50), 2002 (0.75)	B_2	
$Fe(CO)_4(C_2H_4)$[h] (vapor)	C_{2v}	2095 (0.1)	A_1(o)	
		2020 (1.0)	A_1(o)	
		~2000[i]		

[a] Jones, L. H.; McDowell, R. S. *Spectrochim. Acta* **1964**, *20*, 248. [b] Calculated frequencies for gas phase A_1' absorptions. [c] Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276. [d] Ryther, R. J.; Weitz, E. *J. Phys. Chem.* **1991**, *95*, 9841. [e] (o) indicates the symmetry label is our assignment. [f] Andrews, D. C.; Davidson, G. *J. Organomet. Chem.* **1972**, *35*, 161. [g] Weiller, B. H.; Miller, M. E.; Grant E. R. *J. Am. Chem. Soc.* **1987**, *109*, 352. [h] This work. [i] $Fe(CO)_4(C_2H_4)$ and $Fe(CO)_3(C_2H_4)_2$ absorptions near 2000 cm^{-1} were not resolved in the present work. As a result, a relative peak height was not determined. [j] All modes symmetries are indicated for the C_{2v} point group except for $Fe(CO)_5$, where they are indicated for D_{3h} (left), and their correlated symmetries in the C_{2v} point group are also indicated (right).

A study of $Fe(CO)_4(C_2H_4)$ using photoelectron spectroscopy found the iron center in $Fe(CO)_4(C_2H_4)$ to be *more positive* than the iron center in $Fe(CO)_5$.[35] The photoelectron study concluded that C_2H_4 has σ-donating and π-accepting character that are either comparable to or better than that of CO. Similar σ-donating and π-accepting character for CO and C_2H_4 are consistent with the similar bond dissociation energies for $Fe(CO)_4-(C_2H_4)$ and $Fe(CO)_4-CO$. The shifts in the frequencies of the modes in $Fe(CO)_4(C_2H_4)$ relative to $Fe(CO)_4$ are compatible with C_2H_4 being a net electron-withdrawing ligand in $Fe(CO)_4(C_2H_4)$, which is further consistent with significant π-accepting character for C_2H_4 in $Fe(CO)_4(C_2H_4)$. However, CO stretching frequencies in $Fe(CO)_4(C_2H_4)$ are shifted to lower frequency relative to $Fe(CO)_5$.. This is compatible with C_2H_4 being a better σ donor and/or a poorer π acceptor than CO and $Fe(CO)_4(C_2H_4)$ having a more negative iron center than $Fe(CO)_5$.

The three IR absorptions of $Fe(CO)_4(C_2F_4)$ are shifted 40−70 cm^{-1} to *higher frequency* from the corresponding $Fe(CO)_4$ absorptions, taking into account the effect of the matrix. The three highest frequency absorptions of $Fe(CO)_4(C_2F_4)$ are shifted 21−40 cm^{-1} to higher frequency than the corresponding absorptions of $Fe(CO)_5$ (see Table 2), indicating less electron density on the metal center when C_2F_4 replaces CO. Similar trends are observed for $Fe(CO)_3(C_2F_4)_2$. Thus, from these data, C_2F_4 is a poorer σ donor and/or a better π acceptor than CO. This is consistent with the idea that the electron-withdrawing nature of the F atoms on C_2F_4 make it a relatively poor electron donor and a relatively good π acceptor.

D. Comparison of Bond Dissociation Energies. Comparisons of the bond dissociation energy for $Fe-C_2H_4$ bonds with

Cr−C_2H_4 bonds support accepted ideas regarding metal−olefin bonding. As discussed, $Fe(CO)_4(C_2H_4)$ has a bond dissociation energy that is expected to be in the range 36.0 ± 2.5 kcal/mol. The corresponding chromium compound, $Cr(CO)_5(C_2H_4)$, has been reported to have a BDE of 24.7 ± 2.4 kcal/mol.[12] The BDE for $Fe(CO)_3(C_2H_4)_2$ is reported in this work as 21.3 ± 2.0 kcal/mol, and the BDE for *cis*-$Cr(CO)_4(C_2H_4)_2$ has been reported as ∼15 kcal/mol.[36] Two trends are evident: (1) the monosubstituted compounds are more stable than the disubstituted compounds, and (2) the iron compounds are more stable than the corresponding chromium compounds.

To make these comparisons, it must be justified that it is more appropriate to compare the bond dissociation energy for loss of C_2H_4 from *cis*-$Cr(CO)_4(C_2H_4)_2$ than from *trans*-$Cr(CO)_4(C_2H_4)_2$ to that for $Fe(CO)_3(C_2H_4)_2$. There are large differences in the stability of *cis* and *trans* isomers of the bis-olefin-substituted group VI metal carbonyls that have been explained as being due to a competition between CO and olefin π^* orbitals for electron density from the same metal orbital.[37,38] The explanation focuses on the fact that olefins are single-faced π acceptors, i.e., they have a single π^* orbital to accept electron density, while CO has two orthogonal π^* orbitals. In the *trans* bis-olefin group VI metal carbonyls, the olefins orient themselves 90° to each other, and because each has only one π-accepting orbital, the orbitals are orthogonal and do not back-bond with the same metal orbital.[37,38] A diagram illustrating this is in ref 38. With an olefin trans to CO, independent of how the olefin is oriented, the CO will have one of its π-accepting orbitals in the same plane as the olefin's π-accepting orbital, leading to competition for electron density from the same metal orbital. In $Fe(CO)_3(C_2H_4)_2$ the ethylene ligands occupy two of the equatorial sites and compete with each other and a CO group, in the other equatorial site, for electron density from the same metal orbitals. *cis*-$Cr(CO)_4(C_2H_4)_2$ has carbonyl and olefin groups competing for electron density from the same metal orbitals, while in the *trans* isomer the ethylenes do not compete with carbonyl groups, or each other, for electron density from a common metal orbital. For this reason, the bond dissociation energy for loss of C_2H_4 from *cis*-$Cr(CO)_4(C_2H_4)_2$ has been used for comparison purposes with $Fe(CO)_3(C_2H_4)_2$.

This competition for electron density has also been invoked to explain the observed decrease in lifetime of iron carbonyl complexes as the number of olefins increases. There is a limited back-bonding capability of the metal, with more olefins drawing electron density from the same metal orbitals.[24,39] The olefins occupy in-plane equatorial sites when substituted in iron carbonyl, and as a result they compete with each other for electron density from the same metal orbitals.

Experimental results are consistent with this explanation. A number of stable $Fe(CO)_4$(olefin) compounds are known,[40] but only two stable $Fe(CO)_3(\text{olefin})_2$ compounds[39] and one stable $Fe(CO)_2(\text{olefin})_3$ compound, $Fe(CO)_2((E)\text{-cyclooctene})_3$, has been reported.[24] As discussed, previous work has also shown that $Cr(CO)_5(C_2H_4)$ is more stable than *cis*-$Cr(CO)_4(C_2H_4)_2$.[36] In fact, $Cr(CO)_5(C_2H_4)$ has been isolated as a stable solid after UV photolysis of $Cr(CO)_6$ in supercritical ethylene.[41] Also, $M(CO)_5(C_2H_4)$ has been observed to be more stable than *cis*-$M(CO)_4(C_2H_4)_2$ (M = Cr, Mo, W) in alkane solutions.[37]

The greater stability of the ethylene-substituted iron carbonyls compared to the ethylene-substituted chromium carbonyls is consistent with established ideas of metal−olefin bonding. Metals possessing more bonding electrons have the capability to form a stronger π back-bond and thus more stable complexes with π acceptors.[1] Thus, it is not surprising that iron, with two additional electrons, forms stronger bonds with ethylene and perfluoroethylene than chromium.

Comparing the bonding of ethylene and perfluoroethylene to chromium and iron highlights the differences between the two metals. Previous work in this laboratory determined that the bond dissociation energy for $Cr(CO)_5-C_2H_4$ is ∼5 kcal/mol larger than $Cr(CO)_5-C_2F_4$.[12] Although we were not able to make quantitative measurements on the C_2F_4 system, it appears that C_2F_4 in $Fe(CO)_3(C_2F_4)_2$ is more strongly bound than C_2H_4 in $Fe(CO)_3(C_2H_4)_2$.

The rate constant for dissociative loss of C_2F_4 from $Fe(CO)_3(C_2F_4)_2$ is no more than 1/25 000 that of k_d for loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$. This difference in rate constants could, in principle, be due to either a difference in preexponential factors, activation energies, or a combination of both factors. It seems implausible that the entire difference in rate constants could be due to the preexponential since the reverse reactions are unactivated with rate constants that differ by only a factor of 2. Thus, for the entire difference in k_d's to be due to the pre-exponentials, the ratio of preexponentials for the dissociation would have to differ from the ratio of preexponentials for the reverse process by over 12 000. This seems unlikely for reactions that, *a priori*, would be expected to have similar shaped transition states. If this difference in k_d's is solely due to the activation energies, the bond energies for the two systems differ by at least ∼6 kcal/mol.

The stronger perfluoroethylene−iron bond in $Fe(CO)_3(C_2F_4)_2$ relative to the ethylene−iron bond in $Fe(CO)_3(C_2H_4)_2$ is consistent with a similar trend found in a series of $Fe(CO)_4$(haloolefin) compounds.[23] PRDDO calculations predicted C_2H_4 to be slightly (∼1 kcal/mol) more strongly bound to $Fe(CO)_4$ than C_2F_4.[42] However, as previously indicated, our results do not allow us to determine whether the $Fe(CO)_4-C_2H_4$ or $Fe(CO)_4-C_2F_4$ BDE is larger. Nevertheless, only a 1 kcal/mol difference in bond energies is much closer in energy than for the corresponding Cr compounds.

As we have indicated in section III.B, we feel it is highly likely that the second compound we observe is $Fe(CO)_2(C_2F_4)_2$ and have discussed this species in these terms. However, since we cannot rule out the possibility that the second compound is actually a more highly substituted perfluoroethylene species, it seems warranted to indicate once again, that if the second compound we observe is actually an $Fe(CO)_x(C_2F_4)_{5-x}$ ($x \leq 2$) species, then its stability is all the more remarkable.

It was previously concluded, based on bond dissociation energies and CO stretching frequencies, that for $Cr(CO)_5L$ compounds, C_2F_4 is a poorer σ donor and also may be a better π acceptor than C_2H_4.[12] With $Cr(CO)_5$, the better σ donor ability of C_2H_4 appears to be the dominant factor in determining which of the olefins is more strongly bound. In the iron carbonyls, because of the increased electron density on iron compared to chromium, the π-accepting ability of C_2F_4 appears to be more important than the relatively greater σ-donating ability of C_2H_4.

V. Conclusions

The bimolecular rate constants for the processes CO + $Fe(CO)_3(C_2H_4)$, C_2H_4 + $Fe(CO)_3(C_2H_4)$, $Fe(CO)_3(C_2H_4)$ + $Fe(CO)_5$, and $Fe(CO)_4$ + C_2H_4 have been measured as $(4.3 \pm 0.8) \times 10^{-12}$, $(11.1 \pm 0.8) \times 10^{-12}$, $(4 \pm 2) \times 10^{-11}$, and $(1.7 \pm 0.2) \times 10^{-13}$ cm^3 /(molecule s), respectively. All are temperature independent from 24 °C to at least 45 °C. The rate constant for the reaction of $Fe(CO)_3(C_2H_4)$ + C_2H_4 agrees well with a previous determination.[7]

Infrared absorptions observed at 2147, 2091, and 2068 cm^{-1} belong to a compound best assigned as $Fe(CO)_3(C_2F_4)_2$, which is expected to be an analog of $Fe(CO)_3(C_2H_4)_2$. Infrared absorptions observed at 2135, 2074, and 2043 cm^{-1} are assigned to $Fe(CO)_4(C_2F_4)$. The rate constant for addition of C_2F_4 to $Fe(CO)_3$ is $(3.3 \pm 1.2) \times 10^{-11}$ cm^3/(molecule s) at (24 ± 1) °C. The rate constants for addition of C_2F_4 to $Fe(CO)_3(C_2F_4)$ and $Fe(CO)_4$ were determined to be $(5.4 \pm 1.7) \times 10^{-12}$ and $(1.8 \pm 0.4) \times 10^{-14}$ cm ^{3}/(molecule s) respectively at (24 ± 1) °C.

Two prior determinations[29,30] of the bond dissociation energy for the loss of C_2H_4 from $Fe(CO)_4(C_2H_4)$ are compared with current experimental results.

The activation energy for loss of C_2H_4 from $Fe(CO)_3(C_2H_4)_2$ is in agreement, within experimental error, with a previous determination[5] and leads to a bond dissociation energy of 21.3 ± 2.0 kcal/mol. This $Fe(CO)_3(C_2H_4)-C_2H_4$ bond energy is compared to previously determined bond dissociation energies for similar metal−olefin bonds. With the same metal center, the decreased stability of bisethylene-substituted species as compared to monoethylene-substituted compounds has been ascribed to an increase in olefin competition for metal electron density from common d orbitals.[24,37−39] With the same number of ethylene ligands, the iron compounds are more stable than the chromium compounds due to iron being more electron rich and therefore having more electron density available for back-bonding. There appears to be a reversal in the order of stability of the disubstituted compounds of C_2H_4 and C_2F_4 on going from chromium to iron, again explainable based on the relative electron density of the two metals. Though our data do not allow us to definitively reach a similar conclusion regarding the monosubstituted (C_2H_4 and C_2F_4) species, the data are not inconsistent with such a conclusion. Interestingly, the shifts in the three lowest frequency CO modes in $Fe(CO)_4(C_2H_4)$ relative to those in $Fe(CO)_4$ indicate that C_2H_4 is a *net electron-withdrawing* ligand while when C_2H_4 is bound to $Cr(CO)_5$ the shifts in the E mode CO frequencies[12] indicate that C_2H_4 is a *net electron donor*.

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