was found to desorb from the Pt surface with or without microwave discharge. A reinvestigation of the thermal desorption of the OH radical indicates that the desorption energy depends strongly on the O/H ratio of reactant mixtures, varying from 27 kcal/mol at O/H = 100 to 51 kcal/mol at $O/H \simeq 0.037$, with an extrapolated value of $E_{\text{des}} = 60 \pm 3 \text{ kcal/mol at O/H} = 0$. On the basis of the established mechanism for the $H_2 + O_2$ reaction on Pt, it is concluded that, under excess H(ads) conditions, OH(ads) coverage becomes extremely low and the value, 60 kcal/ mol, corresponds to the dissociation energy of the strongest Pt-OH bond.

Registry No. OH, 3352-57-6; Pt, 7440-06-4.

Observation of Photochemical Intermediates in the Low-Temperature Photolysis of Silica-Adsorbed Fe(CO)₅

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The photochemistry of silica-adsorbed $Fe(CO)_5$ has been examined at reduced temperatures with a frequency-tripled Nd:YAG laser (355 nm) as the light source. The only significant photoproduct observed by IR spectroscopy upon photolysis at temperatures between 200 and 300 K is $Fe_3(CO)_{12}$; no $Fe_2(CO)_9$ is detected. Photolysis at 100 to 150 K also yields $Fe_3(CO)_{12}$, but another major product is formed as well. On the basis of IR spectra obtained in the carbonyl stretching region, this product is assigned as $Fe(CO)_4(SiO_2)$, which denotes the species formed upon addition of a silica surface hydroxyl group or siloxane bridging oxo group to the primary photoproduct, $Fe(CO)_4$. This species is a key intermediate in the photoinitiated conversion of $Fe(CO)_5$ to $Fe_3(CO)_{12}$ in this system. Photolysis experiments were also carried out at temperatures below 100 K, but here $Fe(CO)_5$ apparently aggregates on the silica surface, complicating interpretation of the photochemistry.

Introduction

Heterogeneous photochemistry, involving light-initiated processes occurring on solid surfaces, is a growing field which promises to yield a number of important applications.^{1,2} Our work in this area³ has concentrated on the photochemistry of metal complexes adsorbed onto a solid surface, with emphasis on possible applications to heterogeneous catalysis.^{4,5} In a previous paper we discussed ways in which photoinitiated processes could provide an important alternative to present methods for the preparation of supported transition-metal catalysts.³ One attractive approach involves the single-step preparation of supported transition-metal cluster complexes via irradiation of smaller polynuclear or mononuclear carbonyl complexes adsorbed onto a support surface. This idea was illustrated by the photolysis of silica-adsorbed $Fe(CO)_{5}$, which leads almost exclusively to the formation of $Fe_3(C O_{12}$. This was not the expected cluster product, however, since photolysis of $Fe(CO)_5$ in the gas or liquid phase or in solution yields mainly $Fe_2(CO)_{9,6}$ The formation of $Fe_3(CO)_{12}$ was interpreted as evidence that silica plays an active role in photoinitiated reactions of adsorbed Fe(CO)₅. Specifically, we proposed that silica surface hydroxyl

groups or siloxane bridging oxo groups participate as weak ligands, thus altering the outcome of secondary thermal processes involving unsaturated iron carbonyl intermediates.

In an effort to understand these secondary thermal processes, we have examined the photolysis of silica-adsorbed $Fe(CO)_5$ at reduced temperatures. In the present study we have used spectroscopic methods to follow both photochemical and subsequent thermal processes in this system between 10 and 300 K. Our results indicate that silica surface groups indeed act as ligands, trapping the primary photoproduct $Fe(CO)_4$ on the surface as a saturated but thermally labile species, $Fe(CO)_4(SiO_2)$. This species is shown to be a likely intermediate in the silica surface-assisted photochemical conversion of $Fe(CO)_5$ to Fe₃(CO)₁₂.

Experimental Section

 $Fe(CO)_5$ was obtained from Strem and was purified by vacuum transfer to a glass bulb. The bulb was stored in liquid nitrogen except when in use and was thoroughly degassed before each use. The silica used in most experiments was specially prepared in high purity by Dr. John N. Armor and Mr. Emery J. Carlson of Allied Corporate Research Laboratory and is the same as that used in our previous experiments.³ The BET surface area of this material was 470 m² g⁻¹. The silica particles were 20-60 mesh (0.25-0.85-mm diameter). The samples were pretreated in air for ≥ 2 h at 560 °C. Transmittance of the samples was $\sim 25\%$ over a path length of 2.5 mm at the photolysis wavelength. As before,³ a commercial silica (Davison PA-400) was also used in a few experiments, with qualitatively identical results.

All gas manipulations were carried out on a glass vacuum line fitted with greaseless stopcocks and capable of $\sim 10^{-6}$

⁽¹⁾ Wrighton, M. S., Ed. "Interfacial Photoprocesses: Energy Conversion and Synthesis"; American Chemical Society: Washington, DC,

⁽²⁾ Ehrlich, D. J.; Osgood, R. M. Chem. Phys. Lett. 1981, 79, 381.
(3) Jackson, R. L.; Trusheim, M. R. J. Am. Chem. Soc. 1982, 104, 6590.
(4) See also: Nagy, N. B.; Eenoo, M. V.; Derouane, E. G. J. Catal.

^{1977, 58, 230.} (5) See also: Kinney, J. B.; Staley, R. H.; Reichel, C. L.; Wrighton, M.

 ^{(6) (}a) Chem. Soc. 1981, 103, 4273.
 (6) (a) Chisolm, M. H.; Massey, A. G.; Thompson, N. R. Nature (London) 1966, 211, 67. (b) Dewar, J.; Jones, H. O. Proc. R. Soc. London, Ser. A 1905, 76, 558. (c) Braye, E. H.; Huebel, W. Inorg. Synth. 1966, 8, 178.



Figure 1. Low-temperature photolysis cell used in all experiments.

torr. Pressures above 1×10^{-4} torr were measured with a capacitance manometer. Lower pressures were measured with an ionization gauge calibrated for N_2 only.

The cell used in all experiments is shown in Figure 1. The central piece in the figure (cutaway view) was machined from OFHC copper and contained the silica particles in the center. Sapphire windows (1-in. diameter \times 0.040 in.) were placed in the recesses on either side of this piece and thus sandwiched the silica sample firmly in place. A vacuum-tight seal was made between the windows and the cell body by using a loop of 0.050-in. diameter indium wire lightly coated with Apiezon N. The seal was prepared by compressing the indium wire onto the window-cell assembly between the two stainless-steel side plates. Sufficient compression to make a good seal was provided by tightening the six 2-56 machine screws used to hold the entire assembly together. The seal achieved in this way consistently leak tested with helium to $<1 \times 10^{-9}$ sc cm³ s⁻¹.

The cell was connected to the vacuum line by way of a $^{1}/_{8}$ -in. o.d. OFHC copper tube welded to the cell body on one end and to a 1/16-in. stainless-steel Swagelok port connector on the other. This tube opened into the sample-containing area through a 1/16-in. hole in the cell body. Connection from the Swagelok fitting to the vacuum line was made through a 1/16-in. o.d. stainless-steel or copper tube.

Before each photolysis run, the cell was prepared by first sealing one window to the cell body. Silica particles (30–60 mg) freshly removed from the pretreating oven were poured into the open side of the cell and the second window was then sealed to the cell body, requiring about 10 min in the ambient atmosphere. After overnight evacuation to $\leq 10^{-5}$ torr, the cell was filled with Fe(CO)₅ vapor to a final pressure of 0.02–0.10 torr. This translates into an Fe(CO)₅ fractional surface coverage of 0.01–0.05.³ The final seal was then made by using a pinch-off press to crimp the stainless-steel or copper tube which connected the cell to the vacuum line (see Figure 1), thus providing a completely closed system. This pinch-off seal also consistently leak tested with helium to $<1 \times 10^{-9}$ sc cm³ s⁻¹.

wall copper tubing was used; this caused immediate air oxidation of the silica-adsorbed $Fe(CO)_5$, resulting in a brown-colored sample which was discarded.

Cooling of the cell was achieved with an Air Products CSW-202B Displex closed-cycle helium refrigerator. The cell was threaded onto the refrigerator cold finger immediately after the final pinch-off seal was made, and then cooled to the desired temperature. Temperature control was accurate to ± 2 K. The refrigerator Dewar was fitted with four windows: two sapphire and two NaCl. The Dewar could be rotated to switch from one set of windows to the other. For photolysis and UV-visible spectroscopy the sapphire windows were employed, while for IR spectroscopy the NaCl windows were used.

Our light source was a Molectron MY-34 Nd:YAG laser fitted with an MY-THG third harmonic generator, giving a 355-nm output in pulses of ~10-ns duration at a repetition rate of 10 Hz. A uniform, very low fluence beam was obtained by passing the laser output through a 4-mm iris and expanding the beam through a 5× diverging telescope, thus providing full coverage of the sample cell. The laser energy was ~10 mJ pulse⁻¹ measured at the window on the refrigerator Dewar; assuming a uniform beam profile, this translates into a fluence of ~3 mJ cm⁻². The beam was filtered (Schott UG-11) to remove the fundamental and second-harmonic laser output.

The refrigerator-cell assembly was mounted on an optical rail, so that the cell could be alternatively moved into the path of the laser beam or into a spectrometer sample compartment, with good positional reproducibility. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. UV-visible spectra were recorded with a Perkin-Elmer 330 spectrophotometer. A reference cell, identical with the sample cell and filled with an amount of silica equal to that used in a given photolysis run, was always placed in the spectrometer reference beam. The reference cell was not cooled and thus did not provide perfect cancellation of silica absorptions.

In a typical experiment, an Fe(CO)₅/silica sample was cooled and then allowed to equilibrate at the set temperature for approximately 0.5 h. The sample was then irradiated with a sufficient number of laser pulses to induce a clearly observable change in the IR spectrum. This usually required ~500 shots since, at the concentrations employed in our experiments, Fe(CO)₅ absorbs a very small fraction of the incident irradiation. In most cases, photolysis was continued to ~35 000 shots; IR spectra were recorded at several intervals during these prolonged photolyses. Conversion of Fe(CO)₅ to product was frequently >50% in the longest photolyses.

Results

Temperature Dependence of Adsorbed $Fe(CO)_5$ IR Spectrum. With the cell design used in our experiments, nearly all of the $Fe(CO)_5$ in the cell is adsorbed on the silica surface at any given time. This can be verified from our previously reported adsorption isotherm for $Fe(CO)_5$ on silica.³ From this curve, plus the known volume of the cell (1 cm³) and the known mass of the silica employed, we calculate that >99% of the $Fe(CO)_5$ within the cell is adsorbed at 300 K. As the temperature is lowered, the quantity of nonadsorbed $Fe(CO)_5$ is further reduced. Thus, we can neglect spectral and photochemical contributions from nonadsorbed $Fe(CO)_5$.

The carbonyl-region IR spectrum of silica-adsorbed $Fe(CO)_5$, shown in Figure 2A, exhibits peaks at 2024 and 2002 cm⁻¹. This spectrum strongly resembles the spectrum of gas-phase $Fe(CO)_5$ but is slightly red shifted and broadened.⁷ When the sample is cooled, further broad-



Figure 2. IR spectra of $Fe(CO)_6$ adsorbed on silica at (A) 300, (B) 100, (C) 10, and (D) 100 K. In D the final temperature was reached by warming the sample from 10 K.

ening occurs and a shoulder appears at 1980 cm⁻¹, as can be seen in the 100 K spectrum shown in Figure 2B. At temperatures ≤50 K this shoulder becomes the strongest peak, and the spectrum is quite broad, as shown in Figure 2C. These temperature-dependent changes in the spectrum were completely reversible, except in one case: the spectrum obtained at 100 and 150 K depends on whether the sample has been cooled to these temperatures from 300 K, or has been cooled to 10 K and subsequently rewarmed to 100 or 150 K. In the latter case, the spectrum obtained is markedly different, exhibiting sharp peaks as well as several additional bands and shoulders as shown in Figure 2D. Some insight into the origin of this effect is provided by the match between the spectrum in Figure 2D and the spectrum of crystalline $Fe(CO)_{5}$.⁷ These spectra are nearly identical, suggesting that phase transitions occur within the adsorbed layer as it cools to 10 K, such that rewarming to 100 K induces crystallization. Indeed, such phase transitions could be expected in a weakly adsorbed molecular layer under our experimental conditions even at relatively low surface coverages (see Discussion). When the sample is warmed further to ≥ 200 K, the bands of crystalline $Fe(CO)_5$ disappear, and the spectrum reverts to the normal spectrum of silica-adsorbed Fe(CO)₅. Clearly, differences in phase could dramatically affect the photochemistry. Thus, in the photolysis experiments conducted at 100 and 150 K, the photolysis temperature was reached by cooling the sample from 300 K unless otherwise noted.

Photolysis Results. We have previously shown that the N_2 laser photolysis of silica-adsorbed $Fe(CO)_5$ at room temperature leads almost exclusively to the formation of $Fe_3(CO)_{12}$, provided the surface coverage of $Fe(CO)_5$ is submonolayer. This is consistent with the UV-visible and IR spectra obtained here after photolysis of silica-adsorbed $Fe(CO)_5$ at 300 K. After photolysis with the frequency-tripled Nd:YAG laser, the visible bands of $Fe_3(CO)_{12}$ are





Figure 3. IR spectrum of $Fe(CO)_5$ adsorbed on silica at 200 K: (A) before photolysis, (B) after photolysis (1000 laser pulses). A weak silica band is observed at ~ 1880 cm⁻¹.



Figure 4. IR spectrum of Fe(CO)₅ adsorbed on silica at 150 K: (A) before photolysis, (B) after photolysis (1000 laser pulses). A weak silica band is observed at \sim 1880 cm⁻¹ in A.

observed at 440 and 600 nm. In the IR spectrum, the $Fe(CO)_5$ bands diminish upon photolysis while a peak at 2052 cm⁻¹ grows in. We assign the IR spectrum obtained under these photolysis conditions to a mixture of $Fe(CO)_5$ and $Fe_3(CO)_{12}$, with the 2052-cm⁻¹ band assigned to Fe_3 - $(CO)_{12}$. This assignment is consistent with the solution-phase IR spectrum⁸ of $Fe_3(CO)_{12}$, as well as the spectrum of genuine samples of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ coadsorbed on silica. Very similar IR spectra are observed after photolyses carried out at 200 and 250 K, suggesting that at these temperatures $Fe_3(CO)_{12}$ is again the only significant photoproduct. The IR spectrum obtained before and after photolysis at 200 K is shown in Figure 3.

On the basis of the IR spectra alone, we can rule out $Fe_2(CO)_9$ as a significant product of photolyses carried out between 200 and 300 K as the intense bridging CO stretch of $Fe_2(CO)_9$ is not observed at ~1820 cm⁻¹ within our limits of detection (~3% T). Other possible products expected to have intense bridging CO absorptions (e.g., $Fe_2(CO)_8$ and $Fe_2(CO)_8L$) can be similarly excluded. Possible products exhibiting only terminal carbonyl bands are less easily excluded. We find, however, that bands or shoulders other than those attributable to $Fe(CO)_5$ and $Fe_3(CO)_{12}$ are not observed even after photolysis to greater than 50% conversion.

While photolysis at 100 and 150 K also yields $Fe_3(CO)_{12}$, bands due to at least one additional major product are observed. New, poorly resolved bands reproducibly appear at ~1960 and ~1940 cm⁻¹, as shown in Figure 4. We also found that the low-frequency shoulder, which appears in the $Fe(CO)_5$ spectrum at these temperatures, does not

⁽⁸⁾ Knight, J.; Mays, M. J. J. Chem. Soc., Chem. Commun. 1970, 1006.



Figure 5. IR spectrum of Fe(CO)₅ adsorbed on silica at 10 K: (A) before photolysis, (B) after photolysis (1000 laser pulses).

decrease in intensity as rapidly upon photolysis as the other $Fe(CO)_5$ bands.

In photolyses performed at 10 and 50 K, the bands at 1960 and 1940 cm⁻¹ are weak or absent, even in photolyses carried to high conversion; changes in the terminal carbonyl region between 2100 and 1950 cm⁻¹ clearly occur but are not resolved, as shown in Figure 5. Two new bands are noted, however, in the bridging carbonyl region at \sim 1860 and \sim 1820 cm⁻¹. A very sharp peak at 2138 cm⁻¹ is also noted at 10 K arising from CO liberated during the photolysis.⁹ The bridging carbonyl bands do not belong to $Fe_3(CO)_{12}$, since they do not appear upon cooling the cell to 10 K following a 300 K photolysis in which $Fe_3(CO)_{12}$ is produced.

A photolysis experiment at 100 K was carried out on the crystallized form of adsorbed Fe(CO)₅. Prior to photolysis, the sample was cooled to 10 K and then warmed to 100 K, which produced the IR spectrum shown in Figure 2D. After photolysis at 100 K, we observed only a small decrease in the intensity of the $Fe(CO)_5$ bands, relative to decreases obtained after photolysis of an uncrystallized sample carried to the same integrated laser exposure. After prolonged photolysis of the crystallized sample, $Fe_3(CO)_{12}$ formation was observed to a small extent. No other product bands were observed, although the overall conversion was small enough to prevent observation of minor products.

The photochemical behavior of $Fe_3(CO)_{12}$ supported on silica was also examined. The sample was prepared by photolyzing silica-adsorbed Fe(CO)₅ at room temperature in the low-temperature photolysis cell and then removing the remaining $Fe(CO)_5$ under vacuum before sealing off the cell and cooling it in the usual way. Photolysis of this sample at 100 and 300 K under conditions identical with those used in the $Fe(CO)_5$ photolyses produced no observable loss of $Fe_3(CO)_{12}$ after integrated laser exposures 2 times higher than those used in any of the $Fe(CO)_5$ experiments.

We briefly examined the qualitative effects of laser fluence. Reducing the laser fluence by a factor of 2-5yielded the same qualitative results at all temperatures as those found by using our normal fluence level of 3 mJ cm⁻². Increasing the laser fluence by a factor of 3-5, however, led to a decrease in the $Fe(CO)_5$ IR bands, but little or no concomitant increase in product bands at both 100 and 300 K. Higher fluence photolysis was accompanied by the appearance of a brown coloration in the sample, similar to that observed upon air oxidation of silica-adsorbed $Fe(CO)_5$. We thus infer that higher laser fluence photolysis probably induces complete dissociation of Fe(CO)₅, resulting in formation of a surface iron oxide species similar to the oxides observed upon thermal dissociation of metal carbonyls on oxide surfaces containing acidic hydroxyl groups, e.g., silica,¹⁰ alumina,¹¹ MgO,¹² or zeolites.¹³ Such irreversible dissociation does not occur at a fluence level $\leq 3 \text{ mJ cm}^{-2}$, however. Indeed, we found that photoprocesses initiated at lower fluences were almost completely thermally reversible. Allowing the cell to stand at room temperature for 24 h after photolysis results in $\geq 95\%$ recovery of the initial $Fe(CO)_5$ IR band intensity, independent of the temperature at which photolysis was carried out. This indicates that irreversible thermal or photochemical destruction of $Fe(CO)_5$ can be neglected in our experiments.

Thermal Reactions of Photolysis Products. Thermal processes involving the photolysis products were examined by following changes in their IR bands induced by increases in the cell temperature. We are careful in the following discussion to separate irreversible changes in IR bands, resulting from thermal reactions, from simple reversible changes in spectral line shapes, intensities, and frequencies induced by changes in temperature.

After photolysis of silica-adsorbed Fe(CO)₅ at 200 K, the IR spectrum, showing both $Fe_3(CO)_{12}$ and $Fe(CO)_5$, remains unchanged over a period of a few hours. Warming this sample to 250 K increases the intensity of the $Fe(CO)_5$ bands at the expense of the $Fe_3(CO)_{12}$ bands, confirming that a slow thermal reversal of the overall photoprocess occurs at temperatures above ~ 200 K. This reaction is accelerated upon further warming to 300 K.

After photolysis at 100 K, the IR spectrum remains unchanged over several hours if the cell remains at 100 K. The intensities of the 1960- and 1940-cm⁻¹ bands decrease very slowly upon warming the cell to 150 K, with concomitant increases in bands attributed to $Fe_3(CO)_{12}$ and Fe(CO)₅. This process is accelerated at higher temperatures, so that at 200 K no bands were observed at 1960 and 1940 cm⁻¹ while further increases were noted in the Fe₃- $(CO)_{12}$ and $Fe(CO)_5$ bands.

Upon warming a sample photolyzed at 10 K, one observes changes in the bridging carbonyl bands as well as in the CO band. At 50 K the 1860-cm⁻¹ band has diminished, accompanied by a growth in the 1820-cm⁻¹ band; the CO peak is split and broadened, showing a stronger band at $\sim 2160 \text{ cm}^{-1}$ and a weaker band at $\sim 2135 \text{ cm}^{-1}$. Here the spectrum resembles that found after a photolysis performed at 50 K. The observed trend continues on warming further to 100 K, where the 1860-cm⁻¹ band is no longer observed. The CO band is further broadened with increasing temperature until it is no longer apparent at 200 K. Except for the growth in the 1820-cm⁻¹ band noted above, we observed no further changes in this peak up to 250 K. Similarly, the terminal carbonyl region is unchanged up to 250 K, remaining poorly resolved. Increasing the temperature to 300 K, however, leads to loss of the 1820-cm⁻¹ band along with a distinct increase in bands assigned to $Fe_3(CO)_{12}$ and $Fe(CO)_5$. Allowing the

⁽⁹⁾ A peak att 2138 cm⁻¹ was also observed during photolysis of matrix-isolated $Fe(CO)_5$ at 10 K. See: Poliakoff, M.; Turner, J. J. J. Chem. Soc., Dalton Trans. 1973, 1351.

⁽¹⁰⁾ Brenner, A.; Hucul, D. A.; Hardwick, S. J. Inorg. Chem. 1979, 18, 1478.

 ⁽¹¹⁾ Brenner, A.; Hucul, D. A. Inorg. Chem. 1979, 18, 2836.
 (12) Smith, A. K.; Theolier, A.; Basset, J. M.; Ugo, R.; Commeruc, D.; Chauvin, D. J. Am. Chem. Soc. 1978, 100, 2591. We note, however, that some of these same authors have claimed that metal carbonyls decompose to zero valent metal clusters on MgO and other oxide surfaces. Hugues, F.; Besson, B. Bussiere, D.; Dolmon, J. A.; Basset, J. M.; Olivier, D. Nouv. J. Chim. 1981, 5, 207.

⁽¹³⁾ Ballivet-Tkatchenko, D.; Coudurier, G. Inorg. Chem. 1979, 18, 558

cell to stand at 300 K eventually leads to nearly complete recovery of $Fe(CO)_5$, as noted earlier.

Each of our experiments was repeated, using a germanium flat in front of the IR spectrometer light source during the recording of spectra, to assess the importance of photoreactions induced by the visible and near-IR output of the Nernst glower. Studies of $Fe(CO)_5$ photochemistry in low-temperature matrices have shown that Nernst glower output in the 1000-nm region is sufficient to induce rapid photoreactions involving unsaturated iron carbonyl species.¹⁴ No qualitative differences were observed here, however, in photochemical or thermal reaction product spectra obtained with the filter in place vs. those obtained without it.

Discussion

The spectral resolution found in the carbonyl stretching region for silica-adsorbed $Fe(CO)_5$ and the resulting photoproducts is disappointingly poor. The bands do not become narrow at low temperatures, as expected for a homogeneous line shape, but indeed broaden as the temperature decreases. In addition, a shoulder develops at reduced temperatures in the spectrum of silica-adsorbed $Fe(CO)_5$, becoming the dominant peak at temperatures ≤ 50 K. Since this shoulder lies to the low-frequency side of the carbonyl stretching bands found in the room-temperature spectrum, the result is an apparent red shift in these bands as the temperature approaches 10 K. As noted earlier, this behavior is not expected for an isolated molecule of $Fe(CO)_5$, since a similar red shift is not observed in the argon matrix IR spectrum of Fe(CO)₅ at 10 K.¹⁴

It is possible that the red shift is caused by interactions between $Fe(CO)_5$ and the silica surface, resulting in perturbations of the $Fe(CO)_5$ electronic structure. The temperature dependence can be accounted for by adopting the classical picture of surface-adsorbate interactions,¹⁵ in which the surface is depicted as an ensemble of discrete adsorption sites separated from one another by an energy barrier. At 300 K these barriers could be sufficiently low that the equilibrium concentration of $Fe(CO)_5$ molecules confined to single adsorption sites will be very small, suggesting little overall interaction between $Fe(CO)_5$ and the surface. This could explain the similarity between the IR spectrum of siilica-adsorbed $Fe(CO)_5$ and that of gasphase $Fe(CO)_5$ in the carbonyl stretching region at 300 K. As the temperature is reduced, the fraction of $Fe(CO)_5$ molecules trapped in single adsorption sites will increase, resulting in an increasing overall interaction between the silica surface and the population of adsorbed $Fe(CO)_5$ molecules. This interaction may induce the observed red shift, particularly since CO stretching frequencies in metal carbonyls are sensitive to changes in electron density at the metal atom. The result will thus be an increase in the intensity of the red-shifted bands as the temperature is lowered, thereby accounting for the growth of the shoulder at 1980 cm⁻¹.

There is an alternative explanation for the low-temperature red shift, however, which is also consistent with our data. It is possible that the observed perturbations are caused by attractive interactions between adsorbed $Fe(CO)_5$ molecules, such that the shoulder represents an aggregated form of adsorbed $Fe(CO)_5$ which develops on the silica surface as the temperature is lowered. In the limit that the aggregated phase approaches a liquidlike state, a red shift in the strongest CO stretching band of $Fe(CO)_5$ is expected, since this band appears at 1984 cm⁻¹ in liquid-phase Fe(CO)₅ vs. 2012 cm⁻¹ in gas-phase Fe(C- O_{5} .⁷ We have no direct evidence that aggregation occurs in this system, but it is not unreasonable to expect aggregation or condensation in physically adsorbed layers even at relatively low surface coverages. Sharp transitions between well-dispersed and aggregated phases of molecules physically adsorbed on single crystal surfaces have often been inferred from adsorption data.¹⁶ Many examples involve two-dimensional aggregation of inert gases adsorbed on graphite¹⁷ and on metal halide¹⁸ crystal surfaces at low coverages. Adsorbate phase transitions appear in the isotherms of these systems as sharp discontinuities. which are apparent over a limited temperature range. More direct spectroscopic evidence has confirmed that aggregation of the adsorbate is responsible for these discontinuities.¹⁶

Arthur has suggested that aggregation in adsorbed layers should be expected under conditions where the intermolecular attraction between adsorbed molecules is equal to or larger than the attraction between the adsorbed molecule and the surface.¹⁹ An extreme example of this is provided by the behavior of submonolayer metal films on graphite, where the attractive potential between metal atoms is sufficiently strong that the metal atoms aggregate completely into two-dimensional islands at quite low surface coverages.¹⁹ Another demonstration of Arthur's suggestion is given by the adsorption behavior of formic acid on graphite, where hydrogen bonding induces aggregation in the adsorbed formic acid layer at very low surface coverages.²⁰ Clearly, however, the numerous examples of adsorbed inert gas aggregation show that a strong attraction between adsorbate molecules is not necessary to induce adsorbate phase transitions, provided the surface temperature is low and the surface-adsorbate interaction is weak. Thus, we can account for aggregation in the $Fe(CO)_5$ -silica system: while the attraction between Fe- $(CO)_5$ molecules is not exceptionally strong, aggregation may be expected at low temperatures because the interaction between $Fe(CO)_5$ and silica is very weak.³

Another factor which contributes to Fe(CO)₅ aggregation in our experiments is the heterogeneous surface structure of amorphous silica. Aggregation of molecules adsorbed onto the surfaces of polycrystalline or amorphous solids has not been extensively studied, but it has been found that surface steps and defects can serve as specific sites for adsorbate aggregation on single crystal surfaces.²¹ Amorphous silica has a high concentration of these features, as well as an extensive network of capillary type pores. This suggests that the condensed phase of $Fe(CO)_5$ on silica probably consists largely of three-dimensional structures, rather than two-dimensional islands.

Additional evidence supports our proposal that $Fe(CO)_5$ aggregates on silica at low temperatures. We observed that

- (b) Poliakoff, M.; Turner, J. J. J. Chem. Soc. A 1971, 2403.

⁽¹⁴⁾ See paper cited in ref 9.

⁽¹⁵⁾ Ross, S.; Olivier, J. "On Physical Adsorption"; Interscience: New York, 1964; pp 13-6.

⁽¹⁶⁾ Vilches, O. E. Am. Rev. Phys. Chem. 1980, 31, 463. There are a great many examples of adsorbate aggregation on metallic surfaces, al-

^{great many examples of adsorbate aggregation on metallic surfaces, al-}though these examples often involve chemisorbed species and are thus not closely related to our experiments. See: Dash, J. G., Ruvalds, J., Eds., "Phase Transitions in Surface Films"; Plenum Press: New York, 1980. (17) (a) Thomy, A.; Duval, X. J. Chim. Phys. Phys. Chim. Biol. 1969, 66, 1966. (b) Suzanne, J.; Coulomb, J. P.; Bienfuit, M. Surf. Sci. 1973, 40, 414. (c) Lahrer, Y. J. Chem. Soc. Faraday Trans. 1 1974, 70, 320. (d) Chung, T. T. Surf Sci. 1970, 872 - 249. Chung, T. T. Surf. Sci. 1979, 87, 348. (18) (a) Lahrer, Y. J. Colloid Interface Sci. 1971, 37, 836. (b) Nardon,

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(22) (a) Kristoff, J. S.; Shriver, D. F. Can. J. Spectrosc. 1974, 19, 156.

warming a sample to 100 K which had been previously cooled to 10 K yields an IR spectrum of adsorbed Fe(CO)₅ which is nearly identical with the spectrum of pure crystalline $Fe(CO)_5$.⁷ This can be readily explained if $Fe(CO)_5$ aggregates into a relatively disordered liquidlike condensed phase upon cooling to 10 K, such that annealing to 100 K induces crystallization. We did not observe the spectrum of crystallized $Fe(CO)_5$ upon cooling a sample directly to 100 from 300 K, since Fe(CO)₅ does not appear to be strongly aggregated at 100 K. If we assign the 1980-cm⁻¹ shoulder to a disordered aggregated form of adsorbed $Fe(CO)_5$, the relative intensity of this band suggests that most of the aggregation occurs between 100 and 50 K.

Photochemistry. Line broadening obviously complicates our assignment of photoproduct IR bands and probably does not permit observation of minor photoproducts or intermediates. For these reasons, we have made simple spectral assignments consistent with the fewest number of products necessary to explain our data. We discuss photochemical and thermal reaction mechanisms based upon these simple assignments.

As discussed earlier, $Fe_3(CO)_{12}$ appears to be the only significant photoproduct in photolyses carried out at temperatures ≥ 200 K. This complex is again a significant fraction of the photoproducts observed after photolyses carried out at 100 and 150 K, but two additional poorly resolved product bands appear at ~ 1960 and ~ 1940 cm⁻¹ (see Figure 4). The intensity of these bands clearly increases with increasing irradiation. The two bands also appear to maintain the same relative intensity, within a rather large experimental error, indicating that they may arise from a single photoproduct. The frequency of these bands suggests that they may be assigned to an unsaturated iron carbonyl photofragment,²³ such as $Fe(CO)_4$, or to a reactive complex of the form $Fe(CO)_4L$, where L is a weak ligand.²⁴ Both assignments are consistent with the instability of this species, which reacts to give $Fe_3(CO)_{12}$ and $Fe(CO)_5$ at temperatures ≥ 150 K.

We proposed earlier³ that one of the photochemical intermediates expected upon photolysis of silica-adsorbed $Fe(CO)_5$ is $Fe(CO)_4(SiO_2)$, which represents a photosubstitution product formed by addition of a silica surface hydroxyl group or siloxane bridging oxo group to the primary photoproduct, Fe(CO)₄.²⁵ This is consistent with the numerous examples of $Fe(CO)_5$ photosubstitution in the presence of a variety of ligands both in solution and in low-temperature matrices.^{23,24} Assignment of the bands at 1960 and 1940 cm⁻¹ to $Fe(CO)_4(SiO_2)$ is reasonable, since complexes between $Fe(CO)_4$ and ligands with an oxygendonor atom can be quite weak, leading one to expect low thermal stability in addition to CO stretching frequencies below 2000 cm⁻¹.^{23,24} We can model $Fe(CO)_4(SiO_2)$ by a similar weak complex of $Fe(CO)_4$ with an oxygen-donor ligand, $Fe(CO)_4(THF)$ where THF = tetrahydrofuran.

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 $Fe(CO)_4(THF)$ exhibits a strong CO stretching band at 1946 cm⁻¹ plus a slightly less intense band at 1963 cm⁻¹ and a weak band at $2062 \text{ cm}^{-1.29}$ The bands that we observed at 1960 and 1940 cm⁻¹ may also be reasonably assigned to uncomplexed $Fe(CO)_4$, however, since this species also exhibits CO stretching bands below 2000 cm⁻¹ and is thermally unstable. Evidence against this assignment comes from the work of Poliakoff and Turner,²³ who found that $Fe(CO)_4$ readily forms complexes with extremely weak donors such as Xe and CH₄ in low-temperature matrices and is quite unstable at 50 K, reacting with CO to regenerate $Fe(CO)_5$. This suggests that $Fe(CO)_4$ - (SiO_2) is the more reasonable assignment for the bands observed here, and we conclude that $Fe_3(CO)_{12}$ and Fe(C- $O_4(SiO_2)$ are the only major products of photolyses carried out at 100 and 150 K.

It is surprising that $Fe(CO)_4(SiO_2)$ is not also a major product formed upon photolysis at 50 and 10 K, but IR spectra show that it is at best only a minor product (see Figure 5). If $Fe(CO)_5$ remains well dispersed at these temperatures, $Fe(CO)_4(SiO_2)$ should be expected as a major product, since $Fe(CO)_4$ produced upon irradiation will be formed in close proximity to a silica surface ligand site and will not have sufficient thermal energy or mobility to undergo a reaction other than simple addition of this ligand. Indeed, irradiation of well-dispersed $Fe(CO)_5$ at these temperatures should be ideal conditions for formation of $Fe(CO)_4(SiO_2)$. If $Fe(CO)_5$ is strongly aggregated at temperatures ≤ 50 K, however, Fe(CO)₄ will not necessarily be formed near the surface and will likely undergo other reactions, such as dimerization or recombination with CO, as is observed upon irradiation of $Fe(CO)_5$ at relatively high concentrations in low-temperature matrices.²³ Our photochemical results at 50 and 10 K thus provide additional evidence that $Fe(CO)_5$ is not well dispersed at these temperatures.

Because of poor resolution and peak broadening, however, only one of the photoproducts obtained following these lowest temperature irradiations can be clearly identified. One of the photolysis products exhibits an IR band at $\sim 1820 \text{ cm}^{-1}$ and is quite stable up to 250 K, but reacts at 300 K to give $Fe_3(CO)_{12}$ and $Fe(CO)_5$. The stability of this photolysis product, its relatively intense IR band in the bridging carbonyl region, and its reactivity at 300 K suggest that it is $Fe_2(CO)_9$. This is consistent with published IR spectra²² of $Fe_2(CO)_9$ as well as our previous study of the photochemistry of silica-adsorbed Fe(CO)₅.³ Under certain conditions in these earlier experiments, we observed a product band at 1820 cm⁻¹, which we assigned to $Fe_2(CO)_9$, and we found that the product was not stable on silica at 300 K. We also found that a genuine sample of $Fe_2(CO)_9$ reacts on silica to give $Fe_3(CO)_{12}$ and $Fe(CO)_5$ at $\sim 315 \text{ K.}^3$ Thus, our present results establish that, while $Fe_2(CO)_9$ is indeed unstable on silica at 300 K, it is quite stable at temperatures ≤250 K. We do not fully understand the formation of $Fe_2(CO)_9$ in these low-temperature experiments, however.

As noted earlier, the photochemical behavior of the crystallized form of adsorbed $Fe(CO)_5$ is quite different from that of well-dispersed $Fe(CO)_5$ at the same temperature. Very little photochemical conversion of crystallized $Fe(CO)_5$ was observed. This is probably due to the facile recombination of the primary photoproduct, $Fe(CO)_4$, with CO which remains confined within the crystal lattice, resulting in a greatly reduced apparent photochemical efficiency. A similar argument explains our observation that the 1980-cm⁻¹ shoulder observed in the lower temperature

⁽²⁵⁾ $Fe(CO)_4$ is expected to be the only primary photoproduct, despite recent reports of laser-driven, single-photon, multiple fragmentations of both $Fe(CO)_5$ and $Cr(CO)_6$ in the gas phase.^{28,27} These multiple fragmentations appear to involve sequential loss of CO from the vibrationally hot primary photofragments, $Fe(CO)_4$ and $Cr(CO)_5$. Quenching of these species should be very fast on a surface or in solution, and indeed recent picosecond photolysis experiments suggest that $Cr(CO)_{\delta}$ is the only one-photon metal carbonyl product of solution-phase $Cr(CO)_{\delta}$ photolysis.

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 $Fe(CO)_5$ spectra decreases more slowly upon photolysis than the other $Fe(CO)_5$ bands. We have assigned the shoulder to a liquidlike condensed phase of $Fe(CO)_5$, in which recombination of CO with $Fe(CO)_4$ could contribute to an apparent reduction in the photolysis rate over that of well-dispersed $Fe(CO)_5$.

Thermal Reactions of Photolysis Intermediates. In our previous discussion of silica-adsorbed $Fe(CO)_5$ photochemistry,³ we suggested that $Fe_3(CO)_{12}$ was produced in an entirely thermal process, following initial photochemical formation of an intermediate, which we believed to be $Fe(CO)_4(SiO_2)$. Our reasoning was indirect, based on an analogy between the chemistry of $Fe(CO)_5$ on a silica surface and in weakly ligating solvents. Our present experiments indicate that many of our earlier hypotheses are probably correct. We have established that photolysis of $Fe(CO)_5$ on silica does indeed yield an intermediate, which can be observed at 100–150 K. This intermediate, assigned as $Fe(CO)_4(SiO_2)$ based on IR data and on chemical grounds, reacts via an entirely thermal process at temperatures ≥ 150 K to yield $Fe_3(CO)_{12}$ and $Fe(CO)_5$.

The reaction of $Fe(CO)_4(SiO_2)$ to yield $Fe_3(CO)_{12}$ and $Fe(CO)_5$ is sufficiently slow at 150 K (half-life ~8 h) that it can be conveniently followed by IR spectroscopy. The peaks assigned to $Fe(CO)_4(SiO_2)$ steadily disappear with concomitant growth of the bands assigned to $Fe_3(CO)_{12}$ and $Fe(CO)_5$. The formation of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ does not require an induction period, suggesting that there are no long-lived intermediates on the reaction pathway. Also, no $Fe_2(CO)_9$ is formed in the process; this is surprising since we have shown that $Fe_2(CO)_9$ is quite stable on silica at temperatures ≤ 250 K.

These observations offer limited insight into the mechanism for the thermal conversion of $Fe(CO)_4(SiO_2)$ to $Fe_3(CO)_{12}$. We can apparently rule out a process involving a *long-lived* dinuclear intermediate; in particular, we can exclude $Fe_2(CO)_9$ as an important intermediate. This suggests that our earlier proposed mechanism,³ involving stepwise surface migration and subsequent trimerization of $Fe(CO)_4$, is not fully correct; a substantial buildup in the concentration of a dinuclear intermediate would be expected in this process. Thus, we propose the following as the simplest mechanism consistent with our observations:

$$Fe(CO)_4(SiO_2) \Longrightarrow Fe(CO)_4 + SiO_2$$
 (1)

$$Fe(CO)_4 + CO \rightarrow Fe(CO)_5$$
 (2)

 $Fe(CO)_4 + Fe(CO)_4(SiO_2) \rightarrow dinuclear intermediate$ (3)

dinuclear intermediate + $Fe(CO)_5 \rightarrow Fe_3(CO)_{12}$ (4)

The first reaction represents the mechanism for surface migration of $Fe(CO)_4$. Once it is formed in reaction 1, $Fe(CO)_4$ can recombine with the same surface site or can jump to an adjacent site, thereby undergoing a random walk over the silica surface.^{15,30} During this process, Fe-

 $(CO)_4$ may be trapped by CO to give $Fe(CO)_5$ as in reaction 2. Alternatively, by a series of jumps, two molecules of $Fe(CO)_4$ can eventually encounter one another and can combine to yield a dinuclear intermediate. This reaction will most likely occur on every encounter, since dimerization of weakly complexed $Fe(CO)_4$ has been observed in a matrix at temperatures down to 10 K.²³

In the final step leading to $Fe_3(CO)_{12}$, the dinuclear complex must react with an additional mononuclear species. The reaction must proceed at a high rate relative to reactions 1 and 3 to explain the lack of an induction period. For this reason, we have proposed reaction 4, since $Fe(CO)_5$ appears to be very mobile on the silica surface at 150 K, and will thus have a much higher probability of encountering the dinuclear intermediate than will $Fe(CO)_4$. Reaction 4 clearly must have a rather low barrier, however, to be consistent with our observations. This is not unlikely if the dinuclear intermediate is very reactive. The nature of the dinuclear intermediate is unclear, although the most obvious candidate is the 18-electron species $Fe_2(CO)_8(SiO_2)$. Another possibility is $Fe_2(CO)_8$, as this species can also possess an 18-electron configuration with a formal ironiron double bond. $Fe_2(CO)_8$ is expected to be quite reactive,³¹ which could account for the relatively high rate of reaction 4.

Conclusion

We have studied the photolysis of silica-adsorbed Fe- $(CO)_5$ at reduced temperatures. At temperatures ≥ 200 K, the only significant photoproduct is $Fe_3(CO)_{12}$, indicating that thermal reactions of photochemically formed intermediates rapidly occur even at reduced temperatures. Some insight into the nature of these thermal processes was obtained by the observation of a thermally unstable photoproduct in photolyses carried out at 100 and 150 K. This product was assigned, on the basis of its IR spectrum, as $Fe(CO)_4(SiO_2)$, where SiO_2 represents a silica surface hydroxyl group or siloxane bridging oxo group. Fe(C- $O_4(SiO_2)$ was found to react at $T \ge 150$ K, giving $Fe_3(C O_{12}$ and $Fe(CO)_5$, suggesting that this species is an important intermediate in the formation of $Fe_3(CO)_{12}$ upon photolysis of silica-adsorbed Fe(CO)₅ at higher temperatures. A mechanism was proposed for the formation of $Fe_3(CO)_{12}$ whereby $Fe(CO)_4$, formed via dissociation of $Fe(CO)_4(SiO_2)$, undergoes an encounter-controlled dimerization on the silica surface, and the dinuclear intermediate thus formed rapidly reacts with $Fe(CO)_5$.

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Registry No. Fe(CO)₅, 13463-40-6; Fe₃(CO)₁₂, 17685-52-8; silica, 7631-86-9.

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