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Iron/Alkene Reactions: A Matrix Isolation Infrared and Mössbauer Investigation[1]

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The reactions of matrix-isolated iron atoms and clusters with the alkenes ethylene and propylene have been investigated by infrared and Mössbauer spectroscopies. In ethylene at low temperatures (<18 K) and with low iron concentrations (<1%) the major product is $Fe(C_2H_4)$. This is the only monoiron product formed, although unreacted iron atoms can be observed in pure ethylene at 4.2 K. Irradiation with the unfiltered output of a high-pressure Xe lamp causes the unreacted iron atoms to react to $Fe(C_2H_4)$. At higher temperatures and iron concentrations additional products $Fe_2(C_2H_4)_x$ (x = 1, 2) and $Fe_p(C_2H_4)_p$ ($p > 2$) are formed. Mössbauer spectra of Fe/C_3H_6 at both 4.2 and 20 K are very similar to those of Fe/C_2H_4. Hence the products are similarly assigned to $Fe(C_3H_6)$, $Fe_2(C_3H_6)_2$, and $Fe_p(C_3H_6)_p$ ($p > 2$). The Mössbauer spectra of the products indicate that the electronic configuration of the iron atoms in the alkene complexes is approximately $(4s)^1(3d)^7$, in agreement with theoretical work. The Mössbauer spectra of $Fe(C_2H_4)$ and $Fe(C_3H_6)$ are also consistent with the proposal that C_2H_4 and C_3H_6 are primarily σ donors with only minimal $d_\pi \rightarrow \pi^*$ back-bonding.

Introduction

The mechanistic details of the reactions that occur on single-crystal surfaces and on heterogeneous catalysts are not well understood. It has been proposed[2] that well-defined metal clusters or even single atoms are reasonable, simple models of the more complex larger systems. This view has been challenged.[3]

Matrix isolation is one technique whereby a single atom or a few atom cluster is allowed to interact with a reactant under controlled conditions, usually without the complication of additional ligands. In spite of its widespread use in industry as a heterogeneous catalyst, there have been relatively few matrix isolation studies of iron and its reactions. In addition, ^{57}Fe (2.2% natural abundance) shows the Mössbauer effect. This Mössbauer isotope has narrow lines and hence good resolution. It is also one of the most straightforward to use experimentally. The Mössbauer effect allows the direct observation of each type of iron atom present. The resulting spectrum provides information about the electronic environment, the local symmetry, and the stoichiometry of the iron complex. Infrared spectroscopy provides complementary information about the coordinated ligands. Thus together the two forms of spectroscopy give a more complete picture of the iron complex.

We have chosen to investigate the reactions of iron atoms and clusters with simple alkenes in order to provide a model for the reactions of alkenes at an iron surface.

Experimental Section

Detailed descriptions of both the Mössbauer[4] and the infrared[5] vacuum systems have been published.

In brief, the samples for infrared spectroscopy were prepared by deposition onto a NaCl window held at 16–20 K by an Air Products Displex closed-cycle refrigerator. Iron was evaporated either from resistively heated iron powder (Research Organic/Inorganic Corp. 99.99%) in an alumina crucible held in a tantalum furnace or by direct resistive heating of an iron foil (Materials Research Corp. 99.99%) clamped between water-cooled electrodes. Foil evaporation was more difficult to control but resulted in lower temperatures at the cold window. Temperatures were measured with an optical pyrometer and were typically 1450–1550 °C for the crucible and 1250–1350 °C for the foil. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer. This was interfaced to a Radio Shack Model II TRS-80 microcomputer.

Samples for Mössbauer spectroscopy were prepared on a Be disk at 4 K with a Janis liquid-helium cryostat or an Air Products Mössbauer Displex closed-cycle helium refrigerator. This uses a helium exchange gas, resulting in higher temperatures during deposition than the Displex used for the infrared experiments. All the Mössbauer experiments used ^{57}Fe (New England Nuclear 95.85% enriched). This was evaporated from an alumina crucible held in a furnace similar to that used for the infrared experiments. Mössbauer spectra were recorded with a conventional constant-acceleration spectrometer using a $^{57}Co/Rh$ source. A natural-abundance α-Fe foil at room temperature was used for calibration. All isomer shifts are given with respect to α-Fe. The multichannel analyzer output was also interfaced to the TRS-80. The Mössbauer spectra were computer fit to a sum of quadrupole doublets with either the TRS-80 or a VAX/PDP11. The pairs of peaks were constrained to have equal amplitudes and full widths at half-maximum. A Lorentzian line shape was used to each peak. The standard statistical tests X^2 and MISFIT were used as quantitative measures of the quality of the fit.

Argon (Linde 99.999%), ethylene (Linde 99.5%), ethylene-1,2-$^{13}C_2$ (Merck Sharp and Dohme 90 atom % ^{13}C), and propylene (Linde 99.5%) were used without further purification.

Results

Infrared Experiments. When Ar/C_2H_4 gas mixtures are condensed with iron vapor at 16–20 K, new infrared absorptions appear in the regions 1550–1450 and 1250–1150 cm^{-1}. These bands only appear when iron and ethylene are present in the matrix. Background experiments without iron, but under otherwise identical conditions, do not show these bands. When iron is present, the new bands, although weak, occur and are consistently reproducible. These spectral regions are characteristic of ethylene coordinated to metal atoms and clusters. The vibrations correspond mainly to the C=C stretch and C—H bend of the coordinated olefin, although normal-coordinate analyses of ethylene complexes[6,7] show that these vibrations are extensively mixed.

At the lowest iron concentrations two new absorptions appear at 1491 and 1215 cm^{-1}. (The latter band partly overlaps a weak band due to unreacted ethylene at 1220 cm^{-1}.) These bands appear with a constant intensity ratio in matrices containing from 1 to 100% C_2H_4 (Figure 1) and during warm-up experiments. The occurrence of these bands at the lowest iron and ethylene concentrations suggests that the species consists of only one iron atom and one coordinated ethylene. In addition, its presence in pure ethylene implies that this product is the only monoiron complex formed.

The stoichiometry of the complex is confirmed by the concentration dependence of the 1491-cm^{-1} band and by

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[†] Department of Chemistry.
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(1) A preliminary report of this work was presented at the 3rd International Matrix Isolation Conference, Nottingham, England, July 20th, 1981.

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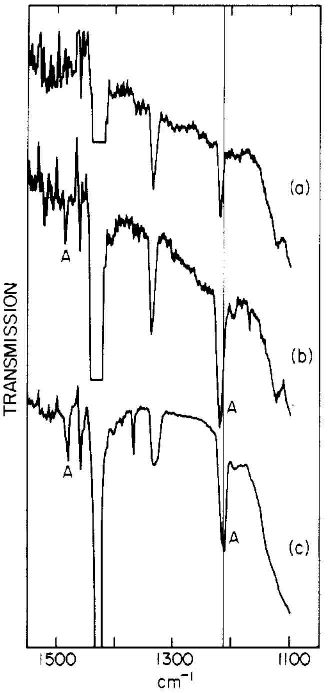

Figure 1. Infrared spectra, showing the absorptions of $Fe(C_2H_4)$ (A), of ethylene-containing matrices in the $\nu_{C=C}$ and δ_{C-H} regions at 15 K: (a) Ar/C_2H_4 (10%); (b) Ar/C_2H_4 (1.5%)/Fe (0.4%); (c) C_2H_4/Fe (0.5%).

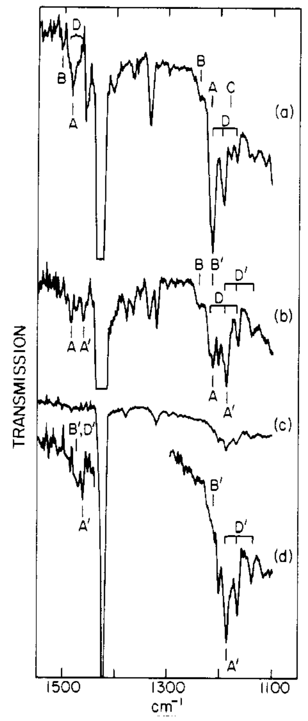

Figure 2. Infrared spectra of (a) $Ar/{}^{12}C_2H_4$ (10%)/Fe (1.5%) (×5 expansion), (b) $Ar/{}^{12}C_2H_4$ (10%)/${}^{13}C_2H_4$ (10%)/Fe (1.2%) (×5 expansion), (c) $Ar/{}^{13}C_2H_4$ (10%)/Fe (1.2%), and (d) ×5 scale expansion of (c) showing the isotope patterns of the iron/ethylene reaction products. Note that (b) is a superposition of (a) and (c).

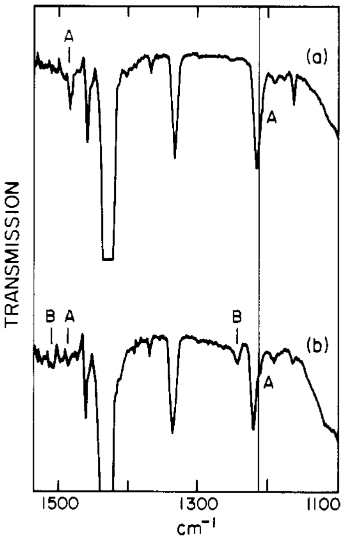

Figure 3. Infrared spectra of Ar/C_2H_4 (10%)/Fe (0.7%) (a) as it is deposited at 17 K and (b) after it is annealed to 35 K and recooled to 17 K, showing the reaction A → B.

mixed-isotope (${}^{12}C_2H_4/{}^{13}C_2H_4$) studies. The intensity of the 1491-cm^{-1} peak is proportional to the first power of the iron concentration. This is good evidence that the absorbing species contains only one iron atom. The mixed-isotope studies (Figure 2), particularly in the 1500–1450-cm^{-1} region, show that the species contains only one coordinated C_2H_4 molecule. The absence of any new absorptions between the 1491/1469-cm^{-1} doublet of $Fe({}^{12}C_2H_4)/Fe({}^{13}C_2H_4)$ respectively is good evidence for a single ethylene coordinated to an iron atom. If the complex were $Fe(C_2H_4)_n$ ($n > 1$), then in addition to the peaks corresponding to $Fe({}^{12}C_2H_4)_n$ and $Fe({}^{13}C_2H_4)_n$ there would have been the absorptions of the mixed ${}^{12}C_2H_4/{}^{13}C_2H_4$ complexes $Fe({}^{13}C_2H_4)_i({}^{12}C_2H_4)_{n-i}$ ($1 \leq i \leq n - 1$).

When the matrices with low concentrations of iron are warmed to 35 K and recooled for spectral recording, two new absorptions at 1510 and 1246 cm^{-1} grow in together. There is a simultaneous loss in intensity of the peaks of $Fe(C_2H_4)$ (Figure 3). The mixed-isotope studies show only a doublet for this new species in the C–H bend region. This is inconsistent with a reaction of the type

$$Fe(C_2H_4) + C_2H_4 \rightarrow Fe(C_2H_4)_2 \qquad (1)$$

because such a product would be expected to show a triplet of absorptions in the mixed-isotope studies as has been observed for $Cu(C_2H_4)_2$.[8] Furthermore, for all the metal/olefin systems that have been examined in pure ethylene, on deposition, the major mononuclear product, $M(C_2H_4)_n$, is the one that has the largest possible value of n for the given metal M; e.g., n = 3 for Ni, Pd. This would imply that the species responsible for the 1510/1246-cm^{-1} bands should be the major product before annealing, which it is not.

The reaction

$$Fe(C_2H_4) + Fe(C_2H_4) \rightarrow C_2H_4\text{–}Fe\text{–}Fe\text{–}C_2H_4 \qquad (2)$$

in consistent with the evidence. If the vibrational coupling between the two ethylene molecules across the Fe–Fe bond were small, then the isotopic spectra would only show a doublet and not a triplet. Minimal vibrational interaction across a metal–metal bond has been observed in a number of systems for both ethylene ($M_2(C_2H_4)_2$, M = Co,[9] Cu[8]) and carbon monoxide ($M_2(CO)_2$, M = Ni,[10] Cu[11]). By analogy to $Ni_2(C_2H_4)_x$ (x = 1,2),[12] the breadth of the bands (~15 cm^{-1}) and their position at higher energy than those of $Fe(C_2H_4)$ also suggest that they are due to a low-nuclearity cluster.

Cocondensation at either a higher temperature, 20 K, or higher iron concentrations results in additional bands (Figure

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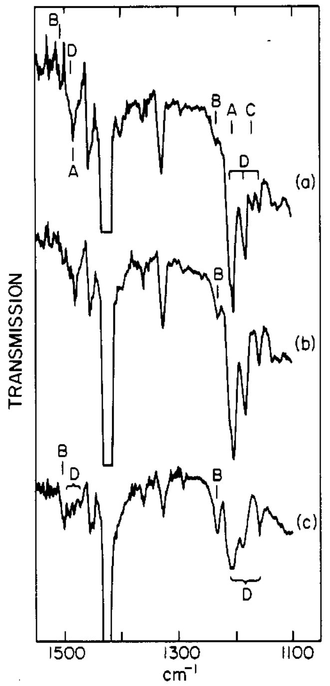

Figure 4. Infrared spectra of an Ar/C_2H_4 (10%)/Fe (1.5%) matrix (a) as it is deposited at 17 K, (b) after it is annealed to 30 K, and (c) after it is annealed to 35 K, showing the reactions C → B and A → B.

4) at 1493 br, 1220, 1200, 1186, and 1172 cm^{-1}. Warm-up experiments indicate that the 1493 br/1220/1200/1172-cm^{-1} bands belong to a single species and that the 1186-cm^{-1} band belongs to a different species.

On warming of the matrix to 30 K the 1186-cm^{-1} band rapidly diminishes in intensity and those of $Fe_2(C_2H_4)_2$ grow in (Figure 4b). This suggests that the species responsible for the 1182-cm^{-1} band can be facilely converted into $Fe_2(C_2H_4)_2$. Such a species would be $Fe_2(C_2H_4)$. This simply adds C_2H_4 to give $Fe_2(C_2H_4)_2$:

$$Fe–Fe–C_2H_4 + C_2H_4 \rightarrow C_2H_4–Fe–Fe–C_2H_4 \quad (3)$$

Annealing to 30 K results in little or no change in the intensity of the bands of $Fe(C_2H_4)$. This is consistent with the difference between reactions 2 and 3. Thus (3) involves reaction with a molecule that is part of the matrix cage, perhaps just a reorientation of the reactants, whereas (2) requires diffusion of the reactants through the matrix, a higher energy process.

The identity of the species responsible for the bands at 1493 br/1220/1200/1172 cm^{-1} is less certain. Its production under conditions of high iron concentration, or considerable surface diffusion, all suggest a low-nuclearity cluster, $Fe_p(C_2H_4)_q$ (p, $q > 2$). Its persistence up to the point where the matrix is boiling off (40–50 K) supports this assignment. The mixed-isotope studies again indicate only a monoethylene product (Figure 2). However, the three C–H bend bands show that there is more than one coordinated ethylene molecule in the complex. Thus for the same reasons as elaborated for $Fe_2(C_2H_4)_2$ the isotope data suggest there is one C_2H_4 per Fe atom. Hence, a reasonable formula would be $Fe_p(C_2H_4)_p$ ($p > 2$). Table I lists all of the observed infrared bands and their assignments.

Mössbauer Results. The Mössbauer spectra (Figure 5) of low concentrations (<1%) of iron in pure ethylene deposited at 4.2 K show the presence of one major product (A) and three minor products (**1**, B, D). The isomer shift of the doublet **1** is characteristic of matrix-isolated iron atoms,[13] the quadrupole splitting arising from the noncubic site symmetry of solid ethylene.[14] Irradiation of the samples with the unfiltered arc of a high-pressure Xe lamp results in the complete loss of the iron monomer (Fe_1) doublet and concomitant growth of the doublet A. This is very similar to the recent demonstration that iron atoms could be isolated in pure CO at 4.2 K and converted solely to $Fe(CO)_5$ on irradiation.[5] This would suggest that A is a mononuclear reaction product of iron atoms with ethylene.

Table I. Infrared Frequencies[a] and Assignments for the Iron/Ethylene System

species	$\nu_{C=C}$	δ_{C-H}	assignt
A	1491	1215	$Fe(^{12}C_2H_4)$
A′	1469	1192	$Fe(^{13}C_2H_4)$
B	1510	1246	$Fe_2(^{12}C_2H_4)_2$
B′	1485	1216	$Fe_2(^{13}C_2H_4)_2$
C		1186	$Fe_2(^{12}C_2H_4)$
D	1493 br	1220, 1200, 1172	$Fe_p(^{12}C_2H_4)_p$ ($p > 2$)
D′	1465 br	1194, 1170, 1144	$Fe_p(^{13}C_2H_4)_p$ ($p > 2$)

[a] All frequencies (±1) are in cm^{-1} for the products in an Ar/$^{x}C_2H_4$ (10%) (x = 12 or 13) matrix at 18 K.

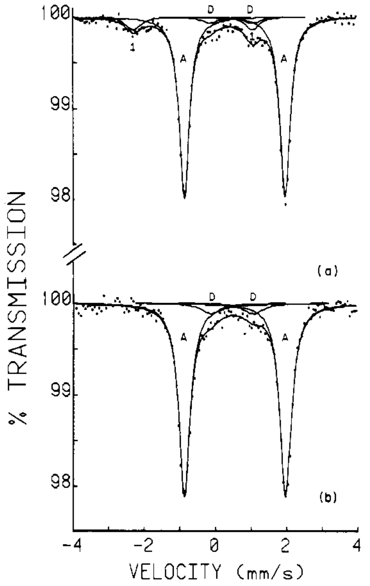

Figure 5. Mössbauer spectrum of C_2H_4/Fe (0.5%) at 4.2 K (a) at the time of deposition and (b) after 2-min irradiation with a high-pressure Xe lamp. Included in the fit but not shown for the sake of clarity is a small contribution from $Fe_2(C_2H_4)_2$ (B).

It has been shown[15] that for a metal cluster of x metal atoms (M) and their associated ligands (L), the ratio of the concentration of the metal cluster (M_xL_y) to that of a mononuclear complex (ML_z) is proportional to the total metal concentration to the power $x - 1$:

$$[M_xL_y]/[ML_z] \propto [M]_{total}^{x-1}$$

This relationship holds for low metal concentrations and excess ligand. For a Mössbauer absorption, the area of the peak is proportional to the product of the number of absorbers multiplied by the recoil-free fraction (probability that a Mössbauer absorption will occur).[16] Hence, a log–log plot of the ratio of the area of A to that of **1**, the iron monomer, vs. total iron concentration will be a straight line of slope x

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(13) McNab, T. K.; Micklitz, H.; Barrett, P. H. *Phys. Rev. B: Solid State* **1971**, *4*, 3787.

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(15) Hulse, J. E.; Moskovits, M. *J. Chem. Soc., Faraday Trans. 2* **1977**, 471.

(16) Note that the recoil-free fractions of Fe_1 and A only appear in a constant term. Measurement of the total area of the spectrum before and after irradiation shows that the total area is approximately (±5%) constant. Thus the individual recoil-free fractions of Fe_1 and A must also be approximately equal, implying that the constant term is nearly zero.

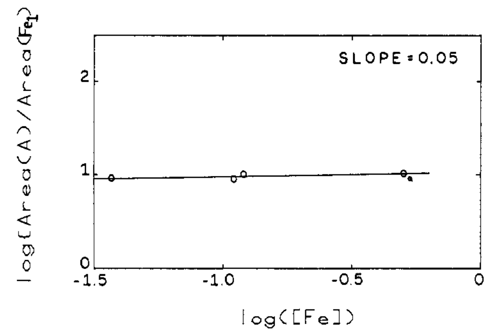

Figure 6. Ratio of the Mössbauer absorption areas of species A:Fe_1 vs. iron concentration. The subscript "a" denotes data from ref 17.

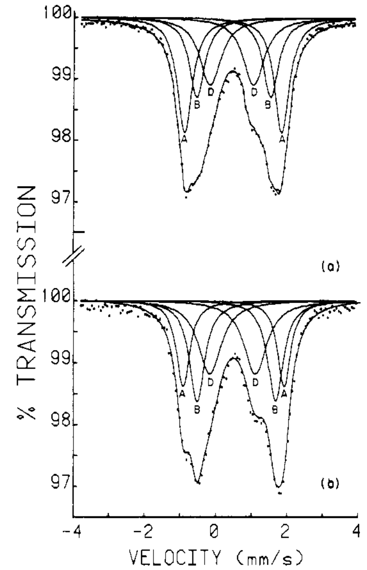

Figure 7. Mössbauer spectra of C_2H_4/Fe (0.7%) at 20 K (a) at the time of deposition and (b) after annealing to 60 K.

$- 1$. From the graph (Figure 6) $x = 1$ so A contains only a single iron atom as expected from the infrared experiments.

In another experiment (not shown) the spectrum consisted of A, larger amounts of B and D, and a well-resolved magnetic hyperfine pattern due to a product E. This has the following Mössbauer parameters: isomer shift +0.52 mm s^{-1}, quadrupole splitting 0.0 mm s^{-1}, and internal magnetic field 450 kG. For iron in argon it has been shown[17] that at least a six-atom cluster is required in order to see a magnetic hyperfine pattern. The positive isomer shift of E suggests that it is an iron/ethylene reaction product. It would seem reasonable that a cluster of several iron atoms is required in order to be able to observe magnetic splitting. Thus, the presence of E shows that considerable diffusion has occurred in this sample even though the total iron concentration is only ~0.1%. Hence, the larger quantities of B and D indicate that they also arise from the reaction of small clusters of iron with ethylene.

The Mössbauer spectra of samples (Figure 7) prepared at 20 K show the presence of products A, B, and D. Annealing of the samples shows the transformation A → B with D remaining approximately constant. This is very similar to the situation seen in the infrared experiments, where $Fe(C_2H_4)$ reacted to give $Fe_2(C_2H_4)_2$ on annealing. Hence, A is assigned to $Fe(C_2H_4)$ and B to $Fe_2(C_2H_4)_2$. A reasonable assignment for D would be to identify it with the $Fe_p(C_2H_4)_p$ cluster. The absence of magnetic splitting indicates that p is small. This is supported by the broad line widths indicative of the wide variety of possible structures for a few-atom cluster. The

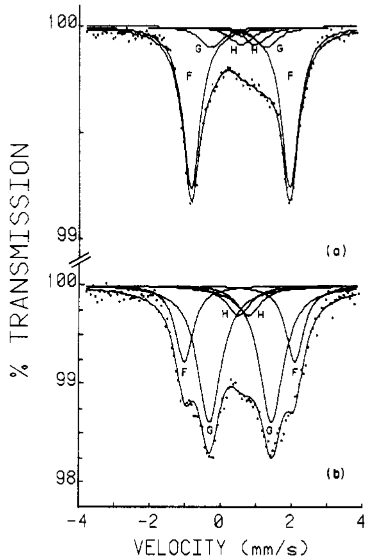

Figure 8. Mössbauer spectra of C_3H_6/Fe (0.6%) (a) at the time of deposition and (b) after annealing to 60 K.

Table II. Mossbauer Parameters[a] for the Iron/Ethylene System in Pure C_2H_4 at 20 K and for the Iron/Propylene System in Pure C_3H_6 at 20 K

species	δ	Δ	Γ	assignt
1	−0.71	3.20	0.50	Fe_1[b]
A	+0.55	2.80	0.43	$Fe(C_2H_4)$
B	+0.52	2.20	0.54	$Fe_2(C_2H_4)_2$
D	+0.54	1.16	0.73	$Fe_p(C_2H_4)_p$ ($p > 2$)
E	+0.52	0.00	1.57	$Fe_q(C_2H_4)_q$ ($q > 2$)[b,c]
F	+0.54	2.95	0.44	$Fe(C_3H_6)$
G	+0.57	1.65	0.60	$Fe_2(C_3H_6)_2$
H	+0.64	0.35	0.84	$Fe_p(C_3H_6)_p$ ($p > 2$)

[a] Isomer shifts (δ), quadrupole splittings (Δ), and line widths (Γ) are in mm s^{-1}. [b] Values at 4.2 K. [c] Internal magnetic field 450 kG.

Mössbauer spectrum suggests that the cluster is very similar to $Fe(C_2H_4)$ and $Fe_2(C_2H_4)_2$, so a formula with an equal number of iron atoms and ethylene molecules would seem reasonable. Thus the stoichiometry $Fe_p(C_2H_4)_p$ ($p > 2$) is in accord with all the available data. However, a formula where the number of coordinated ethylene molecules differs slightly from the number of iron atoms cannot be ruled out. All of the Mössbauer experiments were conducted in pure ethylene. Thus the absence of any absorptions that can be ascribed to $Fe_2(C_2H_4)$ is not surprising. In addition the broad lines would allow small (~5%) amounts of the complex to remain undetected.

The iron/polypropylene system was also investigated by Mössbauer spectroscopy (Figure 8). As expected, the spectra are very similar to those of iron/ethylene. At 4.2 K the major product (~90%) is a quadrupole doublet Fe with parameters virtually identical with those of $Fe(C_2H_4)$; hence, this is assigned to $Fe(C_3H_6)$. Interestingly, there are no unreacted iron atoms in this case, showing a difference in reactivity between ethylene and propylene. Deposition at 20 K produces three products, F, G, and H. These behave very similarly to the three products obtained in Fe/C_2H_4 depositions at 20 K. By analogy to the Fe/C_2H_4 system G and H are assigned to $Fe_2(C_3H_6)_2$ and $Fe_p(C_3H_6)_p$ ($p > 2$), respectively. The Mössbauer parameters for the species observed in the iron/ethylene and iron/propylene systems are given in Table II.

Discussion

The iron/ethylene system proved to be surprisingly difficult to characterize. This was the result of two factors. The first was the critical temperature requirement. To obtain $Fe(C_2H_4)$

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[17] McIntosh, D. F.; Ozin, G. A.; Messmer, R. P. *Inorg. Chem.* **1980**, *19*, 3321.

by itself, a temperature of less than ~18 K was needed. Deposition at 20–25 K gave mainly $Fe_x(C_2H_4)_y$ ($x \geq 2, y \geq 1$) products. Deposition above 25 K resulted in no infrared-observable products. This is corroborated by the Mössbauer spectra. Deposition at 4.2 K gave mainly (~80%) $Fe(C_2H_4)$ whereas deposition at 20 K gave mainly (>70%) iron/ethylene complexes containing more than one iron atom.

The second factor was the extensive band overlap in both the Mössbauer and the infrared spectra. This was particularly so in the C–H bend region. This was further complicated by an ~25-cm^{-1} difference in the positions of the bands. Since the $^{12}C_2H_4/^{13}C_2H_4$ isotope shifts are also ~25 cm^{-1}, there is considerable overlap of $^{12}C_2H_4$ and $^{13}C_2H_4$ products.

We note that the use of isotopic substitution may lead to incorrect conclusions if the vibrational coupling between the coordinated ethylene molecules is small. This is apparently the case for silver.[17] Mixed isotopic substitution, $^{12}C_2H_4/^{13}C_2H_4$, indicated a monoethylene formulation, $Ag(C_2H_4)$. Electron spin resonance (ESR) experiments[18] have demonstrated that the complex is actually $Ag(C_2H_4)_2$. However, the available data suggest that silver may be atypical. Earlier ESR work[19] had indicated that $Ag(C_2H_4)$ was only very weakly bonded, in that the change in the ESR parameters of the silver atom in the complex was within the range caused by matrix perturbations of silver atoms. Presumably the weakness of the bonding causes the expected shifts in the infrared spectrum of coordinated vs. uncomplexed ethylene to be too small to be observed. This behavior is to be contrasted with that of Co,[9] Ni,[12] Cu,[8] Rh, and Pd.[20] For all of these metals the infrared spectra show that bona fide complexes, $M(C_2H_4)_n$ ($n = 1 \rightarrow n_{max}$), are formed. Furthermore, in the cases where isotopic substitution experiments were performed (Co, Cu, Rh, and Pd) the spectra of the mixed $^{12}C_2H_4/^{13}C_2H_4$ complexes were seen. This indicates that the vibrational coupling of the coordinated olefins is reasonably strong and there is no apparent reason why iron should be different from these typical transition metals. Furthermore, both the ethylene concentration study and the isotopic substitution experiments point to a monoligand formulation.

The Mössbauer spectrum of iron in pure ethylene at 4.2 K has been previously reported.[22] In this case the spectrum, identical with that in Figure 5a, was interpreted as being due, in part, to unreacted iron atoms, the major product A was assigned to an iron dimer product, and the remainder of the spectrum to an ethylene reaction product of an iron trimer or higher multimer. The identification of the iron monomer is indisputable. However, the concentration dependence of A shows conclusively that this product contains only a single iron atom. The identification of the third product with an iron multimer reaction product is not unreasonable, although we prefer the more detailed assignment given in this paper. The principal difference between deposition at 4.2 and 20 K is the degree of clustering that occurs. Thus, it seems reasonable to use the more accurate values of the clusters (because of the larger amounts present) obtained from the 20 K work as an aid to the analysis of the minor components in the 4.2 K data.

That iron forms only a monoalkene complex is somewhat surprising. However, it does fit very well with the trend to increasing coordination number that has been observed for matrix-isolated ethylene complexes as the first row of the transition metals is traversed: $Fe(C_2H_4)$, $Co(C_2H_4)_{1,2}$, $Ni(C_2H_4)_{1,2,3}$, $Cu(C_2H_4)_{1,2,3}$. The formation of only a monoalkene complex is not unprecedented although it has only previously been found for Au.[23] Interestingly Pd and Pt form complexes of the same stoichiometry and Rh forms a complex of higher stoichiometry than their congeners in the first transition series.

This work supports the conclusions arrived at from studies of other metal/alkene systems.[8,9,12,23] From these it appears that the alkene is coordinated to the metal with only minimal changes in the coordinated ligand. Thus, the Mössbauer spectra of Fe/C_3H_6 samples are virtually identical with those of Fe/C_2H_4 samples, indicating that propylene is coordinated through the π-bond rather than as an allyl complex.

There have been a number of theoretical studies made on systems relevant to this work. The Fe dimers[24] FeM (M = Mn, Fe, Co, Ni, Cu) have been investigated by a variational technique, Goddard and co-workers have investigated a series of complexes of the type NiX (X = CO,[25] CH_2, CH_3,[26] C_2H_2, C_2H_4,[27] $Ni(C_2H_4)$[12]) by generalized valence bond theory with configuration interaction (GVB–CI). These studies all show a remarkable degree of agreement, in that they all conclude the electronic configuration of the metal atom is changed from $(4s)^2(3d)^n$ to $(4s)^1(3d)^{n+1}$.

The Mössbauer isomer shift gives direct information on the electronic configuration of the iron atom via the relationship

$$\text{isomer shift} = k|\Psi(0)|^2 + \text{constant}$$

where $|\Psi(0)|^2$ is the electron density at the nucleus and k is the isomer shift calibration constant. This is negative for ^{57}Fe; hence, the larger the value of $|\Psi(0)|^2$, the more negative the isomer shift. In a nonrelativistic approximation only s electrons have a non-zero value of $|\Psi(0)|^2$. However, electrons in other shells can affect the value of $|\Psi(0)|^2$ indirectly by shielding of the s electrons. From the known isomer shifts of Fe_1 $(4s)^2(3d)^6$,[13] Fe^+ $(4s)^1(3d)^6$,[28] and Fe^+ $(3d)^7$ [29] together with theoretical values[30] of $|\Psi(0)|^2$, an isomer shift of approximately +1.0 mm s^{-1} may be estimated for Fe_1 $(4s)^1(3d)^7$. The measured isomer shifts of the iron/alkene complexes are all ~+0.5 mm s^{-1}. This is intermediate between the values of Fe_1 $(4s)^2(3d)^6$ and Fe_1 $(4s)^1(3d)^7$ but much closer to the latter. Thus, this study provides strong experimental evidence for the validity of the conclusions from the theoretical work.

The GVB–CI studies also conducted that for ethylene[27] the principal interaction was a σ bond with the π electrons of the olefin donated to the metal 4s orbital and only minimal back-bonding from the metal d orbitals to the ligand π^* orbitals. A similar study of Ni(CO)[25] concluded that in this case there was a small but significant amount of $d_\pi \rightarrow \pi^*$ back-bonding. The Mössbauer results for Fe(CO),[5] $Fe(NH_3)$,[31] $Fe(C_2H_4)$, and $Fe(C_3H_6)$ are in agreement with this conclusion. The removal of an s electron by the rehybridization of the iron atom to $(4s)^1(3d)^7$ increases the isomer shift, while removal of d electrons by $d_\pi \rightarrow \pi^*$ back-bonding decreases the shielding of the s electrons, hence decreasing the isomer shift. The measured order of the isomer shifts in Fe(X) is

$$X = CO < C_2H_4 \approx C_3H_6 \leq NH_3$$

Thus, CO has significant π bonding and therefore shows the most negative isomer shift. NH_3 is a pure σ donor and so has the most positive isomer shift, fairly close to that calculated for Fe_1 $(4s)^1(3d)^7$. C_2H_4 and C_3H_6 have isomer shifts close

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to that of NH_3, reflecting the predominantly σ-donor nature of these alkenes.

The products $Fe(C_2H_4)$, $Fe_2(C_2H_4)_2$, and $Fe_p(C_2H_4)_p$ all have similar isomer shifts and quadrupole splittings, implying similar electronic configurations. Thus, it would appear that addition of further $Fe-C_2H_4$ units to $Fe(C_2H_4)$ itself causes only a small perturbation to the iron atom. This is in agreement with the results of the GVB-CI study of $Ni_2(C_2H_4)$.[12]

One of the unexpected findings of this research was the presence of small amounts ($\sim$10%) of unreacted iron atoms in pure C_2H_4 at 4.2 K in addition to $Fe(C_2H_4)$. Although unreacted atoms in a pure reactive matrix are surprising, they are not unknown. Cobalt[9] and copper[8] atoms have been observed by ultraviolet spectroscopy (UV) in pure C_2H_4 at 12 K. Chromium and vanadium[32] atoms have been observed by UV in pure N_2 at 4.2 K. In the case of iron, unreacted atoms have been detected by Mössbauer spectroscopy in pure N_2 (also by UV[3]), in CO,[5] and in CH_4.[33] So it would appear that the persistence of bare atoms in pure, reactive matrices is apparently not uncommon. This points to the existence of a small activation energy. Our results show that this energy can be supplied either thermally or photolytically. In the latter case whether the mechanism is direct reaction of an excited-state atom or just a local heating of the matrix is difficult to say.

To our knowledge there have been no surface vibrational studies of the iron/ethylene system. Part of the reason for the paucity of data is that iron surfaces are notoriously difficult to clean. However, recent work[34] appears to have overcome this problem. From a study[35] of ethylene on the α-Fe(100) surface using low-energy electron diffraction and ultraviolet photoemission spectroscopy, it was concluded that ethylene is molecularly absorbed at 77 K. Cleavage of the double bond to surface methylene groups started to occur at 98 K and by 123 K was complete. Our matrix isolation study gave no evidence for $C{=}C$ cleavage at any temperature up to the highest annealing temperature used (50 K), the only reaction being clustering of the iron/alkene complexes. (There have been no reports of cleavage of $C{=}C$ bonds by matrix-isolated atoms or clusters.) Thus, while both iron clusters and iron surfaces can molecularly bond alkenes, the small clusters are unable to cleave the double bond. Whether this is due to the temperature being too low to provide the necessary activation energy for the process, or to a fundamental difference between clusters and surfaces, is a question we are unable to answer.

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Preparation, Spectroscopic Characterization, and Photochemical and Electrochemical Properties of Some Bis(2,2′-bipyridyl)ruthenium(II) and Tetracarbonyltungsten(0) Complexes of 6-*p*-Tolyl-2,2′-bipyridyl and of 6-*p*-Styryl-2,2′-bipyridyl and Its Copolymers[1]

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The syntheses of 6-*p*-styryl-2,2′-bipyridyl (6-stybpy) (**1**), 6-*p*-tolyl-2,2′-bipyridyl (6-tolbpy) (**2**), 6,6′-di-*p*-tolyl-2,2′-bipyridyl (**3**), $W(CO)_4$(6-stybpy) (**4**), $[Ru(bpy)_2(6\text{-stybpy})](PF_6)_2$ (**5**), and $[Ru(bpy)_2(6\text{-tolbpy})](PF_6)_2$ (**6**) are described. ^{1}H NMR spectra of **5** and **6** taken between 0 and 75 °C reveal that in these complexes the rotation of the phenylene group is hindered. In contrast to $[Ru(bpy)_3]^{2+}$, **5** and **6** are only weakly luminescent at room temperature in fluid solution. Copolymers of **1** with styrene, methyl methacrylate (MMA), or maleic anhydride and copolymers of **4** and **5** with styrene have been prepared by radical-initiated copolymerization. Polymer-bound $Ru(bpy)_2$ complexes of poly(6-stybpy-*co*-MMA) are formed by reaction of $[Ru(bpy)_2(OH_2)Cl]^+$ and a poly(6-stybpy-*co*-MMA) copolymer. The luminescence and photochemical properties of this polymer-bound $Ru(bpy)_2$ complex and also of poly(sty-*co*-$[Ru(bpy)_2(6\text{-stybpy})]^{2+}$) differ quite markedly from those reported for $Ru(bpy)_2$ derivatives of bipyridylated polystyrene, possibly indicating that in this latter material the bipyridyl function is bound to the polystyrene through its 4-position.

Introduction

Research into the properties of polymer-bound compounds has been stimulated inter alia by their usefulness as reagents or as catalysts[2-4] and as electrode coatings.[5-7] The aim of our work in this area has been to determine how the photochemical and photophysical properties of metal complexes such as metal carbonyls,[8] (bipyridyl)ruthenium complexes,[9,10] and porphyrins[10] are modified upon binding to polymers. It is hoped that this information may lead to the design of more efficient

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(1) Throughout this paper a compound number may designate either the neutral complex or its cation.

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