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J. Am. Chem. Soc. 1993, 115, 2864–2870

Reactions of Atomic and Diatomic Iron with Allene in Solid Argon

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Received August 28, 1992

Abstract: The activation of the C–H bond of allene or propadiene by ground-state atomic iron has been observed in solid argon at 10 K. The new matrix-isolated product, propadienyliron hydride, was characterized via FTIR spectroscopy. The photochemistry of the metal atom and allene was studied and revealed the isomerization of allene into propyne via the formation of the σ-bonded iron propyne complex $Fe(HC\equiv CCH_3)$. The latter underwent interesting and rich photochemistry (which will be treated in greater detail in a future publication) with the activation of the methyl and acetylenic C–H bonds as well as the C–C single bond of $HC\equiv CCH_3$. In contrast, diatomic iron exhibited different reactivity toward allene, with the formation of π-complexes that did not photorearrange to a C–H-activated product. Evidence based on FTIR spectroscopy indicates that diatomic iron is simultaneously bonded to the two π-bonds of allene, forcing the latter into a V-shaped structure for $Fe_2(H_2C\!=\!C\!=\!H_2)$. Isotopic studies with $D_2C\!=\!C\!=\!CD_2$ support these findings.

Introduction

The rearrangements of the C_3H_4 molecular system into different geometrical isomers have been the focus of several studies.[1–14] Experimentally, many stable and metastable C_3H_4 isomers have been generated; theoretically, C_3H_4 turned out to be a model system because of its relative simplicity and small size. Both theory and experiments indicate that propyne, or methylacetylene, is the most stable conformer. SCF and CI calculations[4–7] suggest that the conversion from allene to methylacetylene occurs in four steps, via vinylmethylene, cyclopropene, and propenylidine, and has an activation energy of ~66 kcal/mol. Gas-phase studies of shock waves[1–3] and thermal rearrangement[11] indicate that cyclopropene is indeed a reaction intermediate and that the activation energy for the isomerization of allene into methylacetylene is 63.8 kcal/mol.[11] The interactions of C_3H_4 with metal complexes,[15–17] on metal surfaces, and with supported catalysts have been studied;[18–22] in some cases, a considerable lowering of

the activation barrier for isomerization has been observed. In 1978, Khulbe and Mann[23] reported on the isomerization of allene into methylacetylene on cobalt and iron catalysts and measured the activation energies to be 11.2 and 11.8 kcal/mol, respectively. This 80+% decrease in the activation barrier of the tautomerism represents a significant interaction between the metal catalyst and the C–H bonds of the parent hydrocarbon.

The activation of C–H bonds by metals has drawn tremendous attention over the last decade,[24] especially in its application to delineate mechanisms of catalytic reactions and their specificity. Metal atom chemistry has been explored[25–27] to better understand the exact nature of the interactions between hydrocarbons and the metals. Bond activation by neutral and ionized metal atoms has been noted in the gas phase[25,26] and in condensed phases.[27] Use of the matrix isolation technique has proved especially fruitful in providing information on the interactions between zero-valent metal atoms and/or molecular clusters and small hydrocarbons.[28–31] In most cases, an adduct is formed between the atomic or diatomic metal species and the organic molecule of interest; bond rearrangement involving some form of inert bond activation is usually photolytically induced. For instance, in the Fe/CH_4 reaction,[32,33] a σ-bonded $Fe(CH_4)$ adduct was initially

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formed that was electronically excited with UV light and underwent an oxidative addition reaction with the formation of the C–H-activated photoproduct HFeCH₃. C–H bond activation was also photolytically induced in the iron/acetylene,[28] iron/ethylene[29], iron/ethane,[34] and iron/propane[34] reactions; cyclohexadiene was found[31] to undergo dehydrogenation to benzene under the influence of a photoexcited iron atom. A spontaneous rearrangement to cyclopentadienyliron hydride was found[30] in the Fe/cyclopentadiene reaction, possibly due to the fluxional character of C_5H_6. The C–H-activated product cyclopentadienyliron hydride has been implicated as an intermediate in the mechanism of the formation of substituted ferrocenes by direct condensation of iron vapors with cyclopentadiene and alkynes.[35] Carbon–carbon bond activation was observed for the first time in the iron–cyclopropane reaction;[34] relief from ring strain led to C–C rather than C–H bond activation in this system.

The photochemistry of allene has been studied in cryogenic matrices as early as 1974, when Jacox and Milligan[36] noted its fragmentation upon vacuum ultraviolet photolysis. Fluorine reactions with allene were studied by two groups,[37,38] one of which[38] suggested possible selective vibrational mode excitations in the addition reaction of F_2 to one of the C=C double bonds. An isomerization reaction forming HC≡CCH₂F was also reported.[38] More recently, Chernier, Howard, and Mile[39] reported on the reactions between Cu, Ag, and Au atoms and allene via ESR spectroscopy at 77 K. These studies indicated that the metal atoms inserted into the carbon–carbon double bonds to form H₂CCMCH₂ radicals (M = Cu, Ag, Au) but not any vinyl-metal species. This conclusion was surprising when it is realized that most free-radical attacks upon allene occur at the terminal carbons and not at the central carbon.[40] The present study investigates the interactions between iron and allene via FTIR matrix isolation spectroscopy. A similar study between iron and the isomeric molecule propyne will be the subject of a future publication.[41]

Experimental Section

A multisurface matrix isolation apparatus similar in concept but smaller in scale to the one previously reported[42] was used for the present study. The apparatus was interfaced to a Nicolet 740 FTIR spectrometer. Six polished, gold-plated copper surfaces were used for the deposition experiments. A piezoelectric quartz crystal microbalance mounted directly on the metal block allows for a precise measure of the rate of deposition and the molar ratios of metal, reactant, and matrix gases. The block lies on top of a rotatable closed-cycle helium refrigerator, an Air Products Displex Model CSW-202. Temperatures in the range of 10–20 K were used in this study.

Ultrapure iron (99.9985%) was obtained from Johnson Matthey, Inc. Matheson research grade argon (99.9995%) and Airco allene (97%) were used without further purification. An enriched sample of D₂C=C=CD₂, isotopic purity 98%, was purchased from MSD Isotopes. In a typical experiment, iron was placed in an alumina crucible and heated slowly in vacuo at 1000 °C for several hours. It was normally vaporized between 1300 and 1450 °C. The temperature was measured with a W-5%Re/W-25%Re thermocouple placed at the back of the crucible. After the rates of deposition of iron, allene, and argon were measured, the three gases were cocondensed onto the matrix surface for 0.5–1.0 h. The block was then rotated 90°, and a single-beam FTIR spectrum was recorded at a resolution of 0.5 cm⁻¹. A double-beam spectrum was achieved by taking the ratio of the single-beam matrix spectrum to that of a clean matrix surface. Matrices were usually irradiated subsequent to deposition.

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Table I. Infrared Frequencies (cm⁻¹) of the Fundamental Vibrational Modes of Allene and Allene-d_4 in the Gas Phase[43,44] and in Argon Matrices

vibrational mode	sym species	H₂C=C=CH₂ gas	H₂C=C=CH₂ matrix	D₂C=C=CD₂ gas	D₂C=C=CD₂ matrix
ν_1, CH₂ sym str	A₁	3015 (R)ᵃ	n.o.ᵇ	2195 (R)	n.o.
ν_2, CH₂ def	A₁	1443 (R)	n.o.	1228 (R)	n.o.
ν_3, C=C=C sym str	A₁	1073 (R)	n.o.	874 (R)	n.o.
ν_4, CH₂ torsion	B₁	865	864.7	615	n.o.
ν_5, CH₂ sym str	B₂	3007	3000.1	2230	2221.9
ν_6, C=C=C asym str	B₂	1957	1955.4	1921	1917.4
ν_7, CH₂ def	B₂	1398	1388.7	1034	1028.0
ν_8, CH₂ asym str	E	3086	3091.8	2330	2314.2
ν_9, CH₂ rock	E	999	996.4	830	822.5
ν_{10}, CH₂ wag	E	841	837.5	667	663.4
ν_{11}, C=C=C def	E	355	n.o.	306	n.o.

ᵃ (R) denotes Raman active mode. ᵇ n.o. indicates not observed.
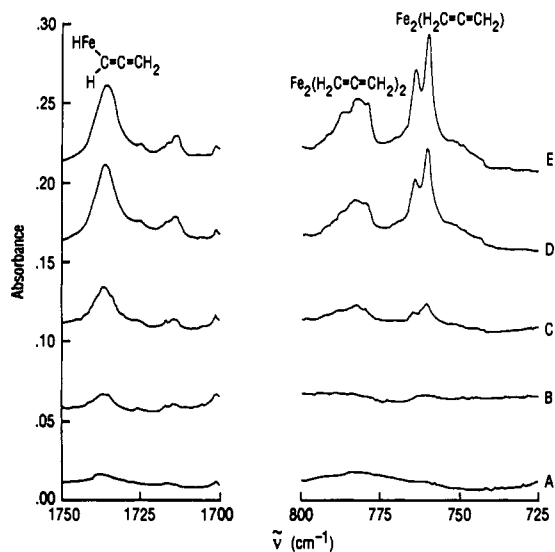
Figure 1. Metal concentration study. FTIR spectra of iron/allene in solid argon. Molar ratios of Fe:H₂C=C=CH₂:Ar are (A) 0.34:-, (B) 0.89:-, (C) 2.3:-, (D) 6.3:-, and (E) 9.8:5.7:1000.

The radiation source is an Oriel 200-W high-pressure Xe/Hg arc lamp. A water filter with various Corning long-pass cutoff filters was used for wavelength-dependent photolysis in the visible region. A band filter, 280 nm < λ < 360 nm, was used for ultraviolet photolysis.

Results

The infrared spectra of matrix-isolated allene and allene-d_4 have been measured in solid argon. The vibrational frequencies and their mode assignments are listed along with gas-phase values[43,44] in Table I. A very small amount of methylacetylene (0.2%) was present in allene but not in the allene-d_4 and did not present any complication in the interpretation of the spectra.

Cocondensation Products. Upon cocondensation of iron vapors with low, constant concentrations of allene in excess argon at 10 K, new absorption bands were observed in the measured FTIR spectra. At low concentrations of iron, one set of new bands was detected, while at higher concentrations a second set of new absorption bands appeared. Figure 1 shows the growth of these Fe/allene product absorption bands versus iron concentration. The absorption bands at 1737.7 and 1714.5 cm⁻¹ appeared at a low iron concentration, about 0.03 mol %. This set of absorption bands increased monotonically and linearly with iron concentration; at high concentrations of iron, however, these bands slowed their growth. A second set of new absorption bands, which includes the peaks at 764.3 and 779.0 cm⁻¹ shown in Figure 1, did not appear until distinctly higher iron concentrations, 0.2 mol %, and continued to increase in intensity with higher metal

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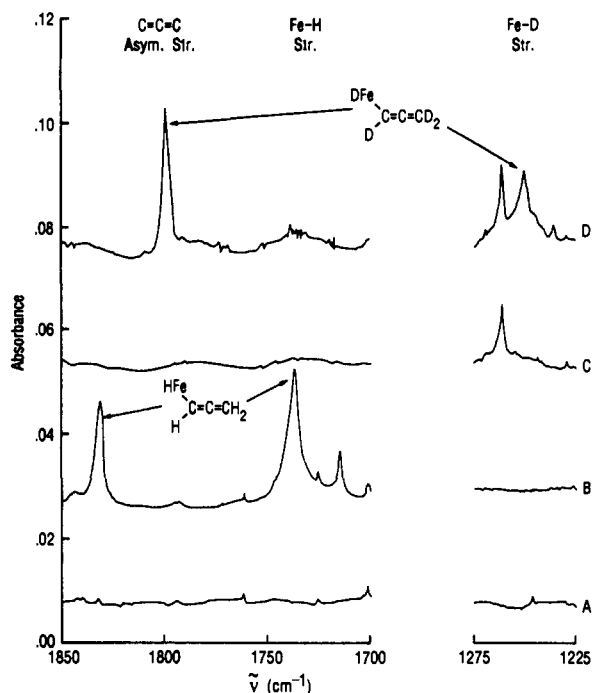
Figure 2. C–H bond activation of allene by ground-state atomic iron. FTIR spectra of the ν(Fe–H/D) and ν_a(C=C=C) stretching regions of propadienyliron hydride. Molar ratios of Fe:H_2C=C=CH_2:Ar are (A) 0:- and (B) 1.3:5.0:1000; those of Fe:D_2C=C=CD_2:Ar are (C) 0:- and (D) 1.0:5.0:1000.

Figure 3. Temperature dependence study of the condensation products. FTIR spectra of iron/allene in argon (spectra collected at 9.5 K). Molar ratio of Fe:H_2C=C=CH_2:Ar is 4.3:5.3:1000. Temperatures of deposition are (A) 9.5, (B) 12.5, (C) 15.0, (D) 17.5, and (E) 20 K.

concentrations. That these sets belong to two separate cocondensation products is also evident in the photolytic behavior of these absorption bands (to be discussed below), and they are assigned to atomic iron/- and diiron/allene products, respectively. Two analogous sets of absorption bands having similar iron concentration behavior were also observed upon cocondensation of iron with allene-d_4. At high concentration of both iron and allene, a broad absorption band appeared in the vicinity of the 779.0 cm^{-1} peak and has been tentatively assigned to Fe_2-(H_2C=C=CH_2)$_2$. No other absorption bands were observed for this complex, and it will not be further considered in this paper.

The new absorption bands at 1737.7 and 1714.5 cm^{-1} assigned to an atomic iron/allene product were accompanied by strong peaks at 428.7, 431.4, and 1832.0 cm^{-1}. Figure 2 shows selected spectral regions, namely 1700–1850 and 1225–1275 cm^{-1}. Upon deuterium isotopic substitution, the peaks at 1737.7 and 1714.5 cm^{-1} shift to 1250.0 and 1234.7 cm^{-1}, as shown in Figure 2. This set of bands occurs in the Fe–H stretching region, and their deuterium isotopic shift confirms this assignment. The peaks at 428.7 and 431.4 cm^{-1} disappear and seem to have shifted beyond the range of the spectrometer. The absorption band at 1832.0 cm^{-1}, identified as the C=C=C asymmetric stretch, shifts only slightly to 1799.0 cm^{-1} upon deuteration. This IR spectral evidence suggests that the cocondensation product contains Fe–H and C=C=C bonds, and we identify it as propadienyliron hydride, or HFeCH=C=CH_2. Formation of this product indicates that spontaneous C–H bond activation with insertion of the metal atom has taken place.

Figure 3 shows selected regions of the IR spectra of the cocondensation of iron with allene in excess argon at different deposition temperatures, from 9.5 to 20 K. The spectral ranges were chosen to be similar to those of Figure 1, where the absorption bands in the 1700–1760 cm^{-1} region have been assigned to the Fe–H stretch of propadienyliron hydride and the absorption bands in the 740–800 cm^{-1} region have been assigned to the as yet uncharacterized (vide infra) diiron/allene products. The bands assigned to propadienyliron hydride decrease with increasing
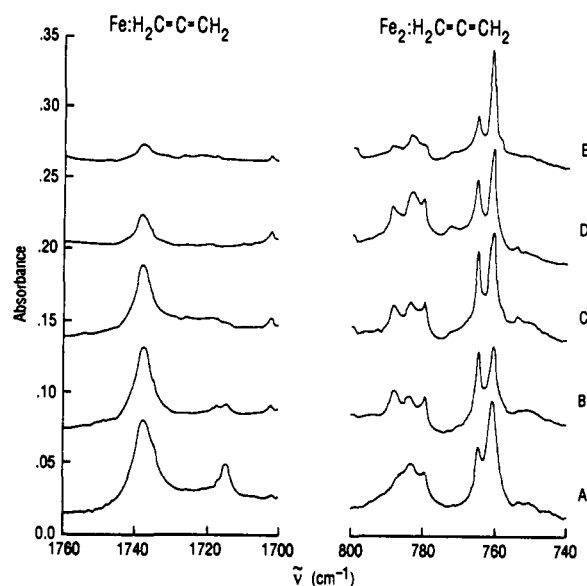
deposition surface temperature, while those assigned to diiron/allene products show little change, except for an alteration of intensities of the two multiplets. While no new chemistry is noted at higher deposition temperatures, the variable temperature behavior confirms the product stoichiometry assignments. The alteration of intensities of the absorption bands assigned to the diiron cocondensation product shown in Figure 3 suggests that there is more than one matrix site or diiron/allene products. Although the iron concentration study indicates that the absorption bands under question are indeed due to diiron, the temperature dependence study shows that certain diiron/allene absorption bands are favored at higher temperatures. For instance, the absorption band at 760.4 cm^{-1} shown in Figure 3 seems to persist at higher temperatures up to 20 K. On the other hand, the peak at 764.5 cm^{-1} shows the opposite effect. The photolytic behavior of the diiron absorption bands, discussed below, suggests that there are indeed two separate isomeric products.

Photolysis Products. Figure 4 illustrates the spectral changes that have taken place with visible ($\lambda > 400$ nm) light photolysis. A decrease of one of the diiron allene adduct absorption bands with concomitant increase in the absorption bands of the other is noted. No evidence is seen to indicate any bond activation of the allene by the diiron. Upon photolysis with UV light, the absorption bands of the more stable diiron/allene adduct decrease slightly but do not bleach entirely. Since no new UV photoproduct absorption bands are detected, we conclude that the diiron adduct has partially photodissociated.

Atomic iron undergoes some interesting photochemistry, as indicated by the new set of absorption bands appearing upon visible photolysis. Figures 5 and 6 show selected regions of the IR spectra that illustrate the photochemistry of the atomic iron/allene system. Upon visible photolysis using a cutoff filter with $\lambda > 400$ nm (Figure 5B), new absorption bands appear that are not present in the initial codeposition spectra. While none of these absorption bands is very intense, many of them are very sharp; further, one of the new absorption bands appears at 3320 cm^{-1} for the Fe/H_2C=C=CH_2 reaction, shifting to 2600 cm^{-1} for Fe/D_2C=C=CD_2 (see Figure 6B). These frequencies are characteristic of acetylenic C–H and C–D stretches, respectively. Two other new peaks appear at 626.9 and 634.3 cm^{-1}, shifting to 490.8 and 493.8 cm^{-1} upon deuteration; these are characteristic of acetylenic C–H and C–D bends. It has been noted[45] that these
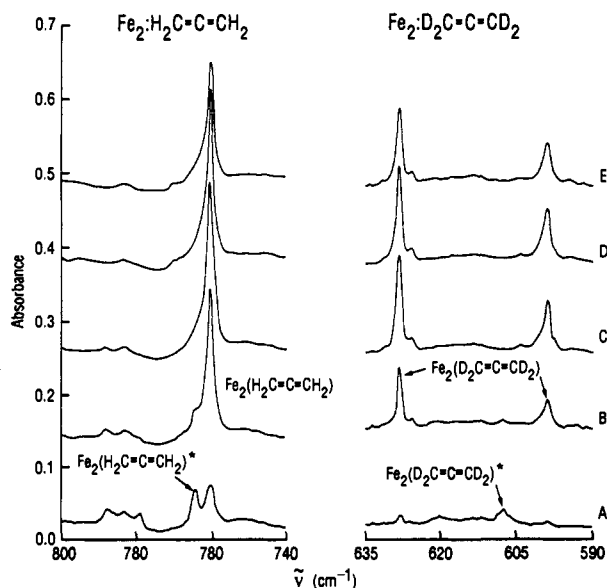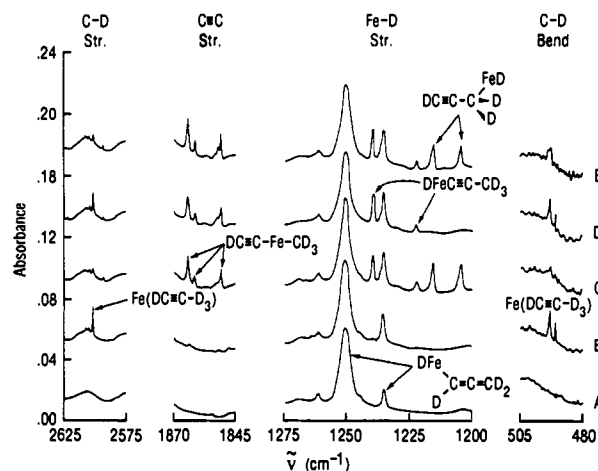
Figure 4. Photoisomerization of Fe$_2$(H$_2$C=C=CH$_2$). FTIR spectra of diiron–allene π-complexes. Molar ratio of Fe:H$_2$C=C=CH$_2$:Ar is 4.3:5.3:1000, and that of Fe:D$_2$C=C=CD$_2$:Ar is 5.5:5.2:1000. Temperature of deposition is 12.5 K. (A) No photolysis. Photolysis with (B) λ > 670 nm; (C) λ > 500 nm; (D) λ > 400 nm; (E) 280 < λ < 360 nm (* indicates another isomer).
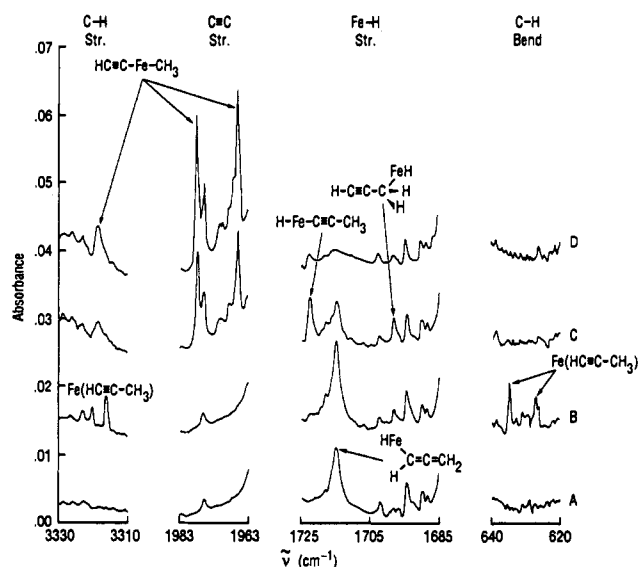
Figure 5. The iron-activated photoisomerization of allene into methylacetylene. FTIR spectra of Fe(HC≡CCH$_3$), HFeC≡CCH$_3$, HC≡CCH$_2$FeH, and HC≡CFeCH$_3$ in argon. Molar ratio of Fe:C$_3$H$_4$:Ar is 1.3:5.0:1000. (A) No photolysis. Photolysis with (B) λ > 400 nm. Photolysis with 280 nm < λ < 360 nm for (C) 30 min and (D) 2 h.

Figure 6. The iron-activated photoisomerization of allene into methylacetylene. FTIR spectra of Fe(DC≡CCD$_3$), DFeC≡CCD$_3$, DC≡CCD$_2$FeD, and DC≡CFeCD$_3$ in argon. Molar ratio of Fe:C$_3$D$_4$: Ar is 4.7:5.2:1000. Photolysis time is 30 min. (A) No photolysis. Photolysis with (B) and (D) λ > 400 nm; (C) and (E) 280 nm < λ < 360 nm.

two acetylenic modes are very strong infrared absorbers. Finally, a separate study subsequently performed[41] on the isomer methylacetylene shows exactly the same absorption bands upon cocondensation of iron vapors with HC≡CCH$_3$ and DC≡CCD$_3$. Therefore this new visible photolysis product is unequivocally assigned to an iron methylacetylene adduct. That is, it appears that some allene has phototautomerized to methylacetylene via the formation of an iron–propyne complex.

The absorption bands due to the iron–methylacetylene adduct show dramatic change upon short-term (<30 min) UV photolysis: they bleach completely. In the same time scale, new bands are observed as illustrated in Figure 5C. Many of these

absorptions appear in IR regions that are characteristic of certain vibrational modes. For example, new absorption bands appearing around 3320 cm^{-1} indicate once again the formation of an acetylenic C–H group; its peak is shifted from that assigned to the C–H stretch of iron methylacetylene adduct. New absorptions (not shown) also appear in the range of 2965–2880 cm^{-1}, characteristic of CH$_3$ symmetric and degenerate stretches, and in the range of 980–1160 cm^{-1}, where CH$_3$ deformations and rocks usually absorb. In addition, absorption bands are observed in the ranges of 1722–1693, 2120–1960, and 540–565 cm^{-1} (not shown) due to Fe–H, C=C and Fe–C stretches.

A photoreversible reaction is observed when previously UV-photolyzed matrices are rephotolyzed with 400-nm cutoff light. This reversibility is illustrated in Figure 6B, where visible photolysis leads to the formation of the iron methylacetylene adduct. Figure 6C shows absorption bands for that adduct bleaching with concurrent formation of new absorption bands. Upon rephotolysis with visible light, as shown in Figure 6D, the infrared absorption bands for the iron methylacetylene adduct reappear, only to disappear upon UV photolysis, seen in Figure 6E. Figures 6C,E also show several photoproduct absorptions that grow in on UV photolysis, bleach on visible photolysis, and grow in again upon rephotolysis with UV light: these absorptions have the opposite photobehavior of the iron methylacetylene adduct and thus represent the photoproduct to which the iron methylacetylene adduct converts. It appears, then, that the iron methylacetylene adduct is photorearranging to several products, only one of which is photoreversible. Assuming that no fragmentation is occurring upon photolysis and considering the moieties that are conclusively identifiable from the infrared spectra as discussed above, we can assign the monotonically increasing UV photoproducts to propynyliron hydride and ethynylmethyliron hydride. This is the only conclusion consistent with the evidence presented by the positions of the new absorptions in the infrared spectra as well as the deuterium shifts of those absorptions. Identification of the photoreversible UV product is less certain because of the paucity of its detected infrared absorption. However, the appearance of an Fe–H (Fe–D) stretch is certain. Further, perturbation of CH$_3$ stretching modes suggests that the iron methylacetylene adduct is coordinated at least partially through the methyl group, suggesting the ability to activate one of the three C–H bonds on that end of the moiety. Therefore, we suggest that the UV photoreversible product is HFeCH$_2$—C≡CH, the methyl C–H-activated insertion product of iron into methylacetylene.

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Table II. Infrared Frequencies (cm^{-1}) of Propadienyliron Hydride in Solid Argon

vibrational mode	HFeCH=C=CH$_2$	DFeCD=C=CD$_2$
Fe—C str or H—Fe—C bend	428.7, 431.4	
CH$_2$ wag	820.2	585.1
CH$_2$ scissor	1413.8	
Fe—H str	1714.5, 1737.7	1234.7, 1250.0
C=C=C asym str	1832.0	1799.0

Table III. C–H Bond Energies of Selected Hydrocarbons and the Spontaneity of C–H Bond Insertion by Iron Atoms

molecule	bond energy, kcal/mol (ref)	spontaneous? (ref)
cyclopentadiene	71.1 ± 1.5 (46)	yes (30)
methylacetylene[a]	89.4 ± 2 (46)	no (41)
allene	92.4 (47)	yes (this work)
propane	99.7 (46)	no (34)
ethane	100.3 ± 1.3 (46)	no (34)
methane	104.8 ± 0.2 (46)	no (32,33)
ethylene	106 (46)	no (29)
cyclopropane	106.3 ± 0.3 (46)	no (34)
acetylene	132 ± 5 (46)	no (28)

[a] Methyl C–H.

Discussion

Atomic Iron Chemistry. The spontaneous reaction between an iron atom and allene resulted in the insertion of the metal atom into one of the C–H bonds of allene and the formation of propadienyliron hydride. The measured vibrational frequencies of propadienyliron hydride and its deuterium-labeled isotopomer are listed in Table II and confirm the identity of this C–H-activated product. Several of the absorptions showed isotopic shifts in the reaction between Fe and D$_2$C=C=CD$_2$. The Fe–H absorptions at 1714.5 and 1737.7 cm^{-1} shifted to 1234.7 and 1250.0 cm^{-1}, respectively, confirming the presence of an iron–hydrogen bond in the product molecule. The absorptions appearing at 428.7 and 431.4 cm^{-1} disappeared, presumably shifting outside the range of the spectrometer. These peaks are assigned to either the Fe–C stretch or the HFeC bend. The absorption at 1832.0 cm^{-1} shifted slightly to 1799.0 cm^{-1}, supporting its assignment to the cumulative C=C=C asymmetric stretch.

The spontaneous formation of propadienyliron hydride is noteworthy because it represents the first case of aliphatic C–H bond activation by a ground-state iron atom. In the previously studied reactions of atomic iron with methane,[32,33] acetylene,[28] ethylene,[29] ethane,[34] and propane,[34] UV photolysis of the matrix-isolated species via electronic excitation of the metal σ-complex[28,29,33] was necessary to induce C–H bond activation. As the studies of interactions between different hydrocarbons with iron atoms in cryogenic matrices increase in number, a correlation is suggested between the spontaneous bond insertion of an iron atom into a C–H bond, i.e., C–H bond activation versus C–H bond energy in the parent hydrocarbon. In the cases of allene and cyclopentadiene,[30] spontaneous insertion is observed; in the cases of CH$_4$, H$_3$CCH$_3$, H$_3$CCH$_2$CH$_3$, H$_2$C=CH$_2$, HC≡CH, and HC≡CCH$_3$, bond insertion does not occur spontaneously and C–H bond activation is photolytically induced. The C–H bond energies are listed in Table III along with a mention of bond activation spontaneity. With the exception of methylacetylene, spontaneous insertion is noted for bond energies <~93 kcal/mol (<~389 kJ/mol). This limited number of results indicates that thermodynamic effects may play an important role in these inert bond activation reactions; on the other hand, one cannot ignore other important factors, like the kinetics of the reaction, that play an obvious role in low-temperature chemistry. However, confirmation of even a general limit to spontaneous C–H bond

Table IV. Infrared Frequencies (cm^{-1}) of the Iron–Propyne σ-Complex in Solid Argon

approximate vibrational mode	Fe(HC≡CCH$_3$)	Fe(DC≡CCD$_3$)
C–H bend	626.9, 634.3	490.8, 493.8
CH$_3$ def	1246.3	
CH$_3$ def	1379.2	
C–H str	3315.7, 3320.2	2601.9, 2604.7

activation can have enormous implications to hydrocarbon chemistry that involves metal centers.

No evidence for rearrangement of allene into propyne was observed during the spontaneous C–H bond activation of allene by atomic iron. Since the bond activation is spontaneous, we can assume that it is thermodynamically favorable and hence that some energy is given off. Apparently, this energy is not enough to cause the isomerization of allene into methylacetylene. Since the energy of activation for this rearrangement is known to be ~64 kcal/mol,[11] it is reasonable to consider this value as the upper limit to the exothermicity of the spontaneous metal atom bond insertion reaction.

Atomic Iron Photochemistry. Molecular photorearrangement of allene into propyne via the formation of a σ-bonded iron methylacetylene complex was observed with visible light. Table IV lists the frequencies of Fe(HC≡CCH$_3$) and Fe(DC≡CCD$_3$). The slightly perturbed C–H stretching and bending frequencies confirm the identity of the complex and the nature of the interaction between the metal atom and the alkyne. The appearance of an absorption in the 3300–3320 cm^{-1} range, shifting to the 2600 cm^{-1} range upon deuteration, is characteristic of an acetylenic C–H stretch. An acetylenic C–H bend is also noted. All absorptions identified for this species occur at frequencies similar to those of methylacetylene.[45] Further, all of the new absorptions are related to C–H or CH$_3$ motions, suggesting that the interaction between the metal atom and the organic moiety occurs through the ends of the methylacetylene and not via the π-electron system of the triple bond. In particular, no new absorptions were observed in the 1700–1900 cm^{-1} region, indicating a perturbed C≡C stretch, which has been previously observed for π-complexes of copper and nickel atoms with acetylene.[49]

That photolysis promotes tautomerism is not surprising: electromagnetic radiation having a wavelength of 400 nm (the cutoff limit of the visible light used for photolysis) has an energy of 71.5 kcal/mol, more than enough energy to overcome the known isomerization barrier. But allene isolated in argon does not show any signs of isomerization with visible light. This result is not surprising since the first absorption of allene occurs at 171 nm.[48] Hence, it appears that isomerization occurs via energy transfer between the electronically excited atomic iron and allene. Further, since no appreciable isomerization is noted with λ > 500 nm (57.2 kcal/mol) photolysis, it appears that the iron atom does not substantially lower the barrier to isomerization. This is in contrast to the results of Khulbe and Mann, who reported[23] an activation energy of only 11.8 kcal/mol for the isomerization of allene to methylacetylene in the presence of iron catalysts.

The iron methylacetylene adduct underwent some interesting and rich photochemistry. Three separate photoproducts were identified, and their measured frequencies are listed in Tables V–VII. 1-Propynyliron hydride (HFeC≡CCH$_3$), 3-propynyliron hydride (HC≡CCH$_2$FeH), and ethynylmethyliron (HC≡CFeCH$_3$) were formed, signaling the acetylenic and methyl C–H and

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Reactions of Iron with Allene in Solid Argon

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Table V. Infrared Frequencies (cm^{-1}) of 3-Propynyliron Hydride in Solid Argon

vibrational mode	$HC\equiv CCH_2FeH$	$DC\equiv CCD_2FeD$
Fe—H str	1697.4	1215.1, 1204.3
C—H str	3319.4, 3318.2	

Table VI. Infrared Frequencies (cm^{-1}) of 1-Propynyliron Hydride in Solid Argon

vibrational mode	$HFeC\equiv CCH_3$	$DFeC\equiv CCD_3$
C—C str	911.2	895.3
CH_3 rock	984.9	
CH_3 def		1112.1
Fe—H str	1716.1, 1721.7	1221.6, 1236.2, 1239.0
$C\equiv C$ str	2110.6, 2114.7, 2123.9	2109.8, 2113.5, 2121.9
CH_3 sym str	2880.4, 2882.4	

Table VII. Infrared Frequencies (cm^{-1}) of Ethynylmethyliron in Solid Argon

vibrational mode	$CH_3FeC\equiv CH$	$CD_3FeC\equiv CD$
CH_3 rock	540.8, 551.0	
Fe—C str	566.0, 564.7	519.2, 520.4
C-H bend	663.7, 669.7	
CH_3 s-def	1155.8, 1161.9, 1163.7	
CH_3 d-def	1455.6, 1439.4	
$C\equiv C$ str	1965.5, 1975.5, 1977.4	1851.0, 1852.3, 1861.4, 1864.2
CH_3 s-str	2880.4	
CH_3 d-str	2963.8	
C-H str	3318.5, 3328.1	

the single C–C bond activation. The formation of 3-propynyliron hydride is indicated by the appearance of an acetylenic C–H stretch around 3320 cm^{-1} and an Fe–H stretch at 1697.4 cm^{-1}, shifting to 1215.1 cm^{-1} upon deuteration. These vibrational frequencies along with their modes assignment are listed in Table V. In the identification of 1-propynyliron hydride, an Fe–H stretch showing the appropriate deuterium shift is noted; also, new absorption bands around 2110 and 910 cm^{-1}, both of which shift only slightly upon deuteration, indicate the presence of $C\equiv C$ and C–C bonds, respectively. The presence of CH_3 stretching and rocking modes at 2880 and 985 cm^{-1} indicates that the methyl group is intact, implying that the iron atom activated only the C–H bond proximal to the carbon–carbon triple bond. The vibrational frequencies assignment for 1-propynyliron hydride are listed in Table VI. Concurrent with the appearance of the absorption bands discussed above, bands characteristic of an acetylenic C–H stretch and bend are observed around 3320 and 665 cm^{-1}, respectively, slightly shifted in position to the previously identified acetylenic modes of the adduct $Fe(HC\equiv CCH_3)$. CH_3 stretches were observed at 2963.8 and 2880.4 cm^{-1}. CH_3 deformation modes were measured around 1160 and 1450 cm^{-1}. The absorption bands at 564.7 and 566.0 cm^{-1} did not shift much upon deuterium substitution and are consistent with their mode assignment to a Fe–C stretch. This assignment, listed in Table VII, verifies that ethynylmethyliron has been formed from the activation of the C–C bond in methylacetylene. Table VIII shows a comparison of the vibrational frequencies of this C–C insertion product with those of ethynyliron hydride and methyliron hydride, previously identified in argon matrices.[28,32,33] A comparison of the frequencies of the ethynyliron group for $CH_3FeC\equiv CH$ and $HFeC\equiv CH$ verifies the identity of the C–C insertion reaction product. This is further confirmed by comparing the frequencies of the methyliron group for ethynylmethyliron and methyliron hydride. This is only the second case of carbon–carbon bond activation by a photoexcited iron atom, but the first case was cyclopropane,[34] which has a very highly strained C_3 backbone. To our knowledge, this is the first case of C–C bond activation of an unstrained, aliphatic hydrocarbon. The strength of the carbon–carbon single bond in methylacetylene has not been

Table VIII. Comparison of the FTIR Measured Frequencies (cm^{-1}) for $CH_3FeC\equiv CH$, $HFeC\equiv CH$, and CH_3FeH in Cryogenic Argon Matrices

	$CH_3FeC\equiv CH$	$HFeC\equiv CH^{28}$	$CH_3FeH^{32,33}$
C—H str	3318.5, 3328.1[b]	3276.2[b]	
$C\equiv C$ str	1977.4, 1975.5, 1965.5	1976.4, 1974.8	
Fe–C str	566.0, 564.7,		523.5
CH_3 rock	551.0, 540.8		544.0, 541.0
CH_3 def	1163.7		1156.1, 1151.1[a]
CH_3 str	2963.8, 2940,8, 2880.4		2929.8, 2895.4, 2878.0

	$CD_3FeC\equiv CD$	$DFeC\equiv CD^{28}$	$CD_3FeD^{32,33}$
C–D str	2593.3	2432.8	
$C\equiv C$ str	1864.2, 1861.4, 1852.3, 1850.0	1862.7, 1861.0	
Fe–C str	520.4, 519.2		480.2
CD_3 def			879.9[a]

[a] In methane matrix. [b] Frequencies of $CH_3C\equiv CH$ and $HC\equiv CH$ are 3322.8 and 3288.5 cm^{-1}, respectively.

Table IX. Infrared Frequencies (cm^{-1}) of the Unstable Diiron–Allene π-Complex

$Fe_2(H_2C\equiv C\equiv CH_2)$	$Fe_2(D_2C\equiv C\equiv CD_2)$
595.1	607.4
764.5	778.2
779.0	910.6
920.4	1107.3
1050.3	1656.2
1055.1	
1516.3	
1671.8	
2013.7	

Table X. Infrared Frequencies (cm^{-1}) of the Stable Diiron–Allene π-Complex

$Fe_2(H_2C\equiv C\equiv CH_2)$	$Fe_2(D_2C\equiv C\equiv CD_2)$
491.6	474.4
557.4	543.9
692.0	598.7
760.4	627.9
812.1	742.4
900.2	824.8
1338.9	1626.7
1642.6	
1683.6	
1713.8	

reported in the literature; however, if we assume that the bond strength is similar to that in ethane, which is 88 kcal/mol,[46] then we see that the strength of this bond is similar to those of the C–H bonds that are attacked spontaneously by iron atoms. Given also that in methylacetylene the carbon–carbon single bond is less spatially hindered than ethane due to the presence of the linear acetylenyl in the place of the methyl group, we might expect a more facile C–C bond attack by the iron atom.

Diatomic Iron Chemistry. Diatomic iron did not appear to activate C–H or C–C bonds, either spontaneously or photolytically. Instead, two diiron π-complexes were formed as indicated by activation of vibrations in the $C\equiv C$ stretching and CH_2 bending regions of the spectrum. While both of these complexes were formed spontaneously upon cocondensation of iron vapors and allene, one of them was preferred, as indicated by the changes in the spectra during visible light photolysis. This same diiron π-complex was also favored at higher deposition surface temperatures, as indicated by the temperature dependence study. The measured vibrational frequencies of the two $Fe_2(H_2C\equiv C\equiv CH_2)$ complexes are listed in Tables IX and X.

The two complexes exhibit different vibrational spectra, which are attributed to different modes of interaction between Fe_2 and $H_2C\equiv C\equiv CH_2$. Two possible modes of π-interaction are offered

V-Shaped π-Complex

$$H_2C = C = CH_2$$
$$Fe — Fe$$

Side-on π-Complex

$$\overset{H}{\underset{H}{}} C = C = C \overset{H}{\underset{H}{}} \qquad \overset{H}{\underset{H}{}} C = C = C \overset{H}{\underset{H}{}}$$
$$Fe_2 \qquad\qquad Fe_2$$
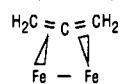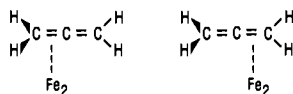
Figure 7. Possible interaction modes of $Fe_2(H_2C=C=CH_2)$ π-complexes.

$$Fe + \overset{H}{\underset{H}{}} C = C = C \overset{H}{\underset{H}{}} \xrightarrow[10K]{Ar} H_2C = C = C \overset{FeH}{\underset{H}{}}$$

Vis ↓↑

σ-Complex $Fe (H—C \equiv C — CH_3) \xrightarrow{UV} H — Fe — C \equiv C — CH_3 + CH_3 — Fe — C \equiv CH$

Vis ↑↓ UV

$$H — C \equiv C — C \overset{FeH}{\underset{H}{\blacktriangleright}} H$$

$$Fe_2 + \overset{H}{\underset{H}{}} C = C = C \overset{H}{\underset{H}{}} \xrightarrow[10K]{Ar} Fe_2 (H_2C = C = CH_2) \qquad \text{Side-on and V-Shaped π-Complexes}$$

↓ hν

$$Fe_2 (H_2C = C = CH_2) \qquad \text{V-Shaped π-Complex}$$
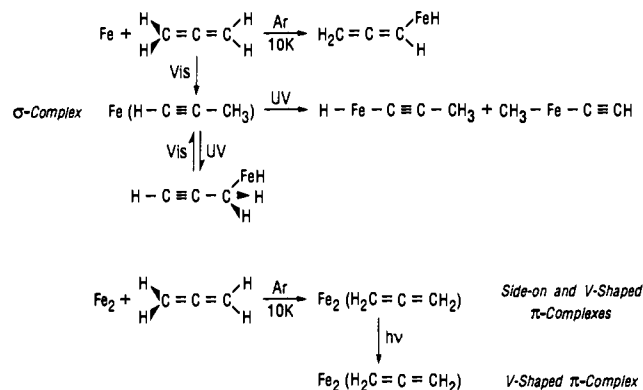
Figure 8. Observed reaction pathways and photochemistry of atomic and diatomic iron with allene in solid argon.

and are displayed in Figure 7. One structure involves the simultaneous interaction of diiron with both π-bonds causing them to twist and bend in a V-shape. The other structure consists of diiron interacting with one of the π-bonds from the side of the allene molecule. In this structure diiron can approach the allene in two different ways with respect to the terminal methylene group, either parallel or perpendicular to the H–C–H plane. The V-shaped structure is proposed for the photostable Fe_2-$(H_2C=C=CH_2)$ π-complex with the C_3 backbone skewed slightly with respect to the Fe–Fe bond. This is supported by the IR data that show the absence of the strong absorption due to the asymmetric $C=C=C$ stretching mode and the appearance of new bands in the $C=C$ stretching region. The bonding in the photo-unstable π-complex takes place through only one of the π-bonds of allene, as indicated by the activation of the $C=C$ stretching mode. This isomer photoconverts to the more stable complex with the V-shaped geometry.

In analogy to this matrix-isolated system, there exist stable metal complexes having two metal centers and an allenic ligand. Bailey et al.[50] determined that the crystal structure of Cp_2M_2-$(CO)_4(C_3H_4)$ (M = W, Mo) has the allene moiety in a V-shape,

where the $C=C=C$ angle is $146°$ and is considered as having one double bond complexing to each metal center. This was the first reported allene complex to two metal atoms that were bonded to each other. Interestingly, the line containing the $C=C=C$ backbone was not collinear with the M–M axis; instead, the two units were skewed with respect to each other. Lewis, Huffman, and Caulton[51] determined a similar structure for $Cp_2Mn_2(CO)_3$-(C_3H_4). More recently, Cayton et al.[52] isolated a stable adduct between allene and $W_2(O\text{-}t\text{-}Bu)_6$. Using a qualitative MO diagram, the researchers reasoned that the allene acts as a four-electron donor and a two-electron acceptor, where electrons from the lowest p orbital of the W_2 moiety are donating into the nonbonding orbitals of allene. A bent C_3 moiety for this complex is also suggested. Finally, Casey and Austin[53] and Hoel et al.[15] have isolated metastable allene complexes to diiron, as in, for example, $Cp_2Fe_2(CO)_2(C_3H_4)$. Their studies also indicate a skewed η^3-type complexation between the allene and the bonded metal centers. Unfortunately, in all studies either minimal or no infrared data were presented; most of the IR data presented dealt with CO absorptions of the initial and final products.

Conclusion

A summary of the reaction pathways and the photochemistry of atomic and diatomic iron with allene in argon matrices is given in Figure 8. Iron vapors were cocondensed with allene in cryogenic argon matrices, and several new species were identified on the basis of the infrared spectra. A spontaneous C–H bond insertion product was seen, forming propadienyliron hydride. Upon photolysis with visible light, an iron methylacetylene σ-complex was detected, indicating an iron-assisted photorearrangement of allene. Subsequent photolysis with UV light caused the formation of 3-propynyliron hydride, which subsequently reacted back to the iron methylacetylene complex upon photolysis with visible light. UV photolysis of the iron methylacetylene complex also provided for the formation of two nonphotoreversible species, identified as 1-propynyliron hydride and ethynylmethyliron. The infrared spectra of the same species using deuterated allene as a starting material provided isotopic shifts that supported these assignments. At higher concentrations of iron, two distinct diiron/allene π-complexes were noted, one of which was found to be more stable than the other in the presence of visible light or higher matrix surface temperatures. No photoactivation of allene by diiron was detected.

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