A Study of FeC$_2$ and FeC$_2$H by Anion Photoelectron Spectroscopy

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The photoelectron spectra of FeC$_2^-$ and FeC$_2$H(D)$^-$ are studied at 3.49 eV photon energy. The electron affinities of FeC$_2$ and FeC$_2$H(D) are determined to be 1.91(10) and 1.41(5) eV, respectively. An excited state of FeC$_2$ at 1 eV above its ground state is also observed. Only one major detachment channel is observed for FeC$_2$H(D)$^-$. A vibrationally resolved spectrum at 2.33 eV photon energy for FeC$_2$D$^-$ is also obtained with a Fe—C stretching progression, yielding a vibrational frequency of 500(100) cm^{-1}. The spectra provide unique information on the bonding between Fe and C$_2$ and C$_2$H(D).

Introduction

Small carbon and hydrocarbon fragments are important in the surface chemistry of many heterogeneous catalysts, usually as intermediates of dehydrogenation reactions and as precursors to carbon films.[1] Metal complexes of these fragments provide interesting models for the study of their bonding with surfaces. Toward this end, several metal complexes of ethynediyl (—C≡C—) and ethynyl (—C≡C—H) as ligands have been synthesized and studied.[2-4] In this Letter, we present a study of these radicals bonded to a single transition metal atom in the gas phase by anion photoelectron spectroscopy (PES), which provides unique information about the electronic structure and the molecular bonding of these simple metal complexes.

The FeC$_2$ and FeC$_2$H complexes may be viewed as reaction products of Fe atom with acetylene. However, they have not been observed due to the low reactivity of iron atom with acetylene.[5] In a matrix-isolation study of its reactions with acetylene,[6] a Fe(C$_2$H$_2$) adduct, formed in the low-temperature matrix, was found to rearrange to ethynyliron hydride, HFeCCH, upon near-ultraviolet photolysis. The ethynyl fragment has been observed to be the intermediate of many dehydrogenation reactions of unsaturated hydrocarbons on transition metal surfaces and catalysts.[1] Several organometallic complexes with FeCC and FeCCH fragments have been synthesized.[2,3] However, there have been no theoretical calculations reported on FeC$_2$ and FeC$_2$H. In the present study, we are interested in how an Fe atom interacts with these simple carbon and hydrocarbon fragments, which may provide insight into the hydrocarbon surface chemistry as model intermediates.

Experimental Section

The FeC$_2^-$ and FeC$_2$H(D)$^-$ anions are prepared by laser vaporization of an iron target with a He carrier gas containing 5% CH$_4$ (CD$_4$). The photoelectron spectrometer used in this study[7] is a newly modified version of a magnetic-bottle time-of-flight photoelectron analyzer.[8] Details of the apparatus will be published elsewhere.[7] Only a brief description of the experimental procedure is presented here. The second harmonic output from a Q-switched Nd:YAG laser operated at 10 Hz is used for the laser vaporization. The laser beam (10 mJ/pulse) is focused to a 1 mm diameter spot onto an iron target that is driven by two computer-controlled stepping motors. The carrier gas containing 5% methane in He at 6.5 atm total pressure is

delivered by two pulsed molecular beam valves (R. M. Jordan Co.) and is synchronized with the vaporization laser pulse. The plasma reactions of CH$_4$ and Fe produce a variety of cluster species which, together with the He carrier gas, undergo a supersonic expansion and are skimmed twice to form a collimated beam. FeC$_2^-$ and FeC$_2$H$^-$ are the smallest Fe-containing anions, and the FeC$_2^-$ signal is quite weak. FeC$_2$H$_2^-$ is also present, but its abundance is rather weak and unstable. About 70 cm downstream from the cluster nozzle, the negative ion species are extracted by a 1 kV high-voltage pulse into a 130 cm long flight tube for mass analyses. The TOF mass spectrometer has a large extraction volume and a modified Wiley-McLaren extraction stack with an added free-flight region between the two acceleration stages.[9] Theoretically, a very high mass resolution can be achieved in this setup with the large extraction volume. We have obtained a mass resolution ($M/\Delta M$) of more than 300, sufficient to resolve all the isotopic species pertinent to the present study.

A three-grid mass gate is used to select only the desired cluster, ^{56}FeC$_2^-$ and ^{56}FeC$_2$H$^-$, to enter the PES interaction zone. The ^{56}FeC$_2$H$^-$ ions can be mass-gated cleanly while the ^{56}FeC$_2^-$ signal may be contaminated by a negligible amount of ^{54}FeC$_2$H$_2^-$. The mass-selected cluster packet is decelerated by a new momentum deceleration procedure[7] down to a very low velocity before photodetachment. This minimizes the Doppler broadening on the photoelectron kinetic energy distribution, a crucial step in achieving high-energy resolution with the magnetic bottle-type analyzer. The third harmonic of a second Q-switched Nd:YAG laser is used in the current study for the photodetachment. There is a cutoff for the transmission of low-energy electrons at about 0.4 eV. The spectrometer is calibrated with the known spectrum of Cu$^-$. The energy resolution (ΔE) in a TOF spectrometer is not constant with respect to the electron kinetic energy (Ek). ΔE is proportional to Ek$^{3/2}$. An energy resolution of 30 meV at 1 eV electron kinetic energy is achieved in the current spectrometer with the new deceleration procedure, as measured from the photoelectron spectrum of Cu$^-$ at 3.49 eV photon energy. This resolution is no longer limited by the Doppler broadening. When the ion signal is weak, full deceleration cannot be achieved to reach this resolution.

Results and Discussion

There have been no theoretical calculations on FeC$_2$ and FeC$_2$H to our knowledge; thus, their ground states and molecular parameters are not known. Therefore, it will be useful to develop a qualitative picture of their molecular bonding before

the results are presented. The simplest bonding picture for FeC_2H involves the interaction of the ground state Fe atom (^5D, $3d^64s^2$) with the singly occupied sp-hybridized orbital on the $H-C\equiv C^{\bullet}$ to form a $3d^6\sigma^2\sigma^{*1}$ FeC_2H. In this case, the Fe 4s forms a σ bonding and a σ^* antibonding orbital with the sp-hybridized orbital. At the same time, the $3d\pi$ orbitals on Fe can interact with the $C-C$ π^* orbitals. Alternatively, the lowest excited state of Fe, with a 4s electron promoted to the $3d(^5F,3d^74s^1)$ and 0.9 eV above the ground state, can form a $3d^7\sigma^2$ FeC_2H with a strong σ bond.

The $Fe-C$ bond, including the FeC double and triple bonds,[10] is much weaker than the CC triple bond. The ground state of C_2 is a double-bonded $^1\Sigma_g^+$ state $(...2\sigma_u^2 1\pi_u^4)$, which cannot bond very effectively to Fe. However, the first excited state $(^3\Pi_u)$ of C_2 is only 0.089 eV higher in energy than the ground state.[11] Furthermore, the strength of the CC triple bond would favor an sp hybridization in C_2 when it can form more bonds, like in C_2H and C_2H_2. Therefore, in our following discussion about the Fe and C_2 bonding, we assume that C_2 has a triple bond with an sp-hybridized orbital on each C atom, similar to that in C_2H. In this case, Fe is expected to interact with one sp-hybridized orbital on the C_2 fragment through its 4s orbital in a linear geometry. The ground state Fe atom interacting with C_2 will yield a $3d^6\sigma^2\sigma_{sp}^1\sigma^{*1}$ configuration, where σ_{sp} represents the nonbonding sp-hybridized orbital on the farthest C atom from Fe in a linear geometry. The excited Fe atom will interact with C_2 to form a $3d^7\sigma^2\sigma_{sp}^1$ FeC_2. The two sp-hybridized orbitals in the C_2 fragment are degenerate initially. In FeC_2, the 4s of Fe interacts with one of the sp orbitals to form the σ bonding and the σ^* antibonding orbitals in FeC_2. Thus, the nonbonding σ_{sp} orbital in FeC_2 is necessarily lower in energy than the σ^* orbital, and a more appropriate configuration, when the ground state Fe atom bonds to C_2, would be $3d^6\sigma^2\sigma_{sp}^2$, with a lone pair electron on the farther C atom. This means that in this case there should be a substantial intramolecular charge transfer from Fe to C_2.[12]

Both $FeCO$[13] and FeH[14] have been extensively studied. In these two molecules, the excited Fe atom is found to participate in the molecular bonding. The major molecular interaction in FeC_2H (4s−sp) is similar to that in FeH (4s−1s). It might be reasonable to expect that the excited Fe atom is involved in the FeC_2H chemical bonding in analogy to that in FeH.[14] However, the bonding between C_2 and CO to Fe should be quite different. The sp-hybridized orbital in CO (the 5σ) already has a lone pair, which can only interact repulsively with the $4s^2$ orbital of Fe. Therefore, a promotion of a 4s electron to the 3d is necessary for a more effective Fe−CO chemical bonding. The C_2 fragment can form two degenerate, singly occupied sp-hybridized orbitals, which can effectively interact with Fe in its ground state. Hence, it is expected that FeC_2 should have a $3d^6\sigma^2\sigma_{sp}^2$ configuration (Fe−C≡C:). The sp lone pair may be similar to that in $H-C\equiv C:^-$, whose photoelectron spectrum has been studied.[15]

Figure 1 shows the PES spectrum of FeC_2^- at 3.49 eV photon energy. Two prominent bands are observed. The FeC_2^- mass signal is very weak. Thus, the spectrum has poor counting statistics. It is also difficult to decelerate the ion to very low velocity in order to achieve the best resolution possible. The resolution is about 90 meV for the band near 2 eV binding energy under the conditions the spectrum is taken. The features on the two bands are due to statistical noise. The first band, labeled X, yields an electron affinity of 1.91(10) eV for FeC_2. The second band, labeled A at 2.9 eV, is an excited state of FeC_2. The weak features at the low binding energy side can be due to the following three factors: (1) hot band transitions,
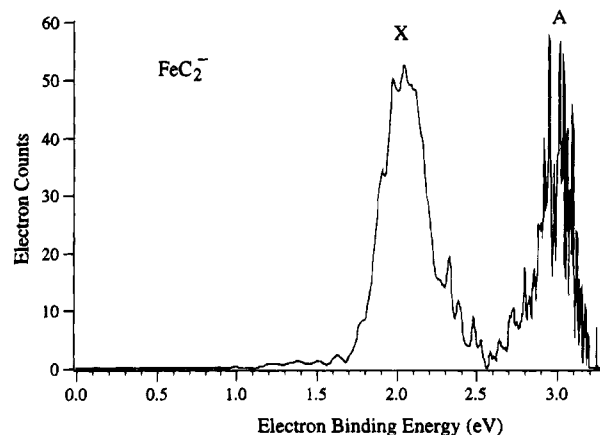

Figure 1. Photoelectron spectrum of FeC_2^- at 3.49 eV photon energy. The fine features are due to statistical noise.

(2) other possible isomers with low electron affinities, and (3) possible contamination from minute amount of $^{54}FeC_2H_2^-$. As discussed above, if we assume the ground state Fe atom is involved in the FeC_2 bonding, then FeC_2^- should have a $3d^6\sigma^2\sigma_{sp}^2\sigma^{*1}$ configuration. The first band would correspond to the removal of the σ^* electron, resulting in the $3d^6\sigma^2\sigma_{sp}^2$ ground state FeC_2. The second band would be due to the removal of an sp lone pair electron. We note that the binding energy of the second band in the FeC_2^- spectrum is the same as that of the removal of a lone pair electron in HC_2^-,[15] thus providing support for the assignment that FeC_2 has an sp lone pair in its ground state. It should be pointed out that the removal of a lone pair electron is expected to result in a vertical transition with little vibrational excitations as is the case in HC_2^-.[15] The A band in Figure 1 has a substantial width that seems to be inconsistent with the removal of a nonbonding lone pair. However, from the above discussion of the possible FeC_2 bonding configuration, the lone pair in FeC_2 involves a charge transfer from Fe to an sp-hybridized orbital. Thus, FeC_2 should have a dipole moment.[12] In this case, the removal of one of the lone pair could induce a change in bonding between the anion and the neutral, resulting in vibrational excitations in the PES spectrum. Nevertheless, the assignment of this band cannot be conclusive without firm *ab initio* calculations.

Figure 2 shows the PES spectrum of FeC_2H^- along with the isotope-substituted version FeC_2D^- (using CD_4 in the carrier gas). The $FeC_2H(D)^-$ mass signal is quite strong, allowing us to decelerate it to a very low energy, thus minimizing the Doppler broadening. We expect to see vibrational structures in the spectra, especially the $C-H$ (D) stretching if it is active. The two spectra look essentially identical, indicating there are no vibrations involving H (D). Only one major band, labeled X, is observed with three very weak features, labeled A, B, and C. The X band is the transition to the FeC_2H ground state, yielding a EA of 1.41(5) eV for $FeC_2H(D)$. We also investigate the FeC_2D^- spectrum at 2.33 eV photon energy (the second harmonic of the Nd:YAG laser) to improve the spectral resolution. This spectrum is shown in Figure 3. At this photon energy, the X band has an electron kinetic energy near 0.9 eV, where the spectral resolution is better than 30 meV. A partially resolved vibrational progression is evident with a frequency of 500(100) cm^{-1}. We assign this to be the Fe−C stretching vibration, which is in good agreement with the Fe−C stretching in HFeCCH, measured in matrix,[6] and the Fe−C stretching on Fe surfaces.[16] The weak feature, A, is better resolved in the 2.33 eV spectrum of FeC_2D^-. Given the instrumental resolution, the Fe−C stretching vibrational structure should be much better resolved. There are three factors that can contribute to
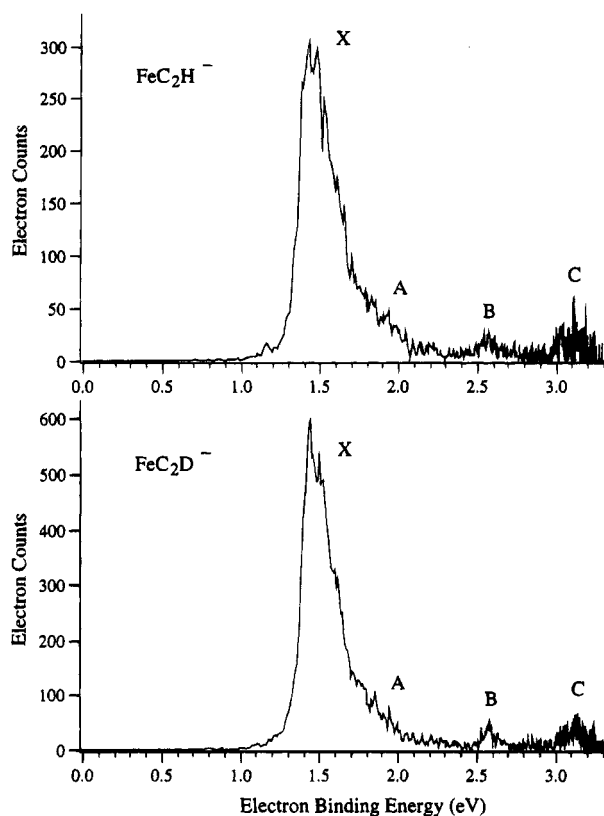
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Figure 2. Photoelectron spectra of FeC_2H^- and FeC_2D^- at 3.49 eV photon energy.
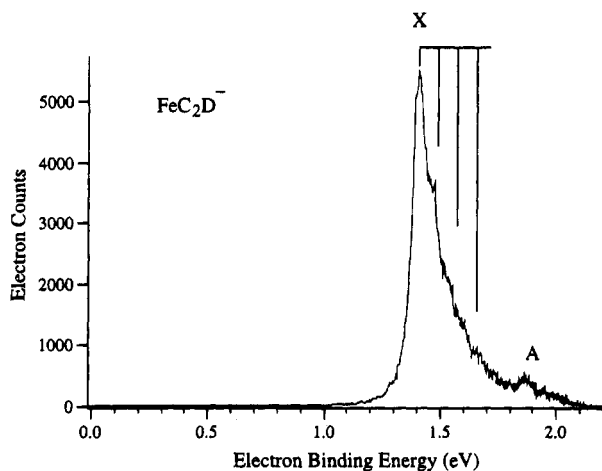

Figure 3. Photoelectron spectrum of FeC_2D^- at 2.33 eV photon energy with partially resolved vibrational structure.

the broadened spectrum observed: rotational broadening, excitation of low-frequency bending mode, and sequence bands from hot band transitions.

The FeC_2H^- should have a $3d^7\sigma^2\sigma^{*1}$ configuration when an excited Fe interacts with C_2H or $3d^6\sigma^2\sigma^{*2}$ configuration when a ground state Fe interacts with C_2H. The latter would indicate that the FeC_2H^- negative ion is very weakly bonded. We observe a rather strong mass signal of FeC_2H^- from the cluster source (much stronger than the FeC_2^- signal). Thus, we do not think this is likely and conclude that FeC_2H^- should have a configuration of $3d^7\sigma^2\sigma^{*1}$ similar to that in FeH^-. In this case, the X band corresponds to the removal of the antibonding σ^* electron. The observation of a vibrational progression in the Fe—C stretching is consistent with this assignment. The three weak bands, A, B, and C, cannot be assigned firmly; their weak intensity is consistent with two possible assignments:

TABLE 1: Spectroscopic Constants and Energies for the States of FeC_2 and $FeC_2H(D)$

	FeC_2	$FeC_2H(D)$
EA (eV)	1.91(10)	1.41(5)
	$X(3d^6\sigma^2\sigma_{sp}^2)$	$X(3d^7\sigma^2)$
ν_{Fe-C} (cm^{-1})		500(100)
excited state (eV)^a	2.9(1)	1.86
	$A(3d^6\sigma^2\sigma_{sp}^1\sigma^{*1})$	A(?)
		2.56
		B(?)
		3.1
		C(?)

^{a} The excited state energies are listed as electron binding energies.

multielectron processes due to electron correlations[17] and one-electron detachments of the 3d electrons. Both of these are expected to have weak intensity.[18] Theoretical confirmations of either assignments should provide interesting insight about the FeC_2H molecular bonding. Compared with the spectrum of FeC_2^-, where two main detachment channels are observed from the σ^* and the sp lone pair, both sp orbitals in FeC_2H form bonds (Fe—C and C—H). Thus, it is reasonable that only one major detachment channel is observed from the σ^*. The spectroscopic constants and energies for the states of FeC_2 and $FeC_2H(D)$ obtained from this study are summarized in Table 1.

In conclusion, we have reported the photoelectron spectra of FeC_2^- and $FeC_2H(D)^-$ at 3.49 eV photon energy. For FeC_2^-, photodetachments from the 4s—sp σ^* and the C sp lone pair take place, resulting in two bands, the ground state and an excited state of FeC_2. For FeC_2D^-, a vibrationally resolved spectrum is obtained at 2.33 eV photon energy, yielding a Fe—C stretching vibration of 500(100) cm^{-1}. Only one major detachment channel is observed for $FeC_2H(D)^-$ at 3.49 eV photon energy. This is assigned to be from the 4s—sp σ^* orbital. Three weak transitions are also observed for $FeC_2H(D)^-$ at 3.49 eV photon energy. These are interpreted to be due to either multielectron processes or one-electron detachments of the 3d electrons. The assignments of both the FeC_2^- and $FeC_2H(D)^-$ spectra are based on very simple bonding arguments. *Ab initio* calculations will be needed to establish the various states and symmetries and confirm the current interpretations.

References and Notes

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