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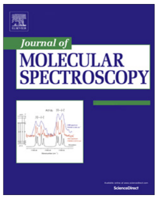

Infrared spectra of M-η^2-C_2H_2 and HM—CCH produced in reactions of laser-ablated Fe and Os atoms with acetylene

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ABSTRACT

The π- and C—H insertion products (M-η^2-C_2H_2 and HM—CCH) are identified in the matrix infrared spectra from reactions of laser-ablated Fe and Os atoms with acetylene isotopomers, but the vinylidene product (H_2CCM) is not, in contrast to the recently studied Ru case. The π-complex is produced in deposition and annealing, and it converts to the insertion complex during photolysis. While the vinylidene product is energetically comparable with the two primary products, the energy barrier is considerably higher in contrast to the Ru case. The relatively short C—C bonds of the π-complexes indicate weak back-donations from the group 8 metals to the acetylene π^* orbitals. The highly bent structure of HOs—CCH evidently originates from the high d contributions to the C—Os and Os—H bonds. The C_{2v} structures of the vinylidene products arise from the p–d π bonding between C and M.

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1. Introduction

The π-system of acetylene makes a good ligand to produce a wide range of acetylene complexes [1]. The subsequent rearrangements after initial coordination vary with the electron-pair acceptor, leading to its characteristic products. Direct reactions with metal atoms have provided interesting small acetylene complexes, which are amenable to high-level theoretical methods to investigate the structures and reaction paths [2–11]. The most investigated are π-complexes (M-η^2-C_2H_2) [4–6,8–11], C—H insertion products (HM—CCH) [4–9,11], vinylidene derivatives (H_2CCM) [8,9,10a], vinyl radicals (·CHCHM) [3,11] and ethynyl complexes (HCCM) [2c,9a,11]. Among them, the π- and insertion products (M-η^2-C_2H_2 and HM—CCH) are the most common in reactions of transition-metals (group 3–11 metals [4–10] and acitinides [11]) while the vinylidenes are relatively rare, mostly provided in the late transition-metal systems (Ru, Rh, Ni, Pt, and Au).

Recent studies have shown that the product characteristics vary significantly with the metal. The group 4 metals form unusually strong π-complexes with strong back-donation from the metal center to the π^*-orbitals in M-η^2-(C_2H_2) [5a], and there is a general trend that the back-donation become weaker with moving right in the periodic table [4–9]. The group 7 metal (Mn and Re) insertion complexes (HM—CCH) own linear or near linear structures unlike the typical, bent structure [7].

Kline et al. have reported observation of a C—H stretching absorption of Fe···H—C≡CH and the C—C and Fe—H stretching absorptions of HFe—CCH, along with several other bands from Fe high-order products [8a]. More recently Wang et al. have identified Ru-η^2-C_2H_2, HRu—CCH, and H_2CCRu in reactions of Ru with acetylene, and their DFT results support that the reaction occurs in the order of coordination to the π-system, C—H bond insertion, and H migration from M to C to generate the products [8b].

Here, we report a spectroscopic investigation for the reactions of Fe and Os with acetylene. While the π- and insertion products are observed in the metal systems, the absence of the vinylidenes contrasts the recently studied Ru system. The back donations in the group 8 metal acetylene complexes are evidently weak, and HOs—CCH shows a highly bent structure.

2. Experimental and computational methods

Laser ablated Fe (Johnson–Matthey) and Os (Metallium, Inc.) atoms were reacted with C_2H_2 (Matheson, passed through a series of traps to remove acetone stabilizer), C_2D_2, and $^{13}C_2H_2$ (Cambridge Isotopic Laboratories, 99%) in excess argon during condensation at 8 K using a closed-cycle refrigerator (Air Products HC-2). These methods have been described in detail elsewhere [12]. Reagent

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gas mixtures range 0.13–0.50% in argon. After reaction, infrared spectra were recorded at a resolution of 0.5 cm^{-1} using a Nicolet 550 spectrometer with an MCT-B detector. Samples were later irradiated for 20 min periods by a mercury arc street lamp (175 W) with the globe removed and a combination of optical filters, and subsequently annealed to allow further reagent diffusion.

Complementary density functional theory (DFT) calculations were carried out using the Gaussian 09 package [13], B3LYP density functional [14], 6-311++G(3df,3pd) basis sets for C, H, Fe, and SDD pseudo potential and basis set [15] for Ru and Os to provide a consistent set of vibrational frequencies and energies for the reaction products and their analogues. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis, and BPW91 [16] calculations were also done to confirm the B3LYP results. The vibrational frequencies were calculated analytically, and the zero-point energy is included in the calculation of binding energy of a metal complex.

3. Results and discussion

The Fe and Os matrix infrared spectra and their variation upon photolysis and annealing (Figs. 1–6 and S1–3, Tables 1 and 2) will be compared with the vibrational characteristics calculated by density functional theory (Figs. 6–11, Tables S1–6). In addition, bands from precursor irradiation common to other metal experiments were also observed [17].

Fe + C_2H_2. Figs. 1–3 show the Fe + C_2H_2, C_2D_2, and $^{13}C_2H_2$ spectra and their variation in the product absorption regions. The product absorptions marked "**π**", "**i**", and "**iA**" (for Fe-η^2-C_2H_2, HFe—CCH, and HFe—CCH···C_2H_2, respectively). The **π** absorptions are weak in the original deposition spectrum, almost disappear on visible ($\lambda > 420$ nm) irradiation, and slightly recover in the early stage of annealing. The **π** absorption regions blown up from Figs. 1–3 for better viewing are shown in Figs. S1–3. The **i** absorptions are most prominent in the product spectra. They increase ~20% on visible irradiation and double on uv ($380 > \lambda > 240$ nm) irradiation. The **iA** absorptions are barely visible on the red side of the **i** absorption in the original deposition spectrum, increase dramatically on uv irradiation, and quickly decrease in annealing. The product absorption frequencies are listed in Table 1, and they are compared with the computed frequencies in Tables S1–3.

The **π** absorptions, while being reasonably consistent with the computed vibrational characteristics, are tentatively assigned to the Fe π-complex (Fe-η^2-C_2H_2) due to their low absorption intensities. Its strongest C—C stretching absorption observed at 1539.8 cm^{-1} shifts to 1458.3 and 1388.0 cm^{-1} on deuteration and ^{13}C substitution (H/D and 12/13 ratios of 1.056 and 1.109). Its frequency and large ^{13}C shift correlate well with the DFT values in Table S1. Another **π** absorption at 701.1 cm^{-1} shows a large D shift to 505.8 cm^{-1} (H/D ratio of 1.386) and a small ^{13}C shift to 698.6 cm^{-1}, and it is designated to the A_1 HCCH in-plane banding mode. The weaker **π** absorption at 667.6 cm^{-1} is assigned to the B_1 HCCH out-of-plane bending mode with its D and ^{13}C counterparts at 482.0 and 674.5 cm^{-1}. Another one at 876.4 cm^{-1} in the ^{13}C spectra is assigned to the B_2 HCCH in-plane bending mode without observation of the isotopic counterparts.

The strong **i** absorption at 1754.8 cm^{-1} shifts to 1258.9 cm^{-1} on deuteration (H/D ratio of 1.394) and shows essentially no ^{13}C shifts. The observed frequencies are compared with 1660.8 and 1204.2 cm^{-1} for FeH_2 and FeD_2 [18], whose absorptions are observed in Figs. 1–3. This Fe—H stretching band is assigned to the insertion complex (HFe—CCH). Another strong **i** absorption is observed at 1976.1 cm^{-1}, and its D and ^{13}C counterparts at 1862.2 and 1905.3 cm^{-1} (H/D and 12/13 ratios of 1.061 and 1.037). It is assigned to the C—C stretching mode on the basis of the frequency and relatively large ^{13}C shift. The weaker CCH in-plane bending and C—Fe stretching absorptions are observed at 668.4 and 470.5 cm^{-1}, and another **i** absorption in the high frequency region at 3310.1 cm^{-1} is assigned to the C—H stretching mode on the basis of its frequency and large D shift (Tables 1 and S2). The observed 5 **i** absorptions substantiate formation of the insertion complex in reaction of Fe with acetylene.

Two **iA** absorptions (1735.5 and 1971.5 cm^{-1}) are observed on the blue sides of the two strong **i** (Fe—H stretching and C—C stretching) absorptions. These absorptions, which dramatically increase on uv irradiation and decrease quickly in annealing, are tentatively designated to the acetylene coordinated insertion complex (HFe—CCH···C_2H_2). Acetylene coordination to an insertion product decreases the M—H stretching frequency [4c], and in annealing it probably converts to a more stable form, such as a sandwiched π-complex ($Fe(C_2H_2)_2$).

The strong C—C and Fe—H stretching absorptions marked "**i**" and "**iA**" (with site absorptions) corresponds to the series of absorptions assigned to the same vibrational modes of the insertion complex by

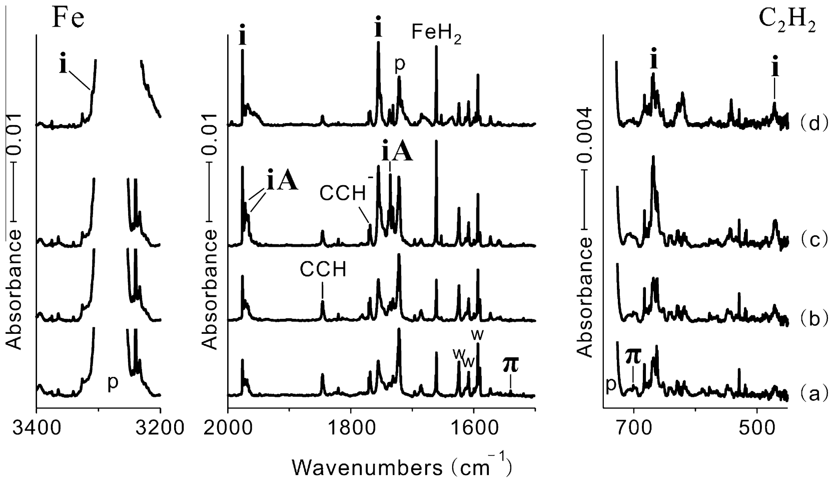

Fig. 1. IR spectra in the product absorptions regions for laser-ablated Fe atoms co-deposited with C_2H_2 in excess argon at 8 K and their variation. (a) Fe + 0.25% C_2H_2 in Ar co-deposited for 1 h. (b) As (a) after photolysis ($\lambda > 420$ nm). (c) As (b) after photolysis ($240 < \lambda < 380$ nm). (d) As (c) after annealing to 28 K. **π**, **i**, and **iA** denote the product absorption groups. p and w stand for precursor and water residue absorptions.

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