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Electronic Structures of (Alkene)iron Tetracarbonyl Compounds

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Baerends and co-workers[1] have reported the photoelectron spectrum of and Xα calculations for (ethylene)iron tetracarbonyl. Their interpretation of the spectrum based upon the computations concluded that the ethylene π MO is not perturbed significantly by the Fe(CO)$_4$ moiety. More recently Cardaci et al.[2] have studied the photoelectron spectra of a series of iron tetracarbonyl complexes. Their conclusion is the same as that reached earlier[1] concerning (ethylene)iron tetracarbonyl. However, they did observe shifts of 0.5 and 0.3 eV, respectively, in the band corresponding to ionization of the ligand π_{cc} orbital when the ligands were acrolein and acrylonitrile. It is interesting that the π ionization energy for the latter complex was lower than the corresponding value for free acrylonitrile given that iron carbonyl complexation normally causes increases in the π ionization potentials of ligands.[3-10]

Extensive work in these laboratories[10] on the photoelectron spectra of iron tricarbonyl complexes of 4π-electron hydrocarbons has shown that the Fe(CO)$_3$ moiety stabilizes the highest occupied π MO of the ligands by ca. 0.8–1.0 eV. For this reason the reported zero perturbation of the ethylene π MO in the (ethylene)iron tetracarbonyl complex did not seem reasonable to us. Thus, we have repeated the photoelectron spectroscopic studies on (ethylene)iron tetracarbonyl and have investigated for the first time the photoelectron spectrum of a related molecule, (tetramethylallene)iron tetracarbonyl.

Experimental Section

The (ethylene)iron tetracarbonyl sample was prepared by the method of Murdoch and Weiss.[12] The sample was purified by fractional vacuum distillation and stored at −196 °C until use. The authenticity of the sample was verified by ^{1}H NMR (singlet at δ 2.45 in CS$_2$ referenced to Me$_4$Si), coupled ^{13}C NMR (triplet at 35.3 ppm; singlet at 212.1 ppm in benzene referenced to Me$_4$Si), and gas-phase, solution, and thin-film infrared spectroscopy (identical spectra with those given in ref 12). The (tetramethylallene)iron tetracarbonyl used in this work was supplied by D. H. Gibson of the University of Louisville.

The photoelectron spectrometer employed in this study was a Perkin-Elmer PS-18. The data presented here represent an average of several spectral runs with argon and xenon being employed as internal calibrants. The sample-inlet probe was held at the lowest temperature possible (ca. 60 °C) to minimize decomposition of the samples.

The mass spectra to be discussed in this note were obtained using a Du Pont 21-491 spectrometer. For these studies the inlet system and ionization chamber were maintained at 30 and 60 °C, respectively, to mimic the conditions in the photoelectron spectrometer.

Results and Discussion

The photoelectron spectrum obtained in this work for (ethylene)iron tetracarbonyl was essentially the same as that reported by Baerends et al.[1] The low-ionization-energy region of the photoelectron spectra for tetramethylallene (TMA) and (tetramethylallene)iron tetracarbonyl (TMACO4) are shown in Figure 1. The low-ionization-energy band in the spectrum of TMA at 8.53 eV (vibrational structure of 0.17 eV with evidence of Jahn–Teller splitting) refers to ionization of the doubly degenerate e π MO for this cumulative diene. Upon complexation of TMA to form TMACO4, the degeneracy of this e MO must be broken. Thus the spectrum of the complex should contain two distinct π ionization bands unless the perturbation introduced by Fe(CO)$_4$ is negligible as has been assumed to be the case[1] for (ethylene)iron tetracarbonyl. One of the bands should remain near 8.5 eV (uncomplexed π orbital), while the other should be shifted according to the magnitude of the perturbation.

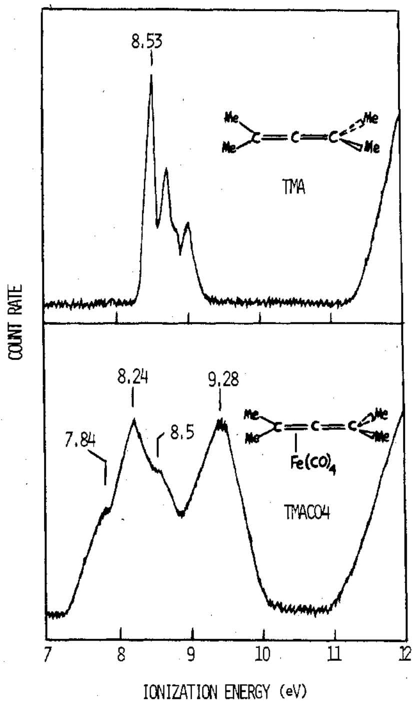

Figure 1. Photoelectron spectra of tetramethylallene and (tetramethylallene)iron tetracarbonyl. The excitation source was the 584-Å resonance line of helium.

Figure 1 clearly shows that a shoulder exists on the high-ionization-energy edge of band A at ca. 8.5 eV. This band can be assigned to the uncomplexed π orbital ionization process. The remainder of band A resembles closely the lowest ionization-energy band system for the numerous iron tricarbonyl complexes which have been studied in these laboratories.[10] Therefore, we assign the two components at 7.84 and 8.24 eV to the various iron d orbital ionization events which overlap extensively. This leaves band B at 9.28 eV to correspond to ionization of an MO which is primarily composed of the perturbed π orbital on the ligand. Thus our results indicate that complexation of the π orbital on TMA by Fe(CO)$_4$ causes a perturbation of ca. 0.75 eV, which is only slightly less than the perturbations which have been measured for the highest occupied π orbital of numerous (diene)iron tricarbonyls (0.8–1.0 eV).[7,10,11]

The results for TMACO4 discussed above would seem to conflict with those obtained earlier[1,2] and in this work for (ethylene)iron tetracarbonyl. One might propose that the alleged photoelectron spectrum of the ethylene complex really corresponds to decomposition products. To this end we have investigated the mass spectra of both complexes discussed in this work at similar temperature and pressure conditions to those existing in the photoelectron spectrometer (Figure 2). It is evident in Figure 2 that the mass spectrum of TMACO4 is as expected with no mass peaks appearing above the parent peak at m/e 264. On the other hand, the mass spectrum of the ethylene complex (Figure 2) contains numerous peaks above the parent at m/e 196 which could indicate at least partial decomposition to ethylene and probably Fe$_3$(CO)$_{12}$ in the high-vacuum systems. Thermal decomposition upon standing of Fe(CO)$_4$(C$_2$H$_4$) to C$_2$H$_4$ and Fe$_3$(CO)$_{12}$ has been observed by Murdoch and Weiss.[12] It should be noted that iron carbonyl compounds such as Fe(CO)$_5$ often yield mass spectra with high mass peaks due to ion–molecule reactions

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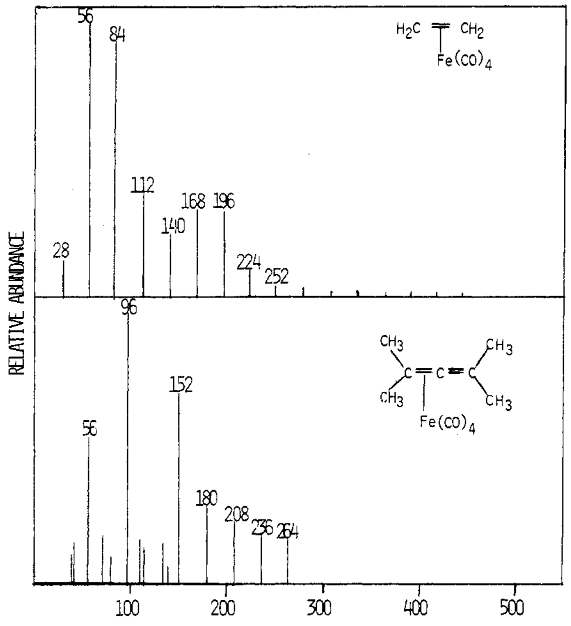

Figure 2. Mass spectra of (tetramethylallene)iron tetracarbonyl and (ethylene)iron tetracarbonyl excited by a 70-eV electron beam.

at high pressure (above 10^{-7} torr)[13,14] but not at the low pressures (ca. 10^{-8} torr) existing in the ionization chamber of our mass spectrometer.[15] We have observed partial sample decomposition for the ethylene complex upon routine vacuum transfer from one vessel to another at ca. 10^{-4} torr. Furthermore, the ethylene complex destroyed our thermal pressure probe on the photoelectron spectrometer, while the TMACO4 sample did not affect it. We would postulate that the metering needle valve on the volatile inlet probe of the photoelectron spectrometer and the gold leak in the mass spectrometer are serving as fractional distillation heads to allow substantial amounts of ethylene and volatile iron carbonyl decomposition products of (ethylene)iron tetracarbonyl into the high-vacuum ionization chambers of the instruments. We further suggest that the broad band (10.01–11.41 eV) in the photoelectron spectrum of (ethylene)iron tetracarbonyl which has been assigned[1,2] to an unperturbed ethylene π orbital really refers to a mixture of complexed and free ethylene, such that the true vertical ionization potential for the complex is not resolved.

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Registry No. TMACO$_4$, 12264-26-5; TMA, 1000-87-9; (CH_2=CH_2)Fe(CO)$_4$, 32799-25-0.

References and Notes

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(11) A referee has suggested that since the two d orbital band components for Fe(CO)$_5$ have equal intensity and are split by ca. 1 eV our assignment for TMACO4 be revised to 7.84 and 8.50 eV for iron orbitals and 8.24 and 9.28 eV for the ligand orbitals. There is a problem with this assignment. It implies that Fe(CO)$_4$ perturbs the two π orbitals of TMA in opposite directions. Such behavior has not been observed for any of the 11 Fe(CO)$_3$ complexes of dienes studied in these laboratories;[10] the latter complexes would seem to be better models for TMACO4 than is Fe(CO)$_5$. However, as suggested by the referee, a comparison of He I and He II spectra would be useful for deciding between the two assignments. In any case the π orbital is *not* unperturbed by Fe(CO)$_4$.
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(15) A mass spectrum of Fe(CO)$_5$ taken under these conditions on our instrument contained no mass peaks above the parent at *m/e* 196.

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Bridging Alkylimido Complexes of the Group 4B Transition Metals

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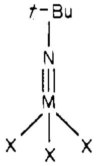
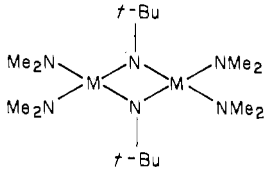
Recently we reported the preparation of group 5B alkylimido complexes of niobium and tantalum[1] and of vanadium.[2] Monomeric complexes Ia–c contain a nearly linear M–N–C arrangement indicating that the formal double bond from metal to nitrogen in fact has considerable triple bond character. In contrast, the known organoimido derivatives of titanium have either dimeric or polymeric structures.[3-5] For instance, compound IIa was prepared by Bradley[3] and a dimeric structure was assigned from solution molecular weight measurements. We have now prepared the zirconium[6] and hafnium analogues IIb and c and have found that these species are imido nitrogen-bridged dimers.

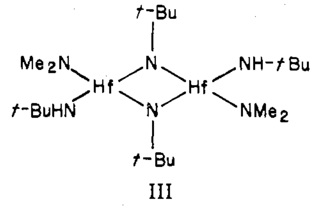


Ia, M = V, X = $OSiMe_3$
b, M = Nb, X = NMe_2
c, M = Ta, X = NMe_2



IIa, M = Ti
b, M = Zr
c, M = Hf

Refluxing a hexane solution of tetrakis(dimethylamido)-hafnium containing 1 equiv of *tert*-butylamine causes the initially colorless solution to become yellow. Removal of the solvent at reduced pressure gave a yellow residue which contained no IIc by NMR.[7] However, heating this material at 150 °C in vacuo afforded a yellow sublimate which was largely IIc apparently contaminated with compound III.[8] The product was purified by recrystallization. Zirconium derivative IIb was prepared in an analogous manner. However, the major impurity in the sublimate in this case appears to be Zr(NMe_2)$_4$.



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