

# Anion states of $\eta^4$ -polyene iron tricarbonyl complexes

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Attachment energies of low energy electrons to  $\text{Fe}(\text{CO})_5$  and to  $\eta^4$  complexes of 1,3-butadiene, 1,3-cyclohexadiene, cyclooctatetraene, and cyclobutadiene with  $\text{Fe}(\text{CO})_3$  have been determined by electron transmission spectroscopy. The spectrum of  $\text{Fe}(\text{CO})_5$  is similar to that of  $\text{Cr}(\text{CO})_6$ , showing an anion resonance near threshold assigned to predominantly  $\text{Fe}3d$  orbitals and two resonances between 1 and 3 eV assigned to predominantly  $\text{CO}\pi^*$  orbitals. The diene complexes show threshold features similar to  $\text{Fe}(\text{CO})_5$ ,  $\text{CO}\pi^*$  resonances around 2 eV, and one or more diene  $\pi^*$  resonances. The resonances from the lowest  $\pi^*$  orbitals of butadiene, cyclohexadiene, and cyclooctatetraene are little different in the free dienes and the complexes, but higher  $\pi^*$  orbitals are substantially destabilized in the complexes, consistent with qualitative symmetry arguments. In the cyclobutadiene complex the  $\pi_3^*$  orbital of cyclobutadiene is strongly destabilized by interaction with the  $\text{Fe}3d$ , giving a resonant feature at 1.2 eV. Dissociative attachment of electrons by the iron tricarbonyl complexes has been observed mass spectrometrically. The phenomenon is observed for electrons of energy less than 2 eV and results primarily in the loss of CO. For the cyclobutadiene complex, however, the attachment of 0 eV electrons results in a complex chemical process leading to the ejection of  $\text{C}_2$ .

## INTRODUCTION

Knowledge of the energy and character of low-lying unoccupied orbitals as determined experimentally may be used in conjunction with MO perturbation theory to predict rates and positions of nucleophilic attack on organic and organometallic substrates.<sup>1,2</sup> Such information can contribute to our understanding of the mechanism of catalysis and metal-ligand bonding at transition metal centers. In order to study the role of both  $\pi$  systems and carbon monoxide as ligands on a singlet metal center, we have undertaken a study of  $\eta^4$ -polyene iron tricarbonyl complexes.

In complexes of conjugated hydrocarbons with metal carbonyls, it can be anticipated that orbitals which are predominantly  $\pi$  and  $\pi^*$  orbitals of the polyene unit will be among the frontier orbitals—the high-lying occupied orbitals and low-lying unoccupied orbitals of the complex. The perturbation of the occupied  $\pi$  orbitals of dienes resulting from complexation with the  $\text{Fe}(\text{CO})_3$  moiety has recently been evaluated by Worley *et al.*<sup>3</sup> using photoelectron spectroscopy (PES). To analyze the perturbation of the predominantly diene orbitals in the iron tricarbonyl complexes it was first necessary to assign the features in the photoelectron spectra so as to distinguish between ionizations arising from orbitals which were predominantly of  $\text{Fe}3d$ , CO, or diene character. For example, analogy between the spectra of  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$ , along with DVM  $X\alpha$  calculations, indicated that in  $\text{Fe}(\text{CO})_4\text{C}_2\text{H}_4$  the highest energy occupied orbitals with IP's around 8.5–10 eV were predomi-

nantly  $\text{Fe}3d$ , the orbitals with IP > 13.5 were predominantly CO, and the intermediate orbitals were predominantly  $\text{C}_2\text{H}_4$ .<sup>4</sup> In the photoelectron spectrum of cyclobutadiene iron tricarbonyl a peak at 8.45 eV was identified as  $\text{Fe}3d$  in character and one at 9.21 eV as diene. This assignment was based primarily on relative intensities for He I vs He II photoionization.<sup>5</sup> Based on systematics in the observed perturbations of the  $\pi$  orbital energies, Worley *et al.*<sup>3</sup> were then able to estimate ionization potentials of 8.3 and 12.0 eV for the  $\pi$  orbitals of free cyclobutadiene, in excellent agreement with later experimentally derived values of 8.2 and 12.2 eV.<sup>6</sup> For the cyclobutadiene iron tricarbonyl complex, Hartree-Fock calculations using both Koopmans' theorem and  $\Delta\text{SCF}$  approaches failed to reproduce the experimental orbital assignment.<sup>5</sup> Fenske-Hall MO calculations<sup>7</sup> and extended Hückel calculations<sup>8</sup> both give the proper ordering of orbital ionizations, but, at the Koopmans' theorem level, significant quantitative discrepancies with experiment remained. MS- $X\alpha$  calculations,<sup>9</sup> INDO calculations,<sup>10</sup> and Hartree-Fock GMO-CI calculations<sup>11</sup> give better agreement with experiment, but discrepancies between calculation and experiment were still of the order of 1 eV.

Information which compliments that obtained by PES may be acquired through a technique called electron transmission spectroscopy<sup>12,13</sup> (ETS). Whereas PES measures the energy required to remove an electron from an occupied orbital, ETS measures the energy of the anion state arising from electron capture into an unoccupied orbital. In this paper we describe an application of this technique in a study



of the perturbation of  $\pi^*$  orbitals caused by the incorporation of polyenes in iron carbonyl complexes. We begin with spectra of iron pentacarbonyl and free dienes and proceed to the study of  $\eta^4$ -polyene iron tricarbonyls.

The experiment involves the measurement of the transparency of a gas to an electron beam as a function of energy. The transparency depends in an adverse fashion upon the electron-scattering cross section. Temporary negative ion formation occurs with large cross section only over a narrow energy range. The negative ion may decay by giving up the trapped electron. This formation and decay process appears only as a fluctuation in the electron-scattering cross section. The process, as well as the corresponding feature in the transmission vs electron kinetic energy spectrum, is referred to as a "resonance."

The electron spectrometer consists of an electron source followed by an electron monochromator, a gas cell, and an electron collector. In practice the first derivative of the transmitted current as a function of electron energy is recorded since the derivative is sensitive to the abrupt change in transmitted current associated with a resonance. The energy associated with a resonance is known as an "attachment energy" (AE) and, with respect to the derivative spectrum, is defined as the point vertically midway between the minimum and maximum that characterize the resonance. For the present purposes an attachment energy can be identified with the negative of the corresponding electron affinity. In some cases the temporary anions formed by electron capture will decay by dissociation into a stable anion and a neutral fragment. In our apparatus a time-of-flight mass spectrometer appended to the gas cell is used to identify ions produced by dissociative attachment.<sup>12(b)</sup>

Among other things, electron transmission spectroscopy has been employed to study the energies of the unoccupied  $\pi^*$  orbitals of dienes as a function of substituent<sup>13</sup> and to identify the unoccupied orbitals of the  $d^6$  hexacarbonyls,<sup>14</sup> the metallocenes,<sup>15,16</sup> and dibenzene chromium.<sup>17</sup> Inspection of the results for  $\text{Cr}(\text{CO})_6$  and the dienes suggests that resonances identifiable with orbitals of mainly metal  $3d$ ,  $\text{CO}$ , and diene character should all occur in the region from 0–3 eV. In an energy derivative mode, the spectra give no direct information on resonance intensities or cross sections, so only the energies are available for orbital assignment (although preliminary results from a new apparatus yielding scattering cross sections directly indicate that cross section magnitudes may be of value in assigning the resonances). As noted above, present quantum mechanical calculations are not sufficiently accurate to quantitatively determine PES energies or assignments. It is not expected that they will be successful for the more difficult problem of attachment energies from ETS which have more features more closely spaced in energy. There is also the inherent problem of using bound state approaches to interpret scattering processes [see, e.g., Refs. 14(b) and 18]. Support for ETS assignments may sometimes be derived from comparison with other data, such as x-ray or UV spectra.<sup>18</sup> Unfortunately, there are no x-ray absorption (or electron energy loss) spectra available for the materials of interest here and the UV spectra<sup>19</sup> are of low resolution and/or restricted energy range. We therefore pro-

ceed by tracing the correlations between the free polyene electron transmission spectra and those of the  $\eta^4$ -polyene iron tricarbonyls using qualitative trends seen in the calculations, and expected from symmetry and orbital overlap arguments. For  $\text{Fe}(\text{CO})_5$  a more definitive approach is possible as described below.

## RESULTS AND DISCUSSION

### Iron pentacarbonyl

The derivative electron transmission spectrum of  $\text{Fe}(\text{CO})_5$  is compared in Fig. 1 with a previously published<sup>14(a)</sup> spectrum of  $\text{Cr}(\text{CO})_6$ . The current of negative ions from dissociative attachment to  $\text{Fe}(\text{CO})_5$  is plotted as a function of electron energy in Fig. 2. As previously reported,<sup>20</sup> the ions which appear at threshold are  $\text{Fe}(\text{CO})_4^-$  due to the detachment of  $\text{CO}$  from the parent anion. The shoulder in the ion current in Fig. 2 appears at the same energy as the first prominent resonance in the electron-scattering cross section and corresponds to the appearance of  $\text{Fe}(\text{CO})_3^-$  due to the loss of 2  $\text{CO}$ 's. The electron transmission spectrum of  $\text{Fe}(\text{CO})_5$ , similar to that of  $\text{Cr}(\text{CO})_6$ , shows a broadening of the characteristic threshold feature (a spike which is the derivative of the turn on of electron current near 0 eV), a resonance at about 0.3 eV and additional resonant features in the range of 1–3 eV. We have employed the transition state approach and the method of Ref. 4 to directly calculate the AE's of the two lowest energy unoccupied orbitals of  $\text{Fe}(\text{CO})_5$ . As shown in Table I, this calculation gives 0.37 eV for both the  $14a'_1$  orbital (which was more than 50%  $\text{Fe}3d$  in character) and the  $4e''$  orbital (about 25%  $\text{Fe}3d$ , 75%  $\text{CO}\pi^*$ ). We can also estimate the  $14a'_1$  AE given the experimental  $10e'$  IP of 8.6 eV,<sup>4,21</sup> the  $10e' \rightarrow 14a'_1$  UV excitation energy of 4.4 eV<sup>19(a),22</sup> and the transition state orbital energy changes calculated by Baerends *et al.*<sup>4</sup> to obtain a  $14a'_1$  AE of about 1.2 eV (although this approach assumes that the magnitude of the change in orbital eigenvalue is the same for removal of, or addition of, half an electron). This procedure is described in more detail in Ref. 18(a). Other DVM  $X\alpha$

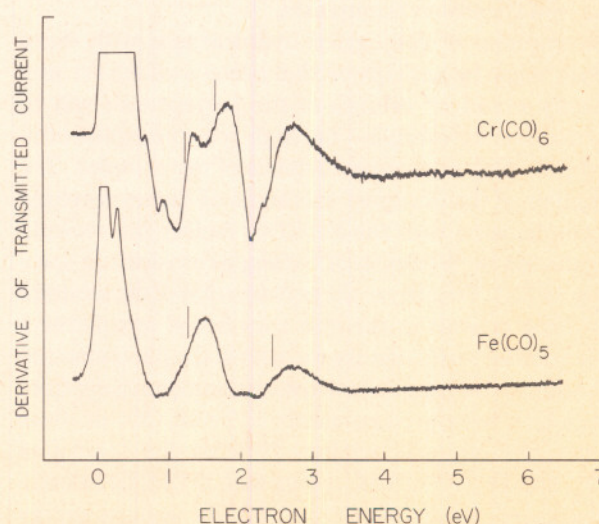


FIG. 1. Derivative electron transmission spectra of  $\text{Cr}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$ .



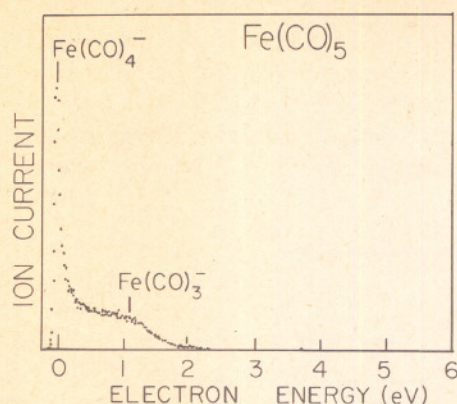


FIG. 2. Negative ion current from electron attachment to  $\text{Fe}(\text{CO})_5$ .  $\text{Fe}(\text{CO})_4^-$  appears at threshold and  $\text{Fe}(\text{CO})_3^-$  at about 1.2 eV.

calculations<sup>23</sup> on  $\text{Fe}(\text{CO})_5$  similar to those of Ref. 4 give a  $10e' \rightarrow 14a_1'$  transition state excitation energy of 4.5 eV, consistent with experiment. The next UV transition lies at 5.1 eV and is probably best assigned to the  $10e' \rightarrow 12e'$  transition, where  $12e'$  is  $\text{Fe}3d$  and  $\text{CO}\pi^*$  in character. The next UV peak at 6.2 eV has a number of possible assignments but  $10e' \rightarrow 5e''$  gives a reasonable energy.<sup>23</sup> The progression of peaks in the UV at 4.4, 5.1, and 6.2 eV in fact correlates with the progression of 0.3, 1.3, and 2.6 eV observed by ETS, indicating that they could have their origins in the same excited states. The symmetries of UV excited states in  $\text{Fe}(\text{CO})_5$  could be probed by magnetic circular dichroism (MCD)<sup>24</sup> and the electron scattering spectrum of  $\text{Fe}(\text{CO})_5$  could perhaps be probed by our total cross section experiment or by MS-X $\alpha$  continuum calculations,<sup>14(b)</sup> but for the present, we are restricted to the above semiquantitative arguments. Our preferred assignment is then that the ETS feature around 0.3 eV is associated with the  $14a_1'$  and  $4e''$  lowest energy orbitals which have substantial  $\text{Fe}3d$  character. Although other empty orbitals may lie lower in energy<sup>23</sup> they are expected to be quite diffuse and so not contribute to the cross section. The higher energy ETS features in  $\text{Fe}(\text{CO})_5$  are probably associated with predominantly  $\text{CO}\pi^*$  orbitals. The  $14a_1'$  (and, to a lesser extent, the  $4e''$ ) orbitals are, of course,  $\text{Fe}3d\text{--CO}\pi^*$  antibonding and so it would not be surprising that their occupation lead to loss of CO, as shown in Fig. 2.

TABLE I. Energies and types for frontier MO's of  $\text{Fe}(\text{CO})_5$ .

Orbital	$\epsilon(\text{eV})^a$	Compositions <sup>b</sup>
$5e''$	1.74	$\text{CO}\pi^*$
$12e'$	1.03	20% $\text{Fe}3d$ , 74% $\text{CO}\pi^*$
$2a_2'$	0.75	$\text{CO}\pi^*$
$11e'$	0.63	6% $\text{Fe}3d$ , 88% $\text{CO}\pi^*$
$9a_2''$	0.57	$\text{CO}\pi^*$
$4e''$	0.37	24% $\text{Fe}3d$ , 74% $\text{CO}\pi^*$
$14a_1'$	0.37	51% $\text{Fe}3d$ , 45% $\text{CO}\sigma$
$10e'$	-3.37	54% $\text{Fe}3d$ , 6% $\text{Fe}4p$ , 32% $\text{CO}\pi^*$
$3e'$	-4.46	73% $\text{Fe}3d$ , 27% $\text{CO}\pi^*$

<sup>a</sup> In  $14a_1'$  electron attachment transition state, with  $0.5 e^-$  in  $14a_1'$  and all orbitals up to  $10e'$  completely filled.

<sup>b</sup> In ground state of neutral molecular with  $10e'$  HOMO.

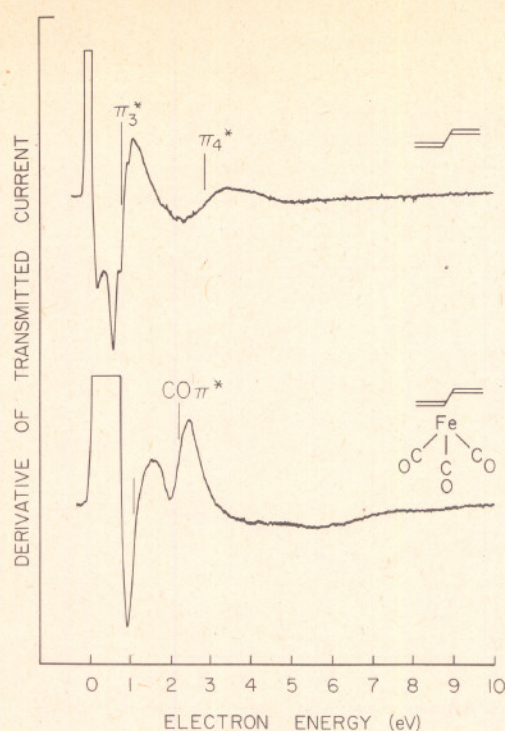


FIG. 3. Derivative electron transmission spectra of 1,3-butadiene and 1,3-butadiene iron tricarbonyl.

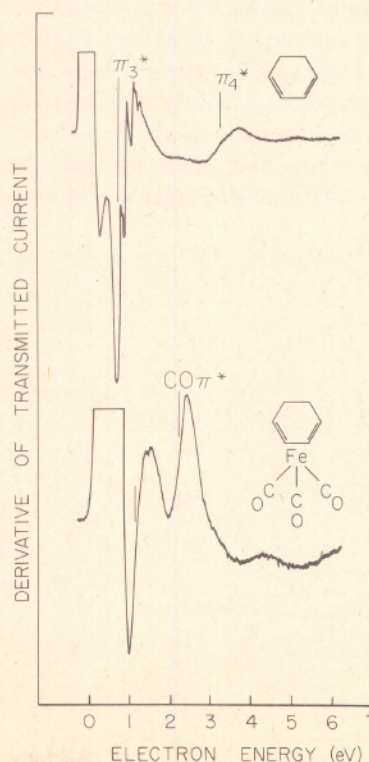


FIG. 4. Derivative electron transmission spectra of 1,3-cyclohexadiene and 1,3-cyclohexadiene iron tricarbonyl.



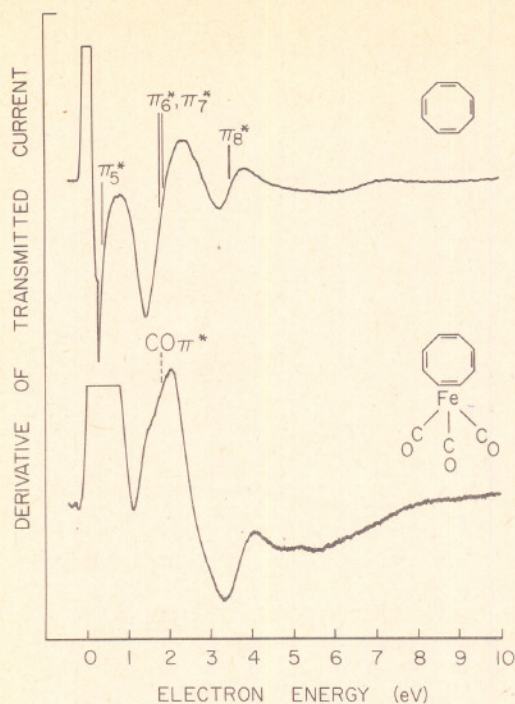


FIG. 5. Derivative electron transmission spectra of 1,3,5,7-cyclooctatetraene and 1,3,5,7-cyclooctatetraene iron tricarbonyl.

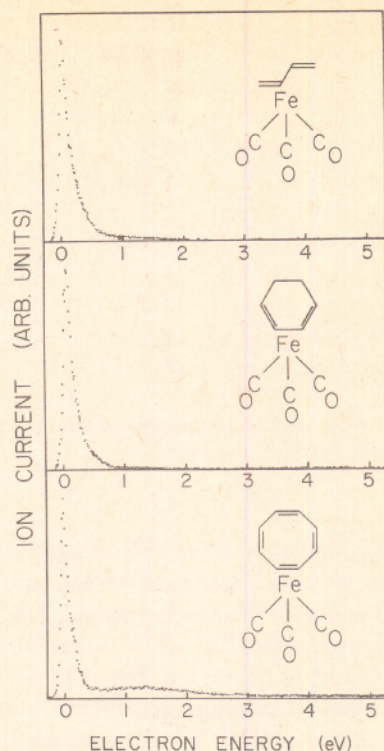


FIG. 7. Negative ion current from electron attachment to butadiene iron tricarbonyl, cyclohexadiene iron tricarbonyl, and cyclooctatetraene iron tricarbonyl. The threshold peak for the first two consists only of the parent ion for cyclooctatetraene the threshold peak is  $(\text{C}_8\text{H}_8)\text{Fe}(\text{CO})_2^-$ .

### Polyene iron tricarbonyls

The electron transmission spectra of the  $\eta^4$ -complexes, butadiene iron tricarbonyl, cyclohexadiene iron tricarbonyl, cyclooctadiene iron tricarbonyl, and cyclobutadiene iron tricarbonyl, along with spectra of the corresponding (stable) free polyenes are shown in Figs. 3–6. The rate of dissociative attachment to these iron tricarbonyl complexes is reflected in the plots of ion current as a function of electron energy presented in Figs. 7 and 8. These data, although more detailed, are in agreement with the available previous

work.<sup>20(c)</sup> In Fig. 7 it can be seen that the ion spectra consist of a threshold peak with a weak shoulder which roughly corresponds in each case to the first prominent resonance in the electron transmission spectrum. In butadiene iron tricarbonyl and cyclohexadiene iron tricarbonyl the ions at threshold are (metastable) parent anions. With increasing electron energy, there appear ions resulting from the loss of either the CO or the polyene ligand. In cyclooctadiene iron tricarbonyl, the only ion which appears is

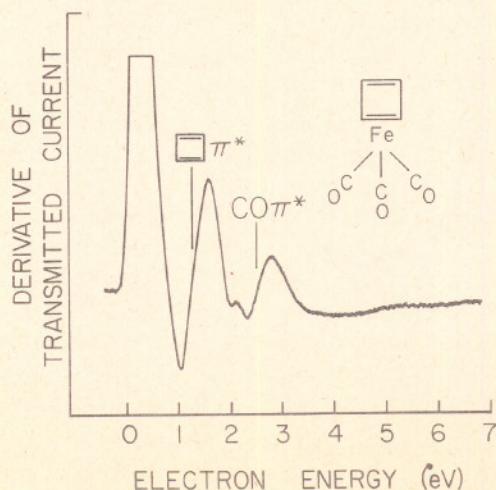


FIG. 6. Derivative electron transmission spectrum of  $\eta^4$ -cyclobutadiene iron tricarbonyl.

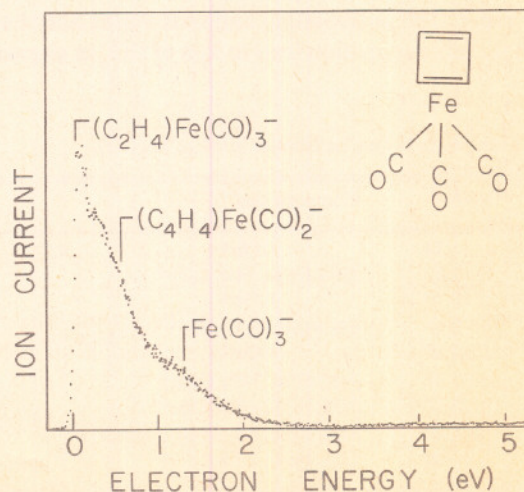


FIG. 8. Negative ion current from electron attachment to cyclobutadiene iron tricarbonyl. The major ions are identified. Note that the threshold peak corresponds to the loss of  $\text{C}_2$ .



$(C_8H_8)Fe(CO)_2^-$ , the ion which results from the loss of a CO ligand. The ion spectrum shown in Fig. 8, for dissociative attachment to cyclobutadiene iron tricarbonyl is considerably more complex. As indicated, we observe ions corresponding to the loss of either ligand, CO or  $C_4H_4$ . More interestingly, at threshold we observe an ion with mass corresponding to  $(C_2H_4)Fe(CO)_3^-$ . This implies a dissociative attachment process which involves a rearrangement to yield the neutral fragment  $C_2$ . The induction of such a complex chemical reaction by the impact of an electron of nearly zero energy is even more remarkable than the chemical process arising from low energy hydride ion impact which have recently been reported by Squires and co-workers.<sup>25</sup>

For each complex we assign the broad turn-on or threshold feature to resonant electron capture into an orbital with  $Fe3d$  and  $CO\pi^*$  character. This will be the analog of the  $32a'$  LUMO in cyclobutadiene iron tricarbonyl which has been identified by Bursten and Fenske.<sup>7</sup> The features in the free diene spectra may be identified with the  $\pi^*$  MO's as indicated in the figures.<sup>13(b)</sup> Experimental IP's for the occupied orbitals of 1,3-butadiene are 11.3 and 9.1 eV,<sup>3</sup> compared to 12.2 and 8.2 eV in cyclobutadiene.<sup>6</sup> The difference of these energies may be qualitatively understood using the  $\pi$  MO energies and plots in Fig. 9 obtained from STO-3G SCF MO calculations assuming a rectangular geometry like that calculated in Ref. 6. Closure of the ring will stabilize  $\pi_1$ , which is bonding between  $C_1$  and  $C_4$ , and destabilize  $\pi_2$ , which is antibonding between  $C_1$  and  $C_4$ . Since  $\pi_{2,3}$  is degenerate and nonbonding in square cyclobutadiene we expect  $\pi_3$  in cyclobutadiene to be more stable than the antibonding  $\pi_3^*$  in butadiene. Assuming that the stabilization of  $\pi_3$  of cyclobutadiene is of the same magnitude as the stabilization of  $\pi_2$  of butadiene (approximately 0.9 eV from the PES data), the AE for  $\pi_3$  of cyclobutadiene should be about 0.9 eV below that of 1,3-butadiene, placing it just about at threshold. Assuming a similar 0.9 eV destabilization for the  $\pi_4^*$  of cyclobutadiene puts its AE 0.9 eV above that of 1,3-butadiene at about 3.8 eV.

In 1,3-butadiene iron tricarbonyl the iron is closest to the terminal carbon atoms of the butadiene.<sup>26</sup> By symmetry we expect the  $\pi_3^*$  MO of the open chain dienes in Fig. 9 to interact weakly with the  $Fe3d$  while the  $\pi_4^*$  will interact strongly so that the energy of the  $Fe3d-\pi_4^*$  antibonding state will be pushed up relative to  $\pi_4^*$  in free butadiene. If this state is destabilized by the same amount by which  $\pi_1$  is stabilized (approximately 0.8–1.0 eV from Ref. 2), then its AE should occur at about 3.7 eV in the 1,3-butadiene complex. The  $\pi_3^*$ , in contrast, should be little changed in energy by covalent mixing in the complex and its AE should be little changed. For cyclobutadiene, in which the Fe is equidistant from the four carbons of the ring,<sup>27</sup> the  $\pi_3$  orbital should mix with and be destabilized by the  $Fe3d$  and the  $\pi_4^*$  should show little interaction.

We then tentatively assign the resonant feature at 1.1 eV in the butadiene iron tricarbonyl spectrum to a little-modified  $\pi_3^*$  orbital and the resonance around 2.2 eV to predominantly  $CO\pi^*$  orbitals. The  $\pi_4^*$  orbital would be displaced to energies above 3 eV resulting in a reduced lifetime and consequent broadening of the feature in the spectrum. A similar

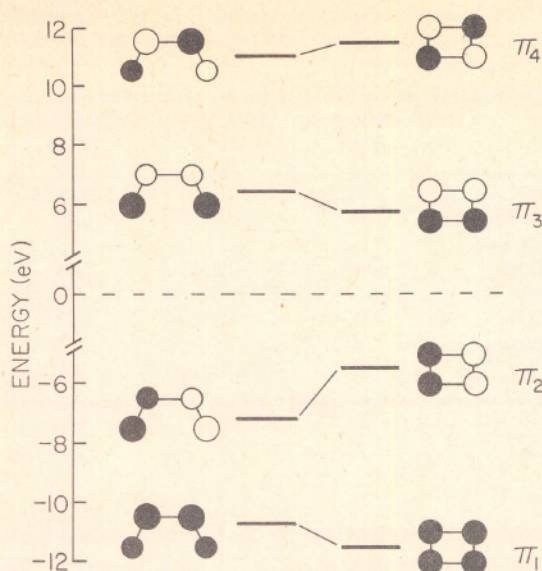


FIG. 9. Qualitative  $\pi$  MO energy levels and orbital compositions for 1,3-butadiene and cyclobutadiene (in rectangular geometry obtained in Ref. 6). Eigenvalues from STO-3G SCF MO calculations.

interpretation is appropriate for the 1,3-hexadiene iron tricarbonyl. It may be that other resonances derived from  $CO\pi^*$  orbitals in the 1–3 eV region are obscured by the diene features, but calculations on the  $Fe(CO)_n$  series<sup>23</sup> do indicate that the set of unoccupied orbitals span a narrow energy range and are less stable in  $Fe(CO)_3$  than in  $Fe(CO)_5$ . Thus the only  $CO\pi^*$  feature in the  $Fe(CO)_3$  complexes may be the one at about 2.2 eV. For cyclobutadiene iron tricarbonyl the feature at about 1.2 eV is assigned to the predominantly  $\pi_3^*$  cyclobutadiene orbital and that at about 2.5 eV to  $CO\pi^*$  type orbitals. The proposition that the  $\pi_3^*$  resonance of the cyclobutadiene complex is close in energy to that in the butadiene iron tricarbonyl does not imply that the  $\pi_3^*$  of cyclobutadiene interacts weakly with  $Fe(CO)_3$ . Rather, as pointed out above, free cyclobutadiene would have its  $\pi_3^*$  resonance near threshold so its high energy in the complex implies a strong interaction.

In free cyclooctatetraene (COT) the lowest energy  $\pi^*$  resonance ( $\pi_5^*$ ) occurs about half an eV lower than in 1,3-butadiene, the nearly degenerate pair ( $\pi_6^*, \pi_7^*$ ) is responsible for the resonance at 1.8 eV and the highest energy  $\pi^*$  orbital ( $\pi_8^*$ ) gives the feature at 3.5 eV.<sup>12</sup> Studies of the ESR of condensed phase anions of the COT complex indicate that the unpaired electron is localized on those COT carbons not bonded to the metal.<sup>28</sup> The four-carbon unit not directly adjacent to Fe seems to be little affected by complexation.<sup>29</sup> For example, the photoemission spectrum of the COT complex shows a considerably smaller perturbation of the occupied  $\pi$  orbitals than those for the other complexes.<sup>30</sup> Studies of the single crystal polarized absorption spectra of cyclooctatetraene iron tricarbonyl indicate a  $Fe3d \rightarrow COT$  charge transfer transition at about 4.1 eV.<sup>31</sup> By analogy with  $Fe(CO)_5$  this indicates that the AE for the COT  $\pi^*$  state should be about 0.5–1.0 eV. Thus, the  $\pi_5^*$  of COT in the complex probably falls in the broadened threshold feature of Fig. 5. By symmetry the  $\pi^*$  LUMO of COT is not expected



TABLE II. Compilation of attachment energies (eV) for  $\text{Fe}(\text{CO})_5$  and the  $\eta^4$ -polyene iron tricarbonyls and proposed assignments of the character of the corresponding molecular orbitals.

	Predominantly $\text{Fe}3d$	Hydrocarbon $\pi^*$	Predominantly $\text{CO}\pi^*$
$\text{Fe}(\text{CO})_5$	0.3		1.34, 2.55
1,3-Butadiene $\text{Fe}(\text{CO})_3$	$\sim 0$	1.08	2.19
1,3-Cyclohexadiene $\text{Fe}(\text{CO})_3$	$\sim 0$	1.13	2.21
Cyclobutadiene $\text{Fe}(\text{CO})_3$	$\sim 0$	1.19	2.52
Cyclooctatetraene $\text{Fe}(\text{CO})_3$	$\sim 0$	$\sim 0.5, \sim 2, \sim 3.7$	$\sim 2$

to significantly mix covalently with the  $\text{Fe}3d$  orbitals since it has the same local symmetry as  $\pi_3^*$  in 1,3-butadiene (Fig. 9). This expectation is supported by INDO calculations.<sup>32</sup> The highest  $\pi^*$  orbital of COT possesses local symmetry of  $\pi_4^*$  of butadiene and can be expected to be destabilized through interaction with the  $\text{Fe}3d$ . The resonance feature near 2 eV in the spectrum of cyclooctatetraene iron tricarbonyl has an irregular shape suggesting two or more overlapping features. These presumably include a resonance which is primarily  $\text{CO}\pi^*$  and a resonance associated with the member of the COT ( $\pi_6^*, \pi_7^*$ ) pair which is stabilized through interaction with the  $\text{Fe}3d$  orbital.

Our proposed assignments of the character of the orbitals associated with the prominent resonances observed in the electron transmission spectral of the iron carbonyl complexes are assembled in Table II.

## SUMMARY AND CONCLUSIONS

Although orbitals of  $\text{Fe}3d$ ,  $\text{CO}\pi^*$ , and hydrocarbon  $\pi^*$  type are all in the energy range to give resonances in electron scattering in the 0–3 eV region, the various features can generally be sorted out on the basis of free hydrocarbon and  $\text{Fe}(\text{CO})_5$  comparisons, MO calculations, and auxiliary spectral information. The observed magnitudes of interaction between the  $\text{Fe}(\text{CO})_3$  unit and the hydrocarbon  $\pi^*$  orbitals are consistent with qualitative symmetry arguments. In general, the lowest energy unoccupied orbitals of the  $\eta^4$ -polyene iron tricarbonyl complexes are predominantly of  $\text{Fe}3d$  character. Antibonding  $\pi^*$  orbitals on the ligands are next highest with the polyene  $\pi^*$  apparently lower than  $\text{CO}\pi^*$ .

## ACKNOWLEDGMENT

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