Valence-band Photoelectron Spectra of some Dicarbonyl(η-cyclopentadienyl)(ligand)iron Compounds and Tetrakis[carbonyl(η-cyclopentadienyl)iron(I)]

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Valence-band photoelectron spectra of $[Fe(CO)_2(\eta\text{-}C_5H_5)X]$ (X = Cl, Br, I, or Me) and $[\{Fe(CO)(\eta\text{-}C_5H_5)\}_4]$ are reported and compared with the previously published spectra of $[Fe(C_5H_5)_2]$ and $Fe(CO)_5$. Analysis of the spectra indicates that a treatment in terms of the local symmetry of the C_5H_5 ring can be used to assign the observed bands.

THE valence-band photoelectron (p.e.) spectra of iron pentacarbonyl and bis(η-cyclopentadienyl)iron have been previously reported.[1–3] In both cases the lowest-energy bands arise from the formally non-bonding *d* orbitals of the iron atom in the σ-bond approximation. In the case of $Fe(CO)_5$ the bands are of approximately equal intensities, as expected from the identical degeneracies of the e' and e'' orbitals. In the case of ferrocene, $[Fe(C_5H_5)_2]$, the intensity of the second peak is approximately twice that of the first, again as expected from the occupancies of the a'_{1g} and e_{2g} orbitals. Both bands have very characteristic shapes. Interestingly this indicates that the a'_{1g} orbital lies above the e_{2g}, contrary to the self-consistent-field calculation of Schustorovich and Dyatkina [4] but in agreement with the calculations of Hillier and Canadine.[5] The calculations by Contiere *et al.*[6] on the energy levels of the ferricinium ion, $[Fe(C_5H_5)_2]^+$, and the applicability of Koopmans theorem to the ferrocene system are also important in this connection. The ferrocene p.e. spectrum also shows a group of ill resolved peaks between 12 and 14 eV,† probably three in number, and these are also certainly due to orbitals such as e_{1g}, e_{1u}, and a_{2u}, from interaction of the ring orbitals with iron orbitals.

Here we report valence-band p.e. spectra of $[\{Fe(CO)_2(C_5H_5)\}_2]$, $[\{Fe(CO)(C_5H_5)\}_4]$, and $[Fe(CO)_2(C_5H_5)X]$ (X = Cl, Br, I, or Me). These compounds are examples of a type in which the overall molecular symmetry is low but in which the bonding in parts of the molecule may be treated, at least qualitatively, in terms of relatively high-level symmetries. Thus in $[\{Fe(CO)(C_5H_5)\}_4]$ the $Fe\text{–}C_5H_5$ interaction may be considered to have C_{5v} symmetry and the cage to have T_d symmetry. In all the others the $Fe\text{–}C_5H_5$ interaction may again be treated as having C_{5v} symmetry and the rest of the molecule as C_s. In making this distinction we are effectly assuming that degeneracies permitted under one symmetry will not be

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† 1 eV ≈ 1.60×10^{-19} J.

[1] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, 1970.

[2] D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, 1969, **8**, 2544.

[3] S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J.C.S. Faraday II*, 1972, **68**, 1847.

[4] E. M. Schustorovich and M. E. Dyatkina, *Doklady Akad. Nauk S.S.R.*, 1959, **128**, 1234.

[5] I. H. Hillier and R. M. Canadine, *Discuss. Faraday Soc.*, 1969, **47**, 27.

[6] M. M. Contiere, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, 1972, **27**, 281.

greatly split by the other. The molecular-orbital (m.o.) energy-level diagram for an Fe–C_5H_5 moiety with assumed C_{5v} symmetry is shown in Figure 1.

RESULTS AND DISCUSSION

The results of the p.e. spectra determinations are given in the Table and shown in Figure 2. Some typical spectra are shown in Figures 3—5. Only those peaks whose positions, because of their sharpness, can be fairly accurately located are given in electronvolts on the Figures.

Photoelectron spectral band values (eV) of some η-cyclopentadienyliron compounds

$[Fe(C_5H_5)_2]$	$[Fe(CO)_2(C_5H_5)Cl]$	$[Fe(CO)_2(C_5H_5)Br]$	$[Fe(CO)_2(C_5H_5)I]$	$[Fe(CO)_2(C_5H_5)Me]$	$[\{Fe(CO)(C_5H_5)\}_4]$	$Fe(CO)_5$ *
6.90	8.00	7.95	7.81	7.65	6.45	
7.20	8.27	8.27	8.18	7.90	6.87	
	8.95	8.91	8.8	8.68	8.58	8.60
			9.35			
8.75	10.15	9.8	10.12	9.25	8.9	9.50
9.40	10.65	10.45	10.48	10.02	9.15	
12.25	12.7	12.79	12.89	12.6	11.30	
12.90	13.88	13.95	13.69	13.44	11.90	
13.50					12.30	
16.45	16.72	16.95	16.81	16.35	15.4	

* From ref. 2.

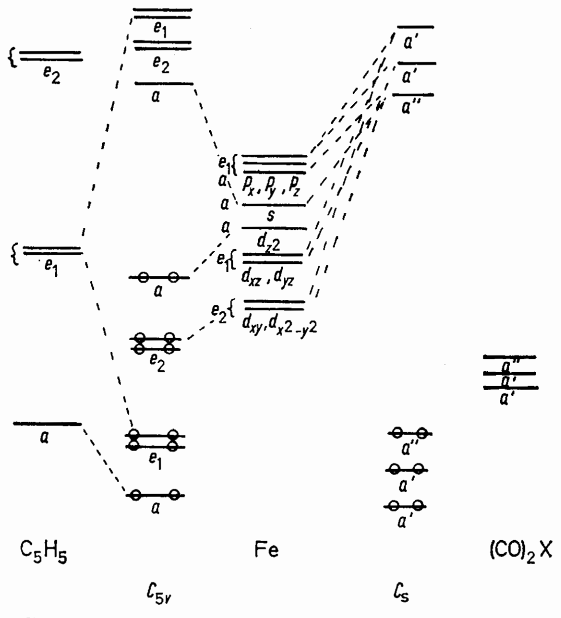

FIGURE 1 Schematic m.o. energy-level diagram for $[Fe(CO)_2(C_5H_5)X]$

The following points emerge from a study of the spectra. In all the spectra there were a pair of low-energy bands with much the same separation as the e_{1g} and e_{2g} bands in ferrocene; the similarity is much closer than that since the gross features of the vibronic structure on these bands is the same as those of ferrocene. We therefore identify these bands as a and e modes of the ' non-bonding ' d electrons of the iron atoms in the field of the C_5H_5 rings. In the case of the $[Fe(CO)_2(C_5H_5)X]$ (X = Me, Cl, Br, or I) compounds there was an additional band, absent in $[Fe(C_5H_5)_2]$ and $[\{Fe(CO)(C_5H_5)\}_4]$, situated between the a and e bands.

The manganese carbonyl halides have been studied by Evans *et al.*[7] and by Lichtenberger *et al.*[8,9] and a comparison of these carbonyl halides with those of rhenium has been made by Ceasar *et al.*[10] Though Evans *et al.*[7] failed to detect the weak bonding p_σ orbital (of symmetry a_1) later identified by Lichtenberger *et al.*[8] and the assignment by the latter workers of the order of the orbitals between 9.56 and 11.18 eV in the manganese carbonyl halides has been questioned by Ceasar *et al.*,[10] all these authors are agreed in assigning the highest-occupied orbital in these systems to the p_π orbitals on the halogen. By analogy with the manganese carbonyl halides, we assign the additional band in the $[Fe(CO)_2(C_5H_5)X]$ systems (X = Cl, Br, or I) to the p_π orbitals

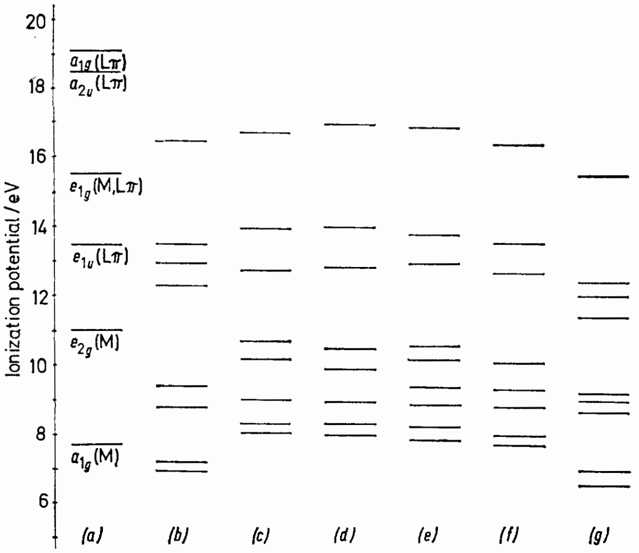

FIGURE 2 Photoionization energies of the various valence levels in the compounds discussed {calculated levels in $[Fe(C_5H_5)_2]$ (a) are included for comparison}: (b) $[Fe(C_5H_5)_2]$; (c) $[Fe(CO)_2(C_5H_5)Cl]$; (d) $[Fe(CO)_2(C_5H_5)Br]$; (e) $[Fe(CO)_2(C_5H_5)_2]$; (f) $[Fe(CO)_2(C_5H_5)Me]$; and (g) $[\{Fe(CO)(C_5H_5)\}_4]$

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[7] S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, 1969, **47**, 112.

[8] D. L. Lichtenberger, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, 1973, **12**, 702.

[9] D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, 1974, **13**, 486.

[10] G. P. Ceasar, P. Milazzo, J. L. Cibouski, and R. A. Levenson, *Inorg. Chem.*, 1974, **13**, 3035.

on the halogen. The actual values of the ionization potentials from this orbital are very similar to those found for the $Mn(CO)_5$ systems, follow the same trends, and like them show no sign of doublet splitting due to spin–orbit effects, except in the case of the iodide. The differing intensities of the iodine doublet in $[Fe(CO)_2(C_5H_5)I]$ are rather puzzling, particularly when compared with the $[Mn(CO)_5I]$ spectrum,[8] but even there the bands are not of equal intensity, and the symmetry in the C_5H_5 compounds is lower. The energies of these levels are very different from those in the alkyl and aryl halides [1] and shift relatively little from Cl to I. This argues some involvement of these orbitals in π bonding and recent n.q.r. studies on these systems confirm this.[11] The band at 8.68 eV in the spectrum of $[Fe(CO)_2(C_5H_5)Me]$ is very close to the position of the band at 8.65 eV in $[Mn(CO)_5Me]$.[7,9] In the manganese compound Evans *et al.* suggested that this band was due to a non-bonding d orbital of e symmetry.

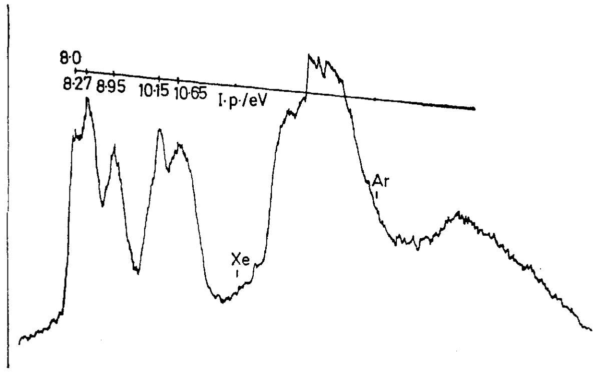

FIGURE 3 The He(I) p.e. spectrum of $[Fe(CO)_2(C_5H_5)Cl]$

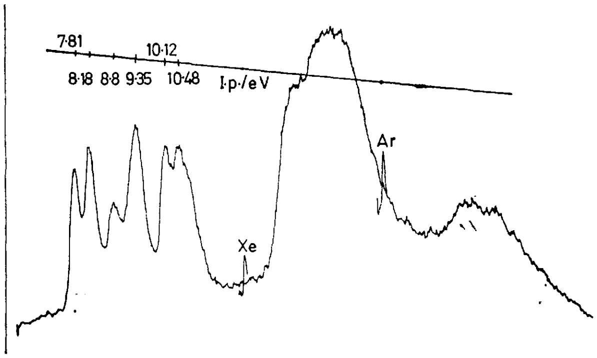

FIGURE 4 The He(I) p.e. spectrum of $[Fe(CO)_2(C_5H_5)I]$

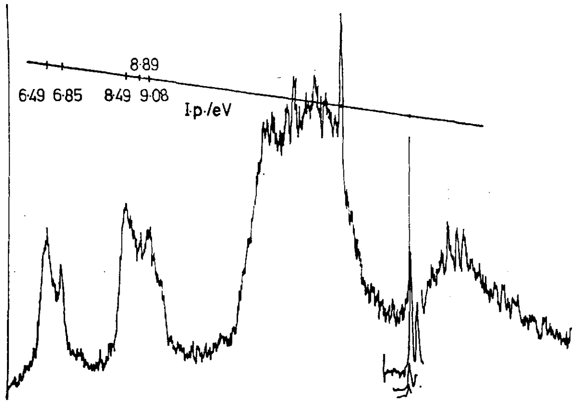

FIGURE 5 The He(I) p.e. spectrum of $[\{Fe(CO)(C_5H_5)\}_4]$

However, approximate m.o. calculations by Hall and Fenske [12] and an *ab initio* calculation on $[Mn(CO)_5Me]$ [13] accompanied by improved data on the low-energy p.e. region of $[Mn(CO)_5Me]$[9] led to the suggestion that this band was perhaps due to the σ-bonding a_1 orbital between the Me ligand and the metal. Because of the much lower ionization energies of the formally non-bonding d orbitals in these iron compounds compared to the manganese carbonyl halides (*ca.* 8 as compared to 9.5 eV for the manganese systems), it is unlikely that this band occurs at much the same energy in the manganese and iron methyl compounds if it is associated with a formally non-bonding d orbital in the σ-bond approximation and we think that the similarity of energies supports the Lichtenberger and Fenske [9] assignment to a σ-carbon–metal bond.

The group of orbitals in the region 12—14 eV are more difficult to interpret, since the bands were less well resolved. In the case of ferrocene they can probably be identified with the e_{1g} and e_{1u} m.o.s of the π-electron system and similar bands are found in $[Fe(CO)_2(C_5H_5)X]$; however, in addition we expect to find bands from the highest of the CO σ orbitals in this region. Thus $[Mn(CO)_5X]$ [7,8] systems and $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ [1] all show bands in this region, which in the case of the Group 6 hexacarbonyls, are relatively insensitive to change in the metal atom.

When we turn to the case of $[\{Fe(CO)(C_5H_5)\}_4]$ we find that again the pattern of molecular orbitals is very similar to that in ferrocene, even to the shape of the two lowest bands. However, the actual ionization potentials of these levels are much lower than for any of the other systems. There may be a weak band at 8.89 eV, inside the first e band of the metal–ring system, which corresponds to the highest-filled m.o. of the Fe_4 system, which is a t mode, but the rest of the p.e. spectrum is very similar to that of ferrocene.

EXPERIMENTAL

All spectra were recorded using a Perkin-Elmer PS18 photoelectron spectrometer with a heated inlet system. Samples were packed into the heated inlet probe under nitrogen, transferred rapidly to the machine, and pumped down. Spectra were internally calibrated with the atomic ionization potentials of argon and zenon. Attempts to obtain a satisfactory p.e. spectrum from $[\{Fe(CO)_2(C_5H_5)\}_2]$ were unsuccessful; the spectrum changed dramatically as the temperature of the inlet system was raised from 110 to 160 °C.

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[11] E. V. Bryukova, I. M. Alymov, and G. K. Sevin, *Bull. Acad. Sci., U.S.S.R., Div. Chem.*, 1973, **22**, 1849.

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[13] M. B. Hall, M. F. Guest, and I. H. Hillier, *Chem. Phys. Letters*, 1972, **15**, 592.

All compounds were prepared by procedures previously reported. Bis[dicarbonyl(η-cyclopentadienyl)iron(I)], $[\{Fe(CO)_2(C_5H_5)\}_2]$, was obtained from Alpha Inorganics. The commercial product was recrystallized from methylene dichloride–hexane. Dicarbonyl(η-cyclopentadienyl)iron chloride,[14] bromide,[15] iodide,[16] and σ-methyl,[17] $[Fe(CO)_2(C_5H_5)X]$ (X = Cl, Br, I, and Me), were prepared by standard literature methods. Tetrakis[(η-cyclopentadienyl)-iron(I)] was prepared by an improvement [18] of the original method of King.[19]

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