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ELECTRONIC STRUCTURE OF HALOGENOFERROCENES STUDIED BY He(I) PHOTOELECTRON SPECTROSCOPY

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Summary

He(I) photoelectron (PE) spectra are reported for chloroferrocene $Fe(\eta\text{-}C_5H_4Cl)(\eta\text{-}C_5H_5)$ and 1,1′-dihalogenoferrocenes $Fe(\eta\text{-}C_5H_4X)_2$ (X = Cl, Br). The difference between the ionization potentials (*IP*'s) of the $e_{2g}(d)$ and $a_{1g}(d)$ level is not affected by the ring substitution. Only the splitting of the $e_{1u}(\pi)$ level of the ligand is observed in the spectra. From the magnitudes of the splittings of this level and halogen non-bonding orbitals it is concluded that there is significant mixing of iron *p* orbitals with the $e_{1u}(\pi)$ level. The spectrum of $Fe(\eta\text{-}C_5H_4Cl)_2$ indicates that there is an interaction between the non-bonding out-of-plane chlorine *p* orbitals.

Introduction

The ultraviolet PE spectrum of ferrocene has been unequivocally assigned [1,2]. Ultraviolet PE spectroscopy is a powerful technique for revealing interactions between non-bonding orbitals [3]. The ultraviolet PE spectrum of halogenoferrocene, recorded by Evans and coworkers [1] for (supposedly) 1,1′-dichloroferrocene, indicates that there is no interaction between halogen non-bonding *p* orbitals. As will be shown below the published spectrum [1] was, however, that of chloroferrocene, and the 1,1′-dichloroferrocene spectrum we have obtained gives a quite different picture.

Experimental

The halogenoferrocenes were prepared by a published method [4]. To make sure that the spectra observed belong to the species studied, we carried out a detailed mass spectrometric examination of our samples and of their behaviour on heating. The mass spectra agreed with those previously published [5,6]. The purity of samples was also checked by gas chromatography (10% SE 30 on silanized Chromosorb W). The mass spectrometric analysis proved that in the range 70–210 °C 1,1′-dichlorofer-

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rocene did not decompose into chloroferrocene. The photoelectron spectrum does not change in this temperature range. This indicates that the sample does not decompose in the spectrometer during the recording of the spectra, which are thus genuinely those of 1,1′-dichloroferrocene.

He(I) PE spectra were recorded on the VG Scientific UVG 3 instrument with FWHM 0.04–0.05 eV on Ar $^2P_{3/2}$. The spectra were calibrated with an Ar/Xe mixture.

Results and discussion

The assignment of the first two bands (**1**, **2**) to the $e_{2g}(d)$ and $a_{1g}(d)$ levels follows the interpretation of the ultraviolet PE spectrum of ferrocene [1,2] (Fig. 1). The presence of one halogen atom raises the *IP*'s of the *d* levels by 0.17 eV. Two halogen atoms increase these *IP*'s by 0.34 ± 0.03 eV. The *IP* difference $e_{2g}(d) - a_{1g}(d)$ is not affected, within the experimental error, by the ring substitution (Table 1).

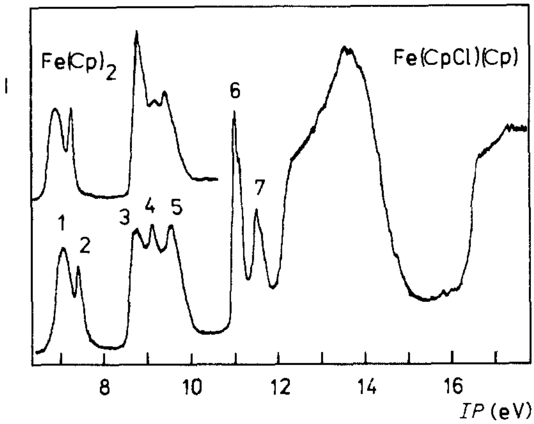

Fig. 1. He(I) photoelectron spectra of chloroferrocene and non-substituted ferrocene.

TABLE 1

VERTICAL IONIZATION POTENTIALS (*IP*) OF HALOGENOFERROCENES (Resolution FWHM 0.04–0.05 eV on Ar $^2P_{3/2}$. Standard deviation 0.03 eV)

Orbitals		Band	*IP* (eV)				
D_{5d}	C_{2h}		$Fe(Cp)_2$	Fe(Cp)(CpCl)	$Fe(CpCl)_2$	$Fe(CpBr)_2$	$Fe(CpCl)_2$ [a]
$e_{2g}(d)$		**1**	6.85	7.02	7.21	7.17	7.03
$a_{1g}(d)$		**2**	7.21	7.38	7.58	7.54	7.37
	b_u	**3**		8.72	8.75	8.65	8.71
$e_{1u}(\pi)$			8.72				
	a_u	**4**		9.09	9.16	9.06	9.09
			9.17				
$e_{1g}(\pi)$		**5**	9.38	9.50	9.63	9.57	9.49
in-plane *p*(Cl,Br)		**6**		10.98	11.08	10.46	10.98
out-of-plane *p*(Cl,Br)		**7**		11.47	11.55	11.09	11.44
out-of-plane *p*(Cl)		**8**			11.87		

[a] Ref 1.

The band shapes of $e_{1u}(\pi)$ and $e_{1g}(\pi)$ ligand ionizations are strongly influenced by the ring substitution. The two-fold degeneracy of $e_{1u}(\pi)$ and $e_{1g}(\pi)$ levels is removed by substitution, and each level is split into two components (a_g–b_g, a_u–b_u in the C_{2h} point group). Only three well resolved bands (3, 4 and 5) are observed in the spectra (Fig. 2). The $b_u(\pi)$ and $a_g(\pi)$ orbitals have non-zero p_z atomic orbital coefficients at the point of substitution. These orbitals can be destabilized by the conjugative interaction with the out-of-plane halogen p orbital. The $a_u(\pi)$ and $b_g(\pi)$ orbitals, having a node at the point of substitution, remain uninfluenced by the conjugative interaction. In ferrocene itself the $e_{1g}(\pi)$ level is located below the $e_{1u}(\pi)$ level. Therefore we have assigned the band **3** to the $b_u(\pi)$ orbital. The **4**/**3** intensity ratio is approximately 1 in chloroferrocenes and less than 1 in 1,1′-dibromoferrocene. The assignment of the middle band **4** to overlapping ionizations of $e_{1u}(\pi)$ and $e_{1g}(\pi)$ level components thus seems unreasonable and we have assigned the band **4** to the $a_u(\pi)$ orbital only. The remaining band **5** is assigned to the a_g,b_g components of the $e_{1g}(\pi)$ level in which the metal d orbitals participate. A similar absence of the splitting of the degenerate ligand π levels which involve participation of the central atom orbitals was observed recently in the He(I) PE spectra of $U(\eta\text{-}C_8H_8)_2$ derivatives [7].

Sharp intense bands located in the 10 to 12 eV region are absent from the spectrum of the parent ferrocene. These bands arise from ionizations involving

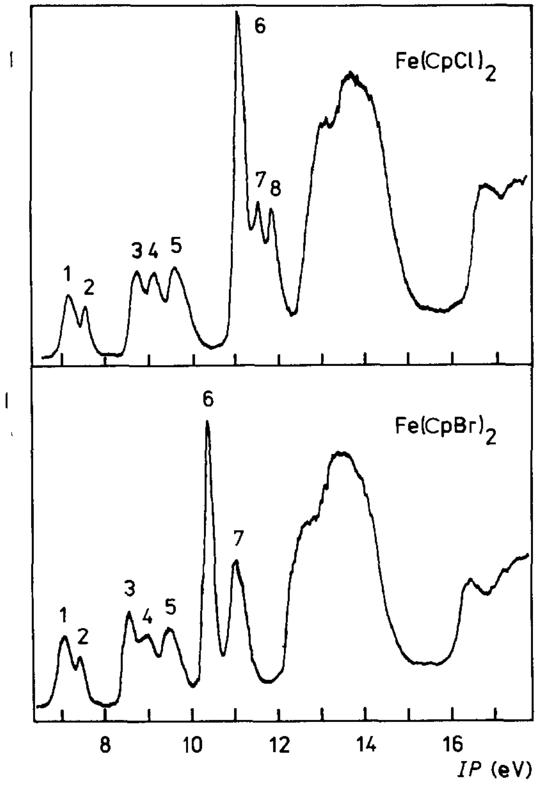

Fig. 2. He(I) photoelectron spectra of 1,1′-dichloroferrocene and 1,1′-dibromoferrocene.

non-bonding *p* orbitals of halogens. In the chloroferrocene spectrum the two non-bonding *p*(Cl) orbitals belong to the two bands **6** and **7**. By analogy with interpretations of the spectra of the halogenobenzenes [8] we have assigned the narrower band **6** to the in-plane *p*(Cl) orbital and the band **7** to the out-of-plane *p*(Cl) orbital which is stabilized by the conjugative interaction with π orbitals.

In the 1,1′-dichloroferrocene spectrum three bands (**6**, **7** and **8**) are present in this region. The band **7** is very near to the *IP* for the chloroferrocene out-of-plane *p*(Cl) orbital. The band **7** intensity was constant over the range 70 to 210 °C. We thus conclude that the band **7** comes from 1,1′-dichloroferrocene.

Evans and coworkers [1] describe only two bands in the Cl-ionization region in the spectrum of 1,1′-dichloroferrocene with *IP*'s of 10.98 and 11.44 eV. Our experiments, however, show three bands in this region for 1,1′-dichloroferrocene, and our *IP*'s for chloroferrocene agree well with those observed by Evans et al. [1] (see Table 1). We thus conclude that the spectrum described by Evans et al. is not that of 1,1′-dichloroferrocene but that of chloroferrocene.

The *IP* of the band **6** is very near to the in-plane *p*(Cl) orbital *IP* of chloroferrocene. The in-plane *p*(Cl) orbitals overlap to a negligible extent in any conformation and are orthogonal to the cyclopentadienyl π orbitals, which play a dominant role in the metal–ligand bonding interaction. It is thus unreasonable to assume that the in-plane *p*(Cl) orbitals can be split by the through-space or through-bond interactions. We have therefore assigned the band **6** to both the symmetrical and antisymmetrical in-plane *p*(Cl) orbitals combinations. The remaining bands **7** and **8** may then be assigned to the out-of-plane *p*(Cl) orbitals. The splitting of these two bands may stem from the fact that the out-of-plane *p*(Cl) orbitals are partly delocalized over the cyclopentadienyl ligand. The combination of the out-of-plane *p*(Cl) orbitals, possessing the proper symmetry (a_g in the C_{2h} point group), can be stabilized by interaction with the *d* orbitals of the same symmetry. This combination is assigned to band **8**. The b_u combination cannot be stabilized by the *d* orbital interaction for symmetry reasons and it is assigned to band **7**. The fact that the separation between bands **6** and **7** in dichloroferrocene is the same as that in chloroferrocene supports this interpretation. Only two bands, **6** and **7**, belonging to the *p*(Br) orbitals are observed in the 1,1′-dibromoferrocene spectrum. The band **6** is assigned to the in-plane *p*(Br) orbitals by analogy with the chloro compound. The out-of-plane *p*(Br) orbitals give rise to a single broad band **7**. In 1,1′-dibromoferrocene the interaction with *d* orbitals is probably weaker, and band **7** is broadened rather than split.

Alternatively the difference between the out-of-plane halogen *p* orbital spectral patterns for 1,1′-dichloro- and 1,1′-dibromoferrocene could be rationalized by taking account of the difference between their rotational barriers [8]. One of the bands **7** or **8** could belong to a conformation of 1,1′-dichloroferrocene which is less favourable in 1,1′-dibromoferrocene. The differences in relative energies of conformers, revealed by the temperature dependence of the dipole moments are low (0.67 kJ mol^{-1} for 1,1′-dichloroferrocene and 2.59 kJ mol^{-1} for 1,1′-dibromoferrocene). The relative proportions of the conformers should be temperature dependent but the spectral band shapes and the relative intensities of the ionizations of the out-of-plane *p*(Cl) and *p*(Br) orbitals do not change with temperature.

Thus interaction with *d* orbitals is the more plausible explanation of the observed splitting of the out-of-plane *p*(Cl) orbitals. This interaction can also be viewed as a through-bond interaction with the a_g component of the $e_{1g}(\pi)$ level acting as a "relay orbital".

The halogen out-of-plane-in-plane *p* orbital splitting can be a measure of the out-of-plane *p*-orbital conjugation with cyclopentadienyl π-orbitals. Compared to halogenobenzenes (0.37 eV Cl, 0.58 eV Br) halogenoferrocenes exhibit greater splitting, implying stronger conjugation. The $e_{1u}(\pi)$ level splitting, which is smaller than the analogous π orbital splitting in halogenobenzenes (0.59 eV Cl, 0.63 eV Br), could, on the other hand, point to a weaker conjugative interaction in halogenoferrocenes. With regard to the absence of the splitting of the $e_{1g}(\pi)$ level by the ring substitution, the smaller $e_{1u}(\pi)$ level splitting may be evidence for non-negligible participation of central atom *p* orbitals in this level.

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References

1 S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard and C.F. Pygall, J. Chem. Soc., Farad. Trans II, 68 (1972) 1847.
2 C. Cauletti, J.C. Green, R.M. Kelly, P. Powell, J. van Tilborg, J. Robbins and J. Smart, J. Electron. Spectrosc. Relat. Phenom., 19 (1980) 327.
3 H.D. Martin and B. Mayer, Angew. Chem., 95 (1983) 281.
4 A.N. Nesmeyanov, V.A. Sazonova and V.N. Drozd, Dokl. Akad. Nauk SSSR, 126 (1959) 1004.
5 L.D. Smithson, A.K. Bhattacharya and F.L. Hedberg, Org. Mass Spectrom., 4 (1970) 383.
6 J. Spilners and J.G. Larson, Org. Mass Spectrom., 3 (1970) 915.
7 G. Bruno, E. Ciliberto, R.D. Fischer, I. Fragala and A.W. Spiegl, Organometallics, 1 (1982) 1060.
8 A.W. Potts, M.L. Lyus, E.P.F. Lee and G.H. Fattahalah, J. Chem. Soc. Farad. Trans II, 76 (1980) 556.
9 S. Sorriso, G. Cardacci and S.M. Murgia, J. Organomet. Chem., 44 (1972) 181.