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Photoelectron Spectra of Biferrocenylene and Biferrocene

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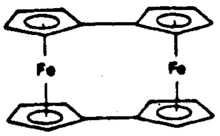
Biferrocenylene (**1**), biferrocene (**2**), and the various charged ions derived from **1** and **2** have found increasing interest in recent years from both experimental[2] and theoretical[3] points of view. The experimental data available indicate a difference between **1** and **2** insofar as in $\mathbf{1}^+$ there is a considerable interaction between the two iron sites while in $\mathbf{2}^+$ both Fe atoms have integral oxidation states leading to a formal $\mathrm{Fe^{II},Fe^{III}}$ system with trapped valences.[4] In order to contribute to the discussion concerning the bonding in **1** and **2**, we have recorded the He I photoelectron (PE) spectra of **1** and **2**. This measurement provides direct insight into the various hole states of $\mathbf{1}^+$ and $\mathbf{2}^+$.[5]



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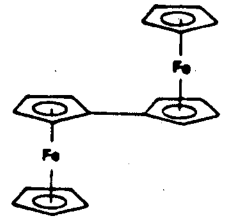

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Due to large relaxation effects in transition-metal compounds[6] (breakdown of Koopmans' theorem[7]), we performed calculations on the various hole states of $\mathbf{1}^+$ and $\mathbf{2}^+$ by using the ΔSCF[8] and the TOM[9] procedures[10] on the basis of a recently developed INDO method for organometallic compounds.[5]

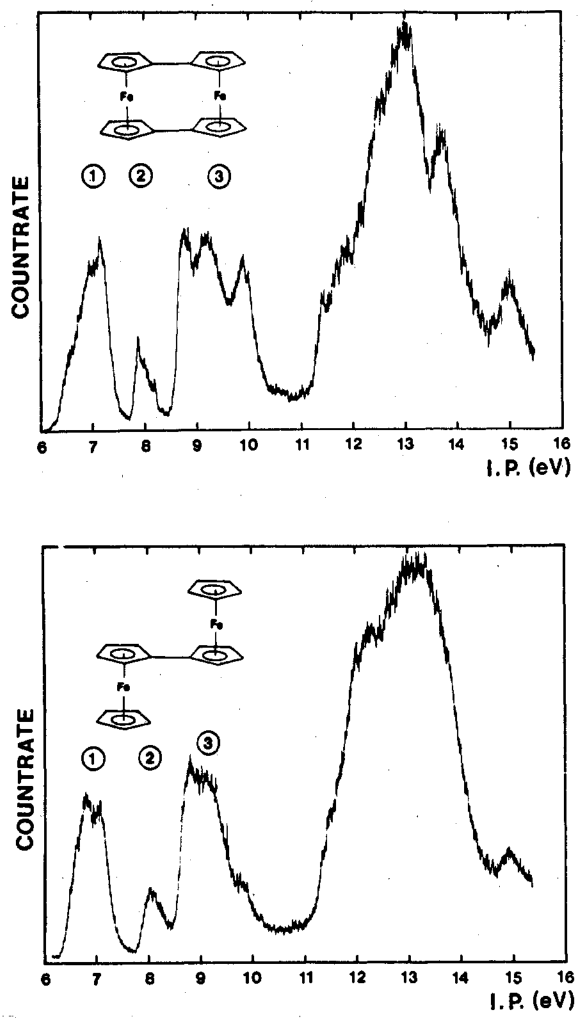

Figure 1. PE spectra of **1** and **2**.

In Figure 1 the PE spectra of **1** and **2** are displayed.[11] By comparison with the PE spectrum of ferrocene[12] it is evident that the first band in both spectra corresponds to ionization events from the six MO's with mainly 3d character (see Table I), mainly the g and u combinations of $3d_{z^2}$, $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals. Inspection of Table I shows the anticipated considerable electronic relaxation in the radical cation. The experimental values are only reproduced satisfactorily if the ΔSCF and TOM calculations were performed without the restriction that the Fe 3d MO's should be symmetry adapted. Both model calculations lead to localized Fe 3d hole states, meaning that the electron has been removed from one of the two iron sites of the molecule. Similar results have been found for the 1s hole states of O_2^+[13] and N_2^+.[14] In all cases it is computed that the relaxation energy of a localized hole contributes twice as much as that of a delocalized one.[15] The

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(10) Both methods of calculation reproduce satisfactorily the PE bands of ferrocene.[12] Experimental: 6.88 (e_{2g}), 7.23 (a_{1g}), 8.72 (e_{1u}), 9.38 (e_{1g}). ΔSCF: 7.85 (a_{1g}), 8.48 (e_{2g}), 9.27 (e_{1u}), 10.41 (e_{1g}). TOM: 6.27 (a_{1g}), 7.08 (e_{2g}), 8.88 (e_{1u}), 10.06 (e_{1g}).

(11) The He I PE spectra were recorded on a PS18 spectrometer of Perkin-Elmer. Both samples were heated to a temperature of 140 °C. The spectra were calibrated with argon, and a resolution of about 25 meV on the argon line was obtained.

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Table I. Observed and Calculated Vertical Ionization Potentials of Biferrocenylene (**1**) and Biferrocene (**2**) (All Values in eV)

peak	$I_{V,J}$	assignt		MO type/dominant contribn[b]	$(-\epsilon_J)I_{V,J}^K$	$I_{V,J}^{\Delta SCF}$		$I_{V,J}^{TOM}$	
		MO	no.			deloc	loc	deloc	loc
				Biferrocenylene					
1	6.55_{sh}	$8b_{3u}$	51	$d_{z^2} - d'_{z^2}$	10.97	9.43	7.83	8.71	6.10
		$9a_g$	49	$d_{z^2} + d'_{z^2}$	11.14	9.47	7.83	8.96	6.10
	7.0_{max}	$5b_{1g}$	46	$d_{xy} + d'_{xy}$	11.34	9.97	8.29	9.25	6.92
		$7b_{3u}$	45	$d_{x^2-y^2} - d'_{x^2-y^2}$	11.42	9.40	8.12	8.48	6.70
	7.1_{max}	$5b_{2u}$	44	$d_{xy} - d'_{xy}$	11.48	9.91	8.29	9.21	6.92
		$8a_g$	42	$d_{x^2-y^2} + d'_{x^2-y^2}$	11.63	9.80	8.12	8.12	6.70
2	7.85	$9b_{3u}$	56	F_π	8.88	8.51	*a*	8.30	*a*
3	8.8_{max}	$6b_{1g}$	55	F_π	10.05	9.74		9.74	
		$6b_{2u}$	54	F_π	10.25	9.94		9.94	
		$10a_g$	52	F_π/Fe $3d_{z^2}$	10.79	9.99		9.28	
	9.1_{max}	$7b_{2g}$	53	F_π/Fe d_{xz}	10.63	10.09		9.92	
		$5a_u$	50	F_π/Fe d_{yz}	11.09	10.84		10.69	
		$5b_{3g}$	48	F_π/Fe d_{yz}	11.22	10.91		10.78	
	9.9_{max}	$8b_{1u}$	47	F_π/Fe d_{xz}	11.33	11.18		11.02	
		$6b_{2g}$	43	F_π	11.61	11.41		11.37	
				Biferrocene					
1	6.6_{sh}	$17a_g$	53	$d_{z^2} + d'_{z^2}$	10.76	9.24	7.68	8.46	6.16
		$16b_u$	52	$d_{z^2} - d'_{z^2}$	10.84	9.44	7.68	8.58	6.16
	6.8	$15b_u$	48	$d_{x^2-y^2} - d'_{x^2-y^2}$	11.30	9.81	8.33	8.90	6.94
	7.1	$9a_g$	47	$d_{xy} + d'_{xy}$	11.32	9.80	*a*	9.09	*a*
		$15a_g$	46	$d_{x^2-y^2} + d'_{x^2-y^2}$	11.33	9.49	8.33	8.91	6.94
		$9a_u$	45	$d_{xy} - d'_{xy}$	11.36	9.80	*a*	9.08	*a*
2	8.0	$18a_g$	57	F_π	9.36	8.87		8.71	
3		$11a_u$	56	F_π/Cp_π	10.09	9.74		9.80	
	8.8_{max}	$11b_g$	55	F_π/Cp_π	10.21	9.91		9.94	
		$17b_u$	54	Cp_π	10.47	10.18		10.14	
		$16a_g$	51	Cp_π/Fe $3d_{xz}$	11.05	10.68		10.44	
	9.2_{max}	$10b_g$	50	$F_\pi/Cp_\pi/3d_{yz}$	11.17	10.82		10.65	
		$10a_u$	49	$F_\pi/Cp_\pi/3d_{yz}$	11.21	10.84		10.73	
	9.8_{sh}	$14b_u$	44	$F_\pi/3d_{x^2-y^2}/3d_{xz}$	11.50	10.64		10.36	

[a] The ΔSCF and TOM procedures did not converge into localized hole states within the $3d_{xy}$ pair. [b] F ≡ fulvalenyl ligand; Cp ≡ cyclopentadienyl ligand.

remaining peaks below 11 eV in both spectra correspond to ionization events from orbitals with dominant ligand character. The second band in both spectra arises from the ionization of the highest occupied orbital (HOMO) of **1** and **2**, $9b_{3u}$ and $18a_g$, respectively. This orbital is closely related to the b_{2g} (HOMO) of fulvalene and is absent in ferrocene. A comparison of the intensity of band 3 with that of band 2 suggests[18] that there are eight ionization processes in **1** and seven in **2**. The first two maxima of band 3 in the case of **1** are assigned as due to the ionization out of $6b_{1g}$, $6b_{2u}$, $5a_u$, and $5b_{3g}$. These linear combinations are related to the ferrocene e_{1u} and e_{1g} orbitals. In **2** band 3 is not resolved. Our calculation predicts that relaxation effects for the latter ionization events are only of minor importance.

Our model calculations on the ground state of **1** and **2** suggest that the highest occupied molecular orbitals of **1** and **2** are levels with dominant ligand character. The most stable cation, however, is generated by removing an electron from a 3d level, due to the large rearrangement effects discussed before. This result, which is consistent with our PE measurements, contradicts a recent study on $\mathbf{2}^+$. On the basis of a Mössbauer spectroscopic investigation on $\mathbf{2}^+$, it was concluded[19] that the unpaired electron of $\mathbf{2}^+$ is predominantly housed in a ligand orbital.

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(15) The hole-state nature of $\mathbf{1}^+$ and $\mathbf{2}^+$ is due to the fact that metal–metal interaction is small as a result of the large separation between the two Fe centers (3.90 Å in **1**,[16] 5.08 Å in **2**[17]). The larger Fe–Fe distance in **2** compared with that in **1** reduces the energy gap between the Fe 3d g/u pairs by a factor of 2–3. Consequently a faster hole exchange between the two iron sites in **1** compared with that in **2** is to be expected.

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Synthesis and Properties of (Triphenylphosphine)pentacarbonylvanadium(0), $V(CO)_5Ph_3P$

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Reactions of hexacarbonylvanadium with triphenylphosphine are known to be very solvent dependent.[1] Thus, $V(CO)_6$ and triphenylphosphine in diethyl ether yield the disproportionation product[2] shown in eq 1, while the same

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(1) For a review on $V(CO)_6$ chemistry see J. E. Ellis, *J. Organomet. Chem.*, **86**, 1 (1975).

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