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Molecular Orbital Calculations on Transition Metal Complexes Part VII

Ground State and Low Energy Ionisations of Manganocene

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INDO SCF Molecular Orbital Calculations have been made for manganocene ($MnCp_2$), its molecular cation ($MnCp_2^+$) and the ferricenium ion $FeCp_2^+$. The computations yield a high spin $^6A_{1g}$ ($e_{2g}^2 a_{1g}^1 e_{1g}^2$) ground state for $MnCp_2$, contrary to that which was assumed to interpret the photoelectron spectrum. The lowest energy ionisations from the $^6A_{1g}$ state have been obtained by differences in total energies of the ion and the neutral molecule. These are in very good agreement with the experimental values. The use of the eigen-values of the neutral molecule to obtain ionisation energies (Koopmans' Theorem) is shown to be inappropriate due to the considerable electronic redistribution which accompanies the formation of the molecular ion from the neutral molecule. The main factor which influences this charge rearrangement is found to be the covalency within the $e_{1g}(d_{xz}, d_{yz})$ orbitals.

Key word: Manganocene

1. Introduction

Manganocene is anomalous among first row transition metallocenes in that hydrolysis and metal replacement are extremely facile and for this reason it has long been considered to be an ionic compound of the Mn^{2+} ion, analogous with sodium cyclopentadienide [2]. The magnetic moment of 5.94 B.M. [3] and the near isotropic g-value of 2.00 [4] are consistent with the formulation of a high spin complex with ground state $^6A_{1g}$ (e_{2g}^2, a_{1g}^1, e_{1g}^2) and in this respect manganocene is unique. All other transition metallocenes are low spin [5]. In view of the fact that the Mn^{II} ion is at the lower end of the spectro chemical series for metal ions and since exchange between electrons is at a maximum with the d^5 (sextet) configuration it is not altogether surprising that manganocene is high spin.

Recently photoelectron spectra have been reported for some first row transition metallocenes including that of manganocene [6]. Despite the fact that the isoelectronic ferricenium ion is known to have the low spin $^2E_{2g}$ ground state [7, 8], the spectrum was interpreted in terms of a low spin $^2A_{1g}$ ground state. Although there have been numerous molecular orbital calculations performed on ferrocene [5, 8–12] and some other first row metallocenes there have been none such as yet for manganocene. Presented below are results of INDO SCF calculations for manganocene and the isoelectronic ferricenium ion.

2. Method

Calculations have been performed under INDO type approximations using the unrestricted Hartree-Fock formalism. Hamiltonian matrix elements and fuller details of the method are given in Ref. [1]. In view of the findings of Beveridge and Dobosh [13] and because the expectation values of S^2 for the INDO wavefunctions reported below do not differ significantly ($<1\%$) from the $S(S+1)$ value the results for manganocene and the ferricinium ion are given without annihilation.

The difference between the well used CNDO method and the INDO approximation lies in the inclusion of the one-centre exchange integrals $(\mu\nu|\mu\nu)$. The retention of these exchange terms makes possible a separation of the different spin configurations arising from the same orbital occupation. Moreover the factors which govern the high spin – low spin behaviour for transition metal complexes involve the orbital energy separation Δ, and the pairing energy of electrons P, which includes increased coulomb repulsion concomitant with pairing electrons in addition to the loss of exchange energy between parallel spins. Thus molecular orbital calculations at the INDO level are in principle able to compare the energies of the high and low spin states of a complex.

Wave functions and total energies have been computed for manganocene, its molecular cation and the ferricenium ion in a number of different electronic configurations. A total of 59 single Slater type orbitals have been included in the basis set for the complexes; H $1s$ (1.2), C $2s/2p$ (1.625), Mn $3d$ (2.60) $4s/4p$ (1.36), and Fe $3d$ (2.722) $4s/4p$ (1.37). Fiftyseven valence electrons are considered for manganocene and the ferricenium ion, with one less for the manganocene ion.

3. Results

Manganocene is reported [14] to have a metal-ring separation of 2.05 Å; this does however seem to be extremely large compared with that found for nickelocene and cobaltocene. Calculations run at this distance and at the shorter distances of 1.95 Å and 1.83 Å produce a high state ${}^6A_{1g}(e_{2g}^2 a_{1g}^1 e_{1g}^2)$ which is more stable than either of the low spin states ${}^2A_{1g}(e_{2g}^4 a_{1g}^1)$ or ${}^2E_{2g}(e_{2g}^3 a_{1g}^2)$. At the larger distance the ${}^6A_{1g}$ state lies lower than the ${}^2E_{2g}$ configuration by 2.55 eV with the ${}^2A_{1g}$ state 1.61 eV higher still. As the bond distance is decreased the separation between the high and low spin forms decreased as expected so that at a metal-ring distance of 1.73 Å the ${}^2E_{2g}$ state becomes the ground state. The minimum in energy for the two states occurs at metal-carbon separation of 2.07 Å and 2.16 Å for the ${}^2E_{2g}$ and ${}^6A_{1g}$ states respectively, with the high spin state being only marginally more favoured energetically by 0.004 a.u.[1]

In contrast the isoelectronic ferricenium ion is known [7, 8] to possess a low spin ${}^2E_{2g}(a_{1g}^2 e_{2g}^3)$ ground state. Although the metal-ring distance is not known

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[1] Since the submission of this paper a more detailed account of the spectra of manganocene and dimethyl manganocene has been reported [16]. Additional low intensity peaks in the low energy region of the photoelectron spectrum have been interpreted in terms of a high spin – low spin equilibrium in these two complexes. In view of the fact that the calculations indicate that the ${}^6A_{1g}$ and ${}^2E_{2g}$ states have equilibrium energies which differ by only $\sim 800\,\text{cm}^{-1}$ a thermal equilibrium between high and low spin states is certainly possible on the present results.

for this ion it is not expected to differ significantly from that of ferrocene since the ion is formed by removal of an electron from an essentially non-bonding or only slightly bonding orbital of ferrocene. Calculations for this complex ion using two metal-ring distances either side of that in ferrocene (1.60 Å and 1.75 Å) yielded the low spin $^2E_{2g}$ state as ground state in both cases, the calculated energy separation between high and low spin forms being 3.58 eV and 1.10 eV at 1.60 Å and 1.75 Å respectively. The other low spin configuration $^2A_{1g}(e_{2g}^4a_{1g}^1)$ was calculated to lie at higher energy than the $^2E_{2g}$ state in both cases. The present calculations therefore satisfactorily account for the high spin ground state for manganocene with the ferricenium ion low spin.

4. Ionisation and Orbital Levels

In their interpretation of the photoelectron spectrum of manganocene Rabelais *et al.* [6] considered ionic states arising only from the low spin configurations $^2A_{1g}$, $^2E_{2g}$ and concluded that the former had a lower energy. The spectrum was therefore interpreted in terms of a $^2A_{1g}$ configuration ionising to the $^1A_{1g}$, $^1E_{2g}$, $^3E_{2g}$, $^1E_{1g}$, $^3E_{1g}$, $^1E_{1u}$, and $^3E_{1u}$ levels of the magnanocene cation. Recent ligand field calculations for d^4 metallocenes [15] suggest that neither of the above ground states is compatible with the observed photoelectron spectrum. Moreover if the first poorly resolved photoelectron band at 6.8 eV is not comprised of several electronic states the spectrum may be interpreted in terms of a high spin $^6A_{1g}$ ground state.

The energies and symmetries of the highest filled orbital levels of manganocene are given in Table 1. The negative value of these should according to Koopman's Theorem correspond to the lowest ionisation energies. Coutière *et al.* [9] have found that the sequence of orbital energies does not necessarily correspond to the ordering of ionisation levels for the ferrocene molecule, particularly when electronic rearrangement in the ionised molecule is significant. Total energies for manganocene and its molecular ion in a number of electronic states are given in Table 2. Differences between the molecular ion energies and the $^6A_{1g}$ ground state of manganocene are also included in Table 2. In this case the ordering of the eigen-values for the neutral molecule again does not correspond exactly to the same sequence of ionisations energies obtained by differences in total energies of the molecule and its ion. The calculated energy of the first photoelectron band

Table 1. Molecular orbital energy levels for manganocene

Symmetry	Energy (eV)
e_{1g} (d)	− 8.10
e_{1g} (ligand $\sigma + \pi$)	−10.99
a_{1g} (d)	−13.44
e_{2g} (d)	−13.96
e_{1u} (ligand π)	−14.42
e_{1u} (ligand σ)	−16.00
e_{2u} (ligand σ)	−16.18

Table 2. Total energies (eV) for manganocene and its ion

$MnCp_2$		Energy	$\Delta E(MnCp_2^+ - MnCp_2, {}^6A_{1g})$	Experimental ionisation energy (eV)
	${}^2E_{2g}$	−2495.18		
	${}^2A_{1g}$	−2493.57		
	${}^6A_{1g}$	−2497.73		
$MnCp_2^+$				
	${}^3E_{2g}$	−2489.14		
	${}^1A_{1g}$	−2488.34		
	${}^5E_{1g}$	−2490.19	7.5	6.8
	${}^5A_{1g}$	−2487.18	10.5	
	${}^7E_{1g}$	−2487.04	10.7	7.9–9.3
	${}^5E_{2g}$	−2486.56	11.2	
	${}^7E_{1u}$	−2483.50	14.2	12.2, 13.3

$({}^6A_{1g} \rightarrow {}^5E_{1g})$ agrees extremely well with that observed. In addition the results suggest that the second broader and more intense band between 7.9 and 9.3 eV is composed of three overlapping bands corresponding to ionisation of both 3*d* (a_{1g} and e_{2g}) and ligand (e_{1g}) electrons, all of which are calculated to lie very close in energy. The higher energy bands were previously assumed to arise from ionisation to states formed by loss of an electron from orbitals which were mainly ligand in character. This interpretation is substantiated by the present calculations where ionisation to the configuration $e_{1u}^1 e_{2g}^2 a_{1g}^1 e_{1g}^2$ (${}^7E_{1u}$) is calculated to occur at 14.2 eV. It should be noted that ionisation to the ${}^3E_{2g}$ and ${}^1A_{1g}$ states of $MnCp_2^+$ is not allowed from ${}^6A_{1g}$ $MnCp_2$. The agreement between computed and experimental ionisation energies is therefore most satisfactory not only for those ionisations involving *d*-electrons but also for the "ligand" ionisations. Thus the MO results suggest that the photoelectron spectrum may be interpreted in terms of a high-spin $MnCp_2$, a conclusion also reached by Warren [15] using ligand-field arguments. The ground state of $MnCp_2^+$ is in fact calculated to be ${}^3E_{2g}$ although at the manganese-carbon distance (2.3 Å) used for the results given in Table 2 the high spin ${}^5E_{1g}$ is lower in energy than either ${}^3E_{2g}$ or the ${}^1A_{1g}$ states.

5. Covalency and Charge Distribution

The $e_{1g}(d_{xz}, d_{yz})$ orbital is found to be the most covalent within the set of *d*-type orbitals. The $a_{1g}(d_{z^2})$ and the $e_{2g}(d_{xy}, d_{x^2-y^2})$ have metal contributions which vary from between 0.94 and 0.98 for the range of metal-ring distances considered, while the highest e_{1g} orbital possesses between 45% and 70% metal 3*d* character for the same range of distances. This covalency within the e_{1g} orbital plays a large part in determining the resultant electronic distribution of both manganocene and its molecular ion. The breakdown of the 3*d* electron densities for $MnCp_2$ and for different states of $MnCp_2^+$ are shown in Table 3. The computed 4*s* and 4*p* populations are almost identical for all cases given in Table 3. When an electron is ionised from a ligand orbital the covalency within the e_{1g} orbital is virtually unchanged from its value in the neutral molecule; thus the overall metal charge

Table 3. *d* electron densities for manganocene and its ion

	e_{2g}	a_{1g}	e_{1g}	Total
$MnCp_2$				
$^6A_{1g}(e_{2g}^2 a_{1g}^1 e_{1g}^2)$	1.986	0.997	2.174	5.157
$MnCp_2^+$				
$^7E_{1u}(e_{1u}^3 e_{2g}^2 a_{1g}^1 e_{1g}^2)$	1.986	0.997	2.197	5.180
$^7E_{1g}(e_{1g}^3 e_{2g}^2 a_{1g}^1 e_{1g}^2)$	1.988	0.999	2.110	5.097
$^5E_{1g}(e_{2g}^2 a_{1g}^1 e_{1g}^1)$	1.994	1.003	1.897	4.894
$^5A_{1g}(e_{2g}^2 a_{1g}^0 e_{1g}^2)$	1.996	0.035	2.692	4.723
$^5E_{2g}(e_{2g}^1 a_{1g}^1 e_{1g}^2)$	1.007	1.006	2.674	4.687
$^1A_{1g}(e_{2g}^4 a_{1g}^0 e_{1g}^0)$	3.956	0.031	0.984	4.971
$^3E_{2g}(e_{2g}^3 a_{1g}^1 e_{1g}^0)$	2.976	0.943	1.003	4.922

also remains unaltered. However when an electron is lost from an orbital which is essentially metal 3*d* the electronic charges may differ quite substantially. For example if the electron is removed from the e_{1g} orbital the increased covalency within this orbital draws more electron density onto the metal through the bonding e_{1g} orbitals in both the α- and β-spin orbitals, and therefore the resultant *d*-electron densities are only slightly less than in the neutral molecule (cases $^5E_{1g}$, $^1A_{1g}$ and $^3E_{2g}$ in Table 3). On the other hand since the a_{1g} and e_{2g} orbitals are considerably less covalent than the e_{1g} orbital the ions formed by the loss of an electron from either of these two orbitals have a significantly smaller amount of *d*-electron density residing on the metal (cases $^5A_{1g}$ and $^5E_{2g}$ Table 3). This is because the α-spin e_{1g} orbitals, both bonding *and* antibonding, are already filled and no increase in covalency can lead to any further shift of electronic charge onto the manganese. This charge rearrangement accompanying the formation of $MnCp_2^+$ from $MnCp_2$ clearly accounts for the differences in the ionisation energies calculated by Koopmans' Theorem and by total energy differences. The greatest difference is seen to occur for ionisation of a_{1g} and e_{2g} electrons, and these two states, $^5A_{1g}$ and $^5E_{2g}$, undergo the largest rearrangement of charge upon ionisation. The charge redistribution is seen to be less significant for e_{1g} ionisation and smaller still for ligand ionisation. A similar observation was noted for the a_{1g}, e_{2g} and ligand ionisations of ferrocene [9].

6. Conclusion

These computations suggest that manganocene possesses a high spin $^6A_{1g}$ ground state and not a low spin $^2A_{1g}$ configuration as was previously assumed [9]. The other doublet state $^2E_{2g}$ is calculated to be the first excited state. Calculations for the molecular cation, $MnCp_2^+$, have been used to obtain ionisation energies which agree very closely with the experimental values. The lowest energy bands in the photoelectron spectrum correspond to ionisation of essentially 3*d* electrons. It is shown that Koopmans' Theorem does not hold for this molecule due to the charge redistribution in the molecular ion.

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