

Journal of Organometallic Chemistry, 116 (1976) C41—C44
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Preliminary communication

MOLECULAR ORBITAL CALCULATIONS ON TRANSITION METAL COMPLEXES

XIV*. ELECTRONIC STRUCTURE OF CHROMOCENE

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(Received June 4th, 1976)

Summary

Equilibrium energy calculations for chromocene using an INDO MO method show that the ground state is ${}^3E_{2g}$ and not ${}^3A_{2g}$ as a recent report using CNDO calculations has indicated, and computed transferred spin densities provide further support for the ${}^3E_{2g}$ ground state.

Introduction

Interest in the critical aspects of metallocenes has been stimulated recently by application of photo-electron spectroscopic [1,2] and single crystal electron spin resonance techniques [3,4] together with ligand field studies [5] aimed towards establishing the ground state electronic configurations in first row transition metal cyclopentadienyl complexes. For species which are, or are close to, axially symmetric there has only ever been any real controversy over the ground states of those complexes which possess either four or five *d*-electrons. Thus chromocene (d^4) may plausibly exist in either of the low spin states ${}^3E_{2g} - e_{2g}^3 a_{1g}^1$ or ${}^3A_{2g} - e_{2g}^2 a_{1g}^2$, or the high spin configuration ${}^5E_{1g} - e_{2g}^2 a_{1g}^1 e_{1g}^1$, while the possibilities are ${}^2A_{1g} - e_{2g}^4 a_{1g}^1$, ${}^2E_{2g} - e_{2g}^3 a_{1g}^2$ (low spin) or ${}^6A_{1g} - e_{2g}^2 a_{1g}^1 e_{1g}^2$ (high spin) for manganocene and the ferricenium ion.

The situation in manganocene has only recently been resolved by photo-electron [1] and ESR [3] spectroscopic studies and theoretical calculations [6] which all indicate that manganocene lies very close to the high spin—low spin crossover point, with the ${}^6A_{1g}$ state marginally favoured over the ${}^2E_{2g}$ configuration in the “free” state. On the other hand magnetic studies [7], PES data [1] and ligand field calculations [5] clearly show that chromocene

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possesses a ${}^3E_{2g}$ electronic ground state. However, recent CNDO type calculations [8] for chromocene have yielded a ${}^3A_{2g}$ ground state, and the PE spectrum was reassigned on this basis.

We now present some INDO MO results for chromocene which produce the correct ground state configuration from an energetic standpoint and which show that the ${}^3A_{2g}$ state cannot constitute the ground state on the basis of spin transfer considerations.

Experimental

The calculational procedure follows the intermediate neglect of differential overlap scheme given in reference 9.

Results

We have examined the total energies of four electronic states of chromocene as a function of the Cr—C distance and find that the ${}^3E_{2g}$, ${}^3A_{2g}$ and ${}^1A_{1g} - e_{2g}^4$ states have similar energy profiles, with ${}^3E_{2g}$ more stable than the other states by 0.73 eV and 0.93 eV, respectively. The ${}^1A_{1g}$ state is calculated to lie closer to the ground state ${}^3E_{2g}$ than is indicated by the ligand field analysis [5], and we believe this to be due to the greater covalency in the e_{2g} molecular orbital compared with the a_{1g} molecular orbital, which effectively reduces $d-d$ electronic repulsions. In fact the isoelectronic $[V(C_7H_7)(C_5H_5)]^+$ ion is diamagnetic [10], and presumably does have a ${}^1A_{1g}$ ground state.

The minimum energy of the ${}^3E_{2g}$ state corresponds to a Cr—C separation of 2.15 Å, which compares very well with the recent electron diffraction measurement of Haaland (2.169 Å) [11]. An earlier structural determination [12] indicated a Cr—C distance of 2.22 Å, and although the CNDO calculations [8] were run at this distance and produced a ${}^3A_{2g}$ ground state our INDO calculations at this distance show that the high spin ${}^5E_{1g}$ state has lowest energy. This finding is in essential agreement with the ligand field diagram [5] which indicates a crossover from ${}^3E_{2g}$ to ${}^5E_{1g}$ as Dt/B is reduced. The difference in the equilibrium energies of these two states is calculated to be 0.98 eV.

Although the energy of the ${}^5E_{1g}$ level was not given in the paper by Perkins et al. [8] it is unlikely that CNDO calculations, which neglect $d-d$ exchange terms, could produce a correct crossover of this type. Thus their CNDO calculations resulted in a low spin ${}^2E_{2g}$ ground state for manganocene while our INDO results have correctly yielded a high spin ${}^6A_{1g}$ state [6].

It is interesting to examine the factors that determine which of the two low spin states lies lowest in chromocene (d^4) and ferricenium ion (d^5). The former prefers e_{2g} occupation, ${}^3E_{2g}$ rather than ${}^3A_{2g}$, while ferricenium ion favours a_{1g} occupation, ${}^2E_{2g}$ as opposed to ${}^2A_{1g}$. In both complexes electronic repulsion terms favour full a_{1g} occupancy i.e. ${}^3A_{2g}$ for chromocene and ${}^2E_{2g}$ for ferricenium, and it is therefore the magnitude of $\Delta_1(e_{2g} - a_{1g}$ splitting) relative to these two-electron terms which decides which ground state occurs. For chromocene if $\Delta_1 > 8B$ the E_{2g} state lies lower while for ferricenium if $\Delta_1 < 20B$ then the ground state becomes ${}^2E_{2g}$. Our calculations show that Δ_1 is about 0.9 eV in chromocene and around 1.1 eV for ferricenium. If the

estimated B values of $\sim 500 \text{ cm}^{-1}$ are used the experimentally observed ground states are reproduced in both cases.

Our results for chromocene molecular ion are in broad agreement with those of Perkins [8] in that the ground state is found to be ${}^4A_{2g}$ with ${}^2E_{2g} - e_{2g}^3$ lying $\sim 3 \text{ eV}$ higher in energy. This ground state has already been assigned for the complex $[\text{Cr}(\text{C}_5\text{H}_5)_2]^+\text{I}^-$ [13]. These ion levels therefore support Orchard's [1] assignment of the PE spectrum of chromocene rather than that of Rabalais et al. [2] who assumed that the first PE band corresponds to ionisation to the ${}^2E_{2g}$ state. It should be pointed out that although the CNDO calculations appear to show reasonable agreement with the PE spectrum, ionisation to some of the molecular ion states given are not allowed to occur from the supposed ${}^3A_{2g}$ state of chromocene. Although we cannot give a complete set of ionised states, since this requires a CI calculation, transitions to states which are single determinantal functions are calculated to occur at 4.75 eV (${}^4A_{2g}$) and 7.40 eV ${}^2E_{2g}$. Bands are observed at 5.71, 7.04, 7.30 and 7.58 eV. Ionisations from the highest ligand orbitals are calculated to lie at 11.5 eV and 14.1 eV.

Finally, ${}^{13}\text{C}$ and ${}^1\text{H}$ NMR shifts can be used to obtain the spin transfer coefficients to the carbon $2s$ and hydrogen $1s$ orbitals of the cyclopentadienyl rings, and Table 1 lists experimental [14,15] and calculated values for the ${}^3E_{2g}$ and ${}^3A_{2g}$ states of chromocene. The agreement in both sign and magnitude between the experimental spin transfer values and those calculated for the ${}^3E_{2g}$ state is extremely good.

TABLE 1
TRANSFERRED SPIN DENSITIES IN CHROMOCENE (%)

Calculated	Experimental		
	${}^3A_{2g}$	${}^3E_{2g}$	
C 2s	-0.04	-0.10	-0.07
H 1s	-0.12	+0.52	+0.49

The results show that the large positive value at the protons arises by direct delocalisation via the open-shell a_{1g} molecular orbital as has also been indicated by extended Huckel calculations [14]. In view of the fact that the carbon $2s$ orbitals are but little involved in the open-shell orbitals, the negative spin densities must occur in these orbitals as a result of exchange polarisation.

It is clear that the observed positive spin density at the protons requires single occupancy of the a_{1g} molecular orbital, and these results confirm the ${}^3E_{2g}$ ground state for chromocene.

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