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Abstract

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THE ELECTRONIC STRUCTURE OF THE FERRICINIUM CATION AND OTHER AROMATIC METAL COMPLEXES

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In previous works we calculated the molecular orbitals (M.O.) of a number of aromatic metal complexes: $(C_5H_5)_2Fe$, $(C_6H_6)_2Cr$, $(C_5H_5)_2Co^+$, and $(C_5H_5)_2Cr$ (^{1,2}). In the present work we have calculated, by the same method and in the same approximations, the M.O. of the ferricinium cation. The form of the M.O. and their energies are given in Table 1. In addition to $(C_5H_5)_2Fe^+$, a calculation was made of the M.O. of the cation $(C_6H_6)_2Cr^+$, but in this calculation we were unable to make a reliable choice between the configurations

$$(a_{1g})^2(a_{1u})^2(e_{1g})^4(e_{1u})^4(e_{2g})^4(a'_{1g})^1 \quad \text{and} \quad \ldots(a'_{1g})^2(e_{2g})^3,$$

although we consider the first to be more probable. However, in both cases the resulting distribution of electron density is approximately the same (charge +1.4 atomic units on the Cr atom and −0.2 on each benzene ring),

Table 1

Molecular orbitals of $(C_5H_5)_2Fe^+$ *and their energies*

Symmetry	Bonding M.O., type of orbital	Bonding M.O., energy, eV	Antibonding M.O., energy, eV	Symmetry	Bonding M.O., type of orbital	Bonding M.O., energy, eV	Antibonding M.O., energy, eV
a_{1g}	$0.87a_{1g}+0.49s$	-22.34	-7.78	e_{1u}	$0.80e_{1u}+0.60p_x$	-18.83	-4.76
a'_{1g}	d_{z^2}	-15.92		e_{2g}	$0.35e_{2g}+0.94d_{x^2-y^2}$	-15.18	-2.01
e_{1u}	$0.99a_{1u}+0.09p_z$	-20.00	-6.45	e_{2u}	–	–	-3.00
e_{1g}	$0.89e_{1g}+0.45d_{xz}$	-17.66	-1.60				

as is also the energy of the highest occupied level, which determines the ionization potential of the cation (the second ionization potential of the dibenzenechromium molecule), ~ 11-12 eV. We also attempted a self-consistent calculation of the molecules $(C_5H_5)_2Co$ and $(C_5H_5)_2V$. In the first of these cases we started from the results of a previously performed calculation of the M.O. of the cobalticinium cation, assuming that the extra electron in the neutral molecule occupies the lowest free level of the cation (symmetry a''_{1g}), consisting mainly of the Co 4*s*-orbital. However, we did not carry out a complete self-consistency of the resulting M.O. because of the great difficulties connected with the fact that $(C_5H_5)_2Co$ is a radical with one unpaired electron located in an antibonding orbital. Therefore we confined ourselves to estimating effective charges. We encountered greater difficulties in the case of the vanadicene molecule $(C_5H_5)_2V$, containing three unpaired electrons, where we likewise established only the electronic configuration of the molecule $\ldots(e_{2g})^2(a'_{1g})^1$ and confined ourselves to estimating effective charges.

Table 2 gives the results of calculations of the effective charges on the central atoms and on the rings in all the molecules considered in the present and preceding papers.

From the results presented one may draw the following conclusions. The distribution of electron density in the cations, as compared with the corresponding neutral molecules, corresponds to removal of an electron from the rings, since the effective charge of the central atom in all the cations is close to the charge in the neutral molecules*. Especially indicative are the most reliable data for ferrocene (charge on Fe +0.7, on the rings −0.35 each) and the ferricinium cation of ferricinium (on Fe +0.6, on the rings +0.2 each). This result is consistent with experimental data showing that, whereas ferrocene (with a negative charge on the rings) is characterized by electrophilic substitution reactions, in the case

Table 2

Effective charges in aromatic metal complexes

Molecule	Effective charges on the central atom	Effective charges in both rings	Effective charges in one ring	Molecule	Effective charges on the central atom	Effective charges in both rings	Effective charges in one ring
$(C_5H_5)_2V$	~ +1.0	~ −1.0	~ −0.5	$(C_5H_5)_2Co$	~ +0.2	~ −0.2	~ −0.1
$(C_5H_5)_2Cr$	+1.7	−1.7	−0.85	$(C_5H_5)_2Co^+$	−0.1	+1.1	+0.55
$(C_5H_5)_2Fe$	+0.7	−0.7	−0.35	$(C_6H_6)_2Cr$	+1.5	~ −1.5	~ −0.75
$(C_5H_5)_2Fe^+$	+0.6	+0.4	+0.2	$(C_6H_6)_2Cr^+$	~ +1.4	~ −0.4	~ −0.2

of the ferricinium cation (with a small positive charge in the rings) nucleophilic substitution reactions are characteristic and electrophilic substitution reactions do not occur (A. N. Nesmeyanov and E. G. Perevalova—unpublished). In the cation $(C_6H_6)_2Cr^+$, according to the calculation, the positive charge is concentrated on the central atom, while the rings bear a small negative charge. This negative charge is considerably smaller than in dibenzenechromium, so that the transition from $(C_6H_6)_2Cr$ to the cation should be accompanied by a weakening of the tendency toward electrophilic substitution. The high electron density in the rings in ferrocene and dibenzenechromium molecules agrees, as we have already indicated (1), with the aromatic character of these complexes. The presence of a large π-electron density is also manifested in the fact that ferrocene, like benzene, forms molecular compounds with electron acceptors (4). It is interesting that the dibenzenechromium cation also forms a complex with $AlCl_3$ (5). Apparently, although the electron density in the rings in the cation is lowered in comparison with neutral dibenzenechromium, it is nevertheless greater than, for example, in the benzene molecule. We have already noted earlier (3) that the cobalticinium cation with a positive charge on the rings is inert toward electrophilic substitution reactions. From the results for the neutral cobalticene molecule it follows that in this case both the central atom and the rings are almost electroneutral, so that, unlike the $(C_5H_5)_2Co$ cation, it should be capable of electrophilic substitution reactions, although possibly to a lesser extent than ferrocene.

The data presented in Table 2 show that, for neutral bis-cyclopentadienyl compounds, the effective positive charge on the central atom in the neutral molecules $(C_5H_5)M$ (Z) increases at the beginning of the transition period, in accordance with the strengthening of the ionic character on going from vanadicene to chromocene (6). This tendency reaches its completion in the case of $(C_5H_5)_2Mn$, which, as is known, is an ionic compound with charge +2 on the central atom, as indicated by the presence of 5 unpaired electrons. Further addi—

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* This result was obtained not simply by considering the removal of an electron from ring orbitals, but by a complete calculation in which removal of an electron from the molecular orbital of the whole complex was taken into account, followed by self-consistency of the M.O. for the cation.

···of the electrons leads to a sharp weakening of the ionic character in ferrocene and, especially, in cobalticene. We also note that the effective charge on V in $(C_5H_5)_2V$ is somewhat greater than on Fe in ferrocene, which is consistent with the more ionic character of the former molecule (^{6}). The course of the charges is presented in Fig. 1.

The results of the calculation of the self-consistent electronic configuration of the ferricinium cation show that the initial valence state of Fe^+ must be $d_{z^2}^2 d_{x^2-y^2}^2 d_{xy} d_{xz} d_{yz}$, with a valence-state energy of $4.5F_2 + 30F_4 + 6$ kcal for excitation of the configuration, i.e., only 33 kcal in all, and not 58 kcal, as we found earlier (7) under the assumption that the initial valence state is $d_{z^2}^2 d_{x^2-y^2}^2 d_{xy}^2 d_{xz} d_{yz}$. It may be supposed that the initial valence state of the ruthenocinium cation should be the same; its energy, by our estimate, is ~ 18 kcal, i.e., only 15 kcal less than for ferricinium. On the other hand, as was shown earlier, the difference in the energies of the valence states of the central atoms in ferrocene and ruthenocene reaches 75 kcal. Therefore, if ruthenocene is more stable than ferrocene owing to the significantly smaller expenditure of energy for excitation of the valence state, then in the case of the ferricinium and ruthenocinium cations (where this difference is much smaller) one should expect a decrease in the difference in stability in comparison with the neutral molecules.

Fig. 1

Note added in proof. A paper by Robertson and McConnell (9) has recently appeared, giving a table of magnetic moments of aromatic metal complexes. It follows from it that the complexes can be divided into two groups: 1) with the purely spin value of the magnetic moment and 2) with an increased magnetic moment, in comparison with the purely spin value. The authors believe that deviations of the magnetic moment of the molecule from its purely spin value are associated with an asymmetric filling by electrons of MOs of the e_{2g} type, which include AOs $3d_{\pm 2}$. Under this assumption, the results of our calculations agree with the experimental data for all compounds considered by us. In addition, Robertson and McConnell found that true orbital degeneracy of the ground state can occur only in the ferricinium cation $Fe(C_5H_5)_2^+$, which also agrees with the results of our calculations.

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Note: Figure translations are in progress. See original paper for figures.