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Relationes

The Electronic State of Butadiene Bonded to an Iron Tricarbonyl Residue

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A theoretical study of tricarbonylbutadieneiron by the all valence electron SCFMO method is presented.

The charge distribution on the butadiene group in the complex appears to correspond to a mixture of excited electronic states of the free molecule and this is found to be consistent both with the experimental geometry of the molecule and its reactions. The charge distribution shows that the iron atom assumes a negative charge in the complex and that this arises from the carbonyl carbon atoms. The bonding pattern of the molecule involves mainly the π electronic levels of butadiene, although the σ set are also somewhat perturbed. When the Fe-diene distance is increased, the excited electronic states are retained in the organic moiety.

Introduction

It is well known that unsaturated organic compounds bonded to transition metals exhibit a different pattern of reactivity to that in the free state, and that this is due to the involvement of the electrons of the organic group with the transition metal [3]. It has further been suggested that, when oxygen or carbon disulphide acts as ligand, the molecules are constrained in excited states [9]. It is clearly, therefore, of great interest to investigate the electronic states in which organic molecules are combined in organometallic compounds so as to be able to predict in what way the reactivity of the organic group will be affected by the transition metal. It is also important to determine whether, on cleavage, the transient organic moiety will exist in the same or some other electronic state, since this will also affect the mode by which it subsequently reacts.

A simple but important compound of this type is tricarbonylbutadieneiron and in this case, Mason [8] has suggested that the butadiene molecule is here constrained in an excited state. In order to study this point in more depth, we have investigated the electronic structure of tricarbonylbutadieneiron so as to illuminate the nature of the electronic state of the combined butadiene. Furthermore, in order to simulate replacement of the butadiene by incoming groups, a second feature which has been investigated is the change in electronic structure of the butadiene when it is gradually withdrawn from the $Fe(CO)_3$ entity.

In carrying out the calculations we have employed throughout a modification of the all-electron SCMO method [6, 7]. The required parameters for the $4s$, $4p$ and $3d$ orbitals of iron (i.e., core Hamiltonian matrix elements and one-centre electron repulsion integrals) were taken from previous work [2, 7] (an independent check of these quantities in the present work did not lead to any significant changes). The parameters for iron, therefore, had the values I_{4s} 7.07; I_{4p} 3.72; I_{3d} 8.68 eV. The one-centre electron repulsion integrals, were given a single value for each atom which was the arithmetic mean of the values for $s-s$ and $d-d$ repulsion; for iron this parameter had the value 12.3 eV. The parameters for carbon, hydrogen and oxygen have been published previously [7]. The bond lengths and angles for the molecules were abstracted from the structural work of Mills and Robinson [10] and all calculations were carried out on the Strathclyde University ICL 1905 Computer.

Results and Discussion

a) Butadiene States

In tricarbonylbutadieneiron the butadiene moiety apparently assumes the *cis* configuration [10] and so, as a first step, the electronic structure of free *cis* butadiene, valence σ electrons included, was calculated. The lower excited states, improved by including interaction between nine excited configurations, were also calculated. The basic calculational scheme involved was closely similar to that used for vinylboranes by Armstrong and Perkins [1]. The eigenvectors of the configuration interaction matrix allow determination of the distribution of electronic charge in all the excited states and this is of crucial importance for comparison with the calculated charge distribution in the combined ligand. The ordering and nature of the first few bonding and antibonding orbitals are illustrated in Fig. 1.

The lowest excited singlet state is due to a $\sigma \rightarrow \pi^*$ transition stemming from the configuration Ψ_1^{-1}. Both for this and the other low-energy $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ transitions the singlet and triplet states have the same energy, since the exchange integral between ground and excited states vanishes by symmetry. Transitions from the ground state to these excited states are of $^{1,3}A_2$ or $^{1,3}B_2$ symmetry and attainment of the former type is formally space-forbidden.

States generated by $\pi - \pi^*$ transitions are allowed and polarised along the long or short axes of the molecule respectively. The energies of these states (symmetries $^1A_1$, $^1B_1$) have been calculated frequently previously [11] and good agreement with experiment has been attained. What is important in the present

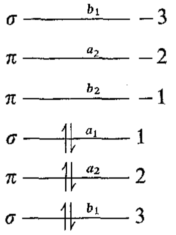
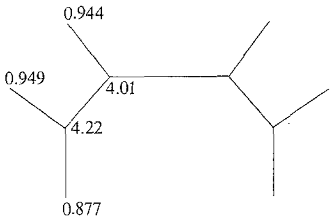


Fig. 1. Orbitals for free butadiene

context is the one-electron orbital sequence for butadiene and the way in which this is perturbed by attachment of an $Fe(CO)_3$ moiety. We now consider the correlation of butadiene states with those of the complex.

b) Tricarbonylbutadieneiron

The charge distribution on the atoms in π complexed butadiene is



If we use the orbitals of free butadiene and generate the charge distribution in the nine excited configurations $\Psi_n^{-m}(n, m = 1, 2, 3)$ of the molecule, then there are two pure excited states which correspond to the above distribution. These are Ψ_1^{-2}, $\sigma - \pi^*$; and Ψ_2^{-1}, $\pi \rightarrow \pi^*$. The first gives rise to an excited state of A_2 symmetry whilst the last corresponds to a B_1 state. It is difficult to distinguish between these and, indeed, the charge distribution over the C atoms in these excited states is rather similar to that in the ground state of the molecule. An examination of the eigenvectors of the highest bonding orbital of the complex shows, however, that it is the *first* excited π^* orbital which becomes partially occupied in the complex. This particular orbital has b_2 symmetry in free butadiene and it possesses nodes between carbon atoms 1,2 and 3,4 but is bonding between atoms 2 and 3. It should be stressed that this orbital only becomes partially occupied in combined butadiene ($\sim 0.3\,e$) whilst the rest of the overall complex molecular orbital contains large contributions from the orbitals of the CO groups.

Further examination of the eigenvectors for the adduct shows that the origin of this "excited" electron density cannot be clearly assigned: thus, the "butadiene part" in both the second and third bonding orbitals (which stem from the first two bonding orbitals of free butadiene) exhibits a loss of electron density compared with the occupancy in the free ligand. However, the loss is greatest from the original butadiene a_2 orbital.

The situation is further complicated by a switching of electron density from the exclusively π orbitals of butadiene to the σ set on lowering the symmetry to C_s in the complex. This shows that the σ levels are involved in the bonding of the ligands to the $Fe(CO)_3$ residue: in fact there is no single butadiene level which remains unperturbed by complex formation.

Hence we consider that to assign the complexed butadiene to a *single* excited state of the free species would be a gross oversimplification of the real situation.

However the entity does seem to bear a resemblance to both A_2 and B_1 states of the molecule. What is most important is that the free butadiene b_2 antibonding orbital does become partially occupied and certain properties associated with the form of that orbital should be manifest.

Table. *Charge distribution in tricarbonylbutadieneiron*

	s	*p*	*d*	*Total*
Fe	1.096	0.816	6.537	8.449
O	1.378	4.652	—	6.030
Carbonyl carbon	1.066	2.817	—	3.883
butadiene carbons (1,4)	0.986	3.234	—	4.220
carbons (2,3)	0.839	3.168	—	4.007
Terminal hydrogens				
H_1, H_2	0.949, 0.877	—	—	0.949, 0.877
H_3	0.944	—	—	0.944

The latter point seems consistent with the known properties of combined butadiene:

(i) the near identity of the C–C bonds [10] and their actual lengths (1.45 Å) is in keeping with the antibonding π character introduced in the 1,2 and the bonding π character introduced in the 2,3 bonds, respectively. The generality of this phenomenon has yet to be established but it is noteworthy that the complex of $Fe(CO)_3$ with sorbic acid shows a similar lengthening and decrease of the equivalent internuclear distances [4].

(ii) the susceptibility of the carbon atoms towards electrophilic attack is the same as that of the free hydrocarbon and occurs at the 1,4 positions. There is also, of course, a second factor which helps bring this about i.e., the allyl transition state for the 1,4 substitution is energetically more favoured than that for 2,3 substitution and indeed, a Friedel-Crafts allyl intermediate has been isolated [5].

(iii) the inertness of combined butadiene in the Diels-Alder reaction is consistent with the removal of electrons from the periphery to the central region of the molecule.

It is of great interest, and of potential importance, that the combined butadiene incorporates contributions from excited A_2 states of the free molecule. Under C_{2V} symmetry the translational degrees of freedom transform like the A_1, B_1 and B_2 representations. Hence in *cis* butadiene, electronic excitations are space-allowed to A_1, B_1, and B_2 states of the molecule. It seems therefore that the A_2 states, unattainable by interaction with dipole radiation from the ground state, are attained at least partially in a fixed form in butadiene complexed to $Fe(CO)_3$. This type of result is potentially important for a number of compounds which will form complexes with transition metals.

The rest of the charge distribution over the atoms is shown in the table. It is interesting that the iron atom carries a negative charge whilst the carbonyl groups are polarised in the $\overset{\delta^+}{C}$–$\overset{0}{O}$ sense. Thus, the electron density on the iron atoms seems to be almost wholly drawn from the C atoms of the carbonyl groups.

c) Removal of Butadiene

It is of interest to enquire to what extent the occupation of the excited states persists when the Fe-butadiene distance is increased in the complex. Since this simulates removal of the moiety, it should give a guide as to what the reactivity of the molecule released from the complex would be before relaxation to the ground state. A series of calculations was therefore performed in which the Fe-butadiene-plane distance was varied from 0.16 nm to 0.21 nm in steps of 0.01 nm.

The results can be summarised briefly as follows: firstly, the total electronic charge on the carbon atoms is virtually unchanged by the perturbation due to elongation of the Fe-butadiene distance. Secondly, examination of the contributions to the highest bonding orbitals of the distorted complex reveals that the same antibonding orbital of butadiene that becomes occupied in the molecule at equilibrium distance also remains occupied as the moiety is removed from the $Fe(CO)_3$ unit. Furthermore, the number of electrons associated with the butadiene remains at 22. This means that we should expect separation of the molecule into two neutral entities and that the butadiene should be in an excited state.

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