The Edward Davies Chemical Laboratories, University College of Wales ,Aberystwyth (U. K.)

The Stability of Silver-Olefine Complexes

By

W. H. Prichard and W. J. Orville-Thomas

Molecular orbital calculations are carried out which throw some light on the factors determining the electron densities of the double-bonds in 3- and 4-alkylcyclopentenes. The results support Dewar's views on the structure of silver-olefine complexes since the compounds with higher 'double-bond' electron densities form complexes of greater stability.

Es werden Rechnungen nach der MO-Methode für 3- und 4-Alkylcyclopentene mit dem Ziel durchgeführt, Aufschlüsse über die Faktoren zu gewinnen, welche die Elektronendichte an den Doppelbindungen bestimmen. Die Resultate stehen im Einklang mit den Vorstellungen Dewar's über Silber-Olefin-Komplexe, da diejenigen Komplexe stabiler sind, deren Liganden eine größere Elektronendichte an der Doppelbindung aufweisen.

Nous avons effectué des calculs d'orbitales moléculaires qui donnent de renseignements sur la densité électronique dans la liaison double des 3- et 4-alcyl-cyclopentènes. Les résultats renforcent l'avis de Dewar sur la structure des complexes argent-alcène, car les composés à plus haute densité électronique dans la double liaison forment des complexes plus stables.

Compounds possessing a double-bond form complexes with metal ions such as Ag^+. A number of possible explanations including the influence of steric factors [1], the extent to which conjugation occurs [27], participation of the olefine anti-bonding π-orbital [9], and ring strain [25], have been put forward to account for the relative stabilities of these compounds.

The differing stabilities of silver complexes have been used as a basis for the separation of the isomeric cyclohexenes [11] and alkylcyclopentenes [24] using gasliquid partition chromatographic techniques. During this work by a comparison of retention volumes of olefins of similar boiling point it was shown that the silver complexes formed by the 4-alkylcyclopentenes, were more stable than those formed by the 3-alkylcyclopentenes.

For these compounds no conjugation of double bonds exists and the rings are free from strain [8]. In addition the side-chain groups R are relatively far from the double bonds and so steric factors should not greatly affect the stability of the complexes. These series are ideal then to test Dewar's model [9]. In this paper some molecular orbital (MO) calculations on cyclopentenes are reported. They throw some light on the factors which determine the electron densities of the double bonds and hence influence the stabilities of the metal-olefine complexes.

Method of Calculation

Two factors can be expected to influence the electronic density (bond order) of the double bond in 3-alkylcyclopentenes (Fig. 1a) as compared with 4-alkylcyclopentenes (Fig. 1b).

They are (i) hyperconjugation,

and (ii) the difference in the values of the Coulomb integrals of atoms 1 and 2′ owing to their differing electronegativities.

1. Effect of Hyperconjugation. If it is assumed that the ring carbons are co-planar the methylene hydrogen atoms are above and below this plane. With these configurations hyperconjugation of the ordinary 'sacrificial' type [18] can occur between the π-electrons of the double-bond and the quasi- $C = H_2$ double-bonds (Fig. 2).

Fig. 1a u. b
3- and 4-alkylcyclopentenes

The distribution of π-electrons is indicated in Fig. 2c and d.

Using the LCAO approximation the general MO for the system shown in Fig. 2a is:

$$\psi = c_1 \varphi_1 + c_2 \varphi_2 + c_3 \varphi_3 + c_4 \varphi_4$$

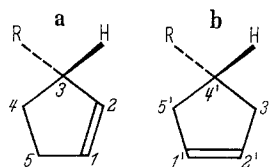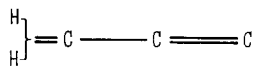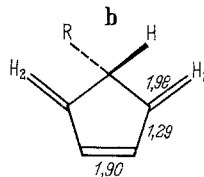where φ_1 is a π-type atomic orbital (AO) of the composite hydrogen group and $\varphi_2 \ldots \varphi_4$ are $C : 2p\,\pi$ AO's.
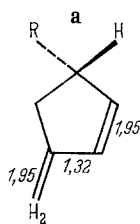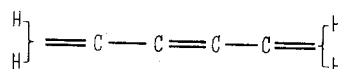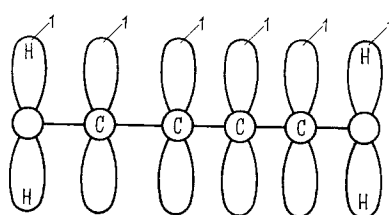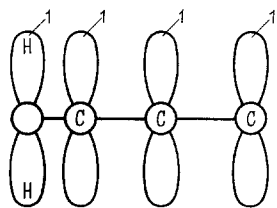

Fig. 2a—d. Hyperconjugation in Cyclopentenes

The fourth order secular determinantal equation, was obtained by standard procedures [6, 19], and solved by using the following parameters suggested by Coulson and Crawford [5] and by I'Haya [15]

$$\alpha\,(C) = \alpha \qquad \beta\,(CC) = \beta$$
$$\alpha\,(H_2) = \alpha - 0.3\,\beta \qquad \beta\,(C = H_2) = \beta\,.$$

The values of the normalized coefficients appropriate to the filled molecular

orbitals were used to calculate the bond orders* (using Coulson's definition [4]) given in Fig. 2a. A similar calculation led to the values given in Fig. 2b.

2. Effect of Electronegativity on Coulomb Integrals. Let us consider the atoms involved in the double bonds. Carbon atoms, 1, 1' and 2' are in similar environments since they are immediately adjacent to methylene groups. Hence their effective electronegativities, χ, and therefore their Coulomb integrals, α, are sensibly equal [23, 26]. Atom 2, however, is in a different environment since it is adjacent to a carbon attached not to a methylene group but to a carbon attached to three other carbons and one hydrogen atom.

Gordy [12] has used nuclear quadrupole coupling data to show that for XY_4 molecules as the electronegativity of the substituents Y increases so does the effective electronegativity of the central atom. Consequently a consideration of the nature and relative numbers of the attached atoms shows that $\chi\,(C_3) > \chi\,(C_{3'})$. This means that C_3 will have a greater power to draw electrons to itself and hence using Gordy's argument a stage further, it is reasonable to infer that $\chi\,(2) > \chi\,(2')$. This difference in electronegativity will be mirrored in differing values for the Coulomb integrals for these atoms and [23, 26]

$$\frac{\alpha\,(C_2)}{\alpha\,(C_{2'})} = \frac{\chi\,(C_2)}{\chi\,(C_{2'})}\ .$$

χ values for carbon in various environments [13] range from 2.3 to 2.8. The *maximum* ratio of Coulomb integrals is then

$$\frac{\alpha\,(C_2)}{\alpha\,(C_{2'})} = \frac{2.8}{2.3} = 1.218$$

and hence since $\alpha\,(C_{2'}) = \alpha\,(C_{1'}) = \alpha\,(C_1) = \alpha$,
$$\alpha\,(C_2) = 1.218\,\alpha\ .$$

If β/α is put equal to 0.54 [6] then $\alpha\,(C_2) = \alpha + 0.408\,\beta$; if we use the alternative value [23] $\beta/\alpha = 0.244$, $\alpha\,(C_2) = \alpha + 0.894\,\beta$. The extreme values are then $\alpha \leq \alpha\,(C_2) \leq \alpha + 0.894\,\beta$ $(\alpha + \delta\beta)$.

Using the LCAO approximation the π-type molecular orbital (MO) has the form

$$\Phi = a_1\,\varphi\,(C_1{:}2p) + a_2\,\varphi\,(C_2{:}2p)$$

where $\varphi\,(C{:}2p)$ represents a $2p$ π-type atomic orbital. The Pauling-Wheland procedure [21] leads to a determinantal equation, whose roots given by

$$E = \alpha + \frac{\beta}{2}\,(\delta \pm \sqrt{\delta^2 + 4}) \tag{1}$$

yield the energies of the allowed molecular orbitals. The two π-electrons possessed by the system suffice to fill the lowest energy bonding orbital [given by the plus sign in eq. (1)].

The values of the (normalized) coefficients a_1 and a_2 for various values of δ are given in the table, bond orders are also included.

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* The effect of taking the compression energies of the σ-bonds into consideration will not significantly alter the bond orders. For this reason and because it is doubtful (see Discussion) whether hyperconjugation is at all important in the ground state of these systems the 'compression' effect has been ignored.

When the Coulomb integrals have the same value ($\delta = 0$) the calculated bond order ($N = 2$) is that appropriate to both the 3-alkyl and 4-alkylcyclo-pentenes.

Table. *M. O. energies and coefficients*

δ	Energy	a_1	a_2	N
0	$\alpha + \beta$	0.707	0.707	2.00
0.4	$\alpha + 1.220\,\beta$	0.634	0.773	1.98
0.6	$\alpha + 1.344\,\beta$	0.597	0.802	1.96
0.8	$\alpha + 1.477\,\beta$	0.561	0.828	1.93
0.9	$\alpha + 1.547\,\beta$	0.543	0.840	1.91

Discussion

Olefines are amongst the most strongly trans-directing ligands [21]. DEWAR explains this in terms of the existence of (i) a σ-molecular orbital, ψ_1 formed by the overlap of the vacant Ag: $5s$ *atomic* orbital with the bonding π-*molecular* orbital, (Fig. 3a), and (ii) a π-molecular orbital, ψ_2, formed by overlapping of the Ag: $4d$ and the vacant anti-bonding $\pi^\star$-molecular orbital (Fig. 3b). Electrons to fill these composite molecules orbitals are donated by the π-bond (i) and a doubly occupied Ag: $4d$ orbital (ii) [9].

The nett bonding is therefore the sum of the σ- and π-bond contributions. Any factor that alters these components will show itself in a variation in the stabilities of the complexes.

Since the constituent orbitals are the same ψ_1 and ψ_2 do not change as we go from one complex in a closely related series to another. Since ψ_2 is filled by two Ag:$4d$ electrons there seems no reason to expect fluctuations in the bonding power of the 'complex' π-bond as the olefine changes. As we have seen there are, however, reasons for expecting differences in the electronic

Fig. 3a u. b. Bond formation in a Silver-Olefine complex. a formation of σ-bond, b formation of π-bond

structures of the donor π-bonds of the olefines and hence any variation in the stabilities of the complexes have to be explained on this basis.

One factor that could affect the olefine π-bond order is hyperconjugation. The concept of hyperconjugation was received a great deal of attention since its introduction in 1935 but recently the situation has become controversial [10]. A number of observations have been made which cannot be explained simply by hyperconjugation. RAO [22] has summarized the position by saying that *all* the physical evidence seems to rule out hyperconjugation in the *ground state*.

The results obtained in this study indicate that when the C $=$ C bond is hyperconjugated with one methylene group its order is 1.95; this falls to 1.90 when hyperconjugation involves two methylene groups. In each case the order of the
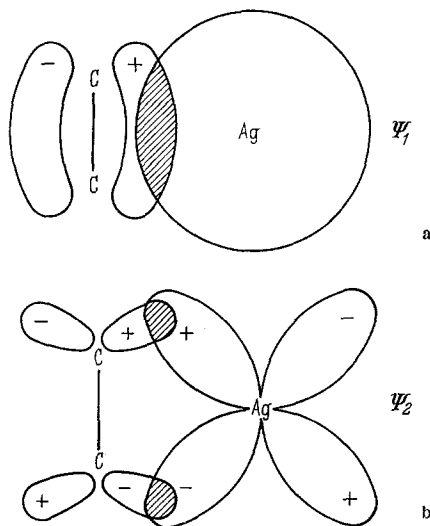
C — C bond situated between the C = C and C = H_2 groups increases to $\sim$ 1.3. In this connection it may be pointed out that hyperconjugation has never been considered to be as effective as ordinary conjugation in increasing the bond order of links lying between conjugated or hyperconjugated bonds. If we consider butadiene the semi-empirical Hückel theory [14] leads to values ranging from 1.325 to 1.45 for the bond order of the central bond. These are clearly overestimated and more refined treatments [2, 16, 17, 20] based on the LCAO-SCF (Self Consistent Field) and AIM (Atoms in Molecules) methods lead to values centred about 1.22. This value though considerably in excess of 1.0 (as indicated by the classical formula, H_2 C = CH — CH = CH_2) is still appreciably less then the values obtained for 'hyperconjugated' single bonds in this and other similar studies [19]. The bond orders calculated for the 1 — 5 and 1′ — 5′ bonds (Fig. 2), are extraordinarily high and completely unacceptable as being due merely to hyperconjugation. Our results therefore support Coulson's belief [7] that the 'standard' type of hyperconjugation calculation considerably exaggerates the degree of mobility of the electrons of the CH_2 groups, and that some improvement is the general theory is needed. Clearly the values recommended for Coulomb and resonance integrals for the pseudo-atom H_2 and the quasi-double bond H_2 = C are considerably in error. Until the discrepancy between the available physical evidence and the theoretical predictions is resolved it seems best to conclude that hyperconjugation is unimportant for molecules in the ground state. i. e., hyperconjugation is not expected to be a considerable factor in changing the orders of the 'double' bonds in the cyclopentenes.

This rejection of hyperconjugation as an important contributing factor leaves us with the effect of varying electronegativity on Coulomb integrals as a possible explanation for differences in the electronic structures of the double bonds.

An analysis of the data given in the table shows that the bond order of the 1′ — 2′ link in 4-alkylcyclopentenes is 2 (corresponding to δ = 0). The bond order of the corresponding bond in 3-alkylcyclopentenes however is always less 2 because of the effect of environment on Coulomb integrals (see section 2). For example for the maximum value of δ, N = 1.91 and hence the donor properties are less. Since the double-bonds are isolated and relatively far from the alkyl groups R conjugation is absent and steric factors should not affect the stability. It seems, then, that the increased stability of the Ag complex formed by the 4-cyclopentenes, as compared with the 3-cyclopentenes, is due to the higher bond order (and hence greater donor power) of the double-bond.

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