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ELECTROPHILICITY AND NUCLEOPHILICITY IN SINGLET CARBENES.

I. DEPENDENCE ON ELECTRONEGATIVITY.

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Abstract. Based on one-electron perturbation theory the electrophilic and nucleophilic reactivity of a singlet carbene :CX_2 depends (a) on the electronegativity of X and (b) on its position in the periodic table (first row versus second row).

The 1,2-addition of singlet methylene towards olefines can be viewed in terms of an orbital interaction diagram (Figure 1) as charge transfer of electron density from the bonding π-orbital of the olefine into the empty p-AO (type I) at the σ^2-methylene and vice versa from the σ-orbital into the π^*-orbital (type II). These interactions correspond to an electrophilic (type I) or nucleophilic (type II) attack by the methylene on the olefine[1].

In this communication we present a theoretical model which characterises the electrophilicity and nucleophilicity of singlet carbenes (σ^2-configuration) of the general type :CX_2 (X=F,Cl,OR etc.) on the basis of one-electron perturbation theory. Consider within the same interaction scheme (Figure 1) the substitution of :CH_2 by :CX_2. The π-type orbitals at X overlap with the p-AO at the central carbon. This gives rise to the three MO's φ_1 to φ_3.

(A) For the type I interaction the charge transfer from π to φ_3 (type I1) is now opposed by charge transfer from φ_1 to π^* (type I2). Hence, contrary to σ^2-methylene, the :CX_2 acts as an electrophilic (type I1) and nucleophilic (type I2) species towards the olefine and within the same approach path. According to one-electron perturbation theory without overlap[2] the total interaction energy is given by (1)

$$(1) \qquad \delta E = \delta E_{I1} + \delta E_{I2} = \frac{<\pi|H|\varphi_3>^2}{E(\varphi_3)-E_\pi} + \frac{<\pi^*|H|\varphi_1>^2}{E_{\pi^*}-E(\varphi_1)}$$

Figure 1.

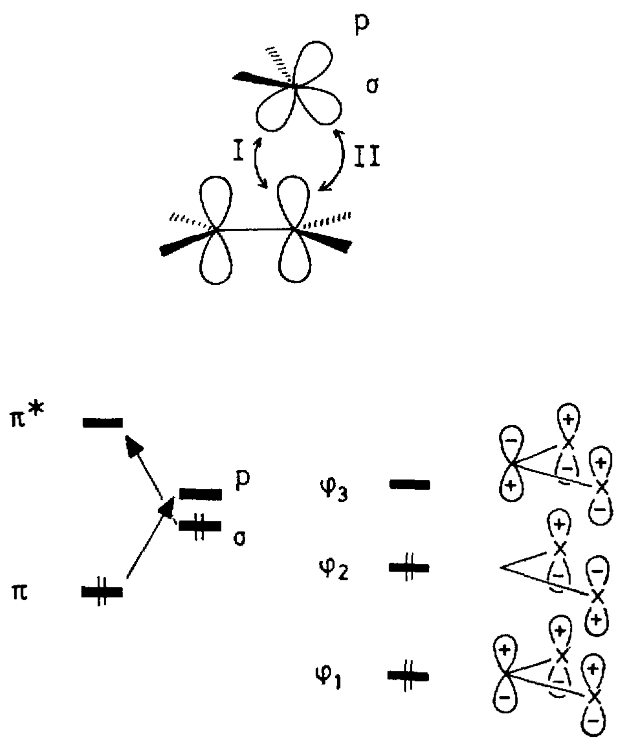
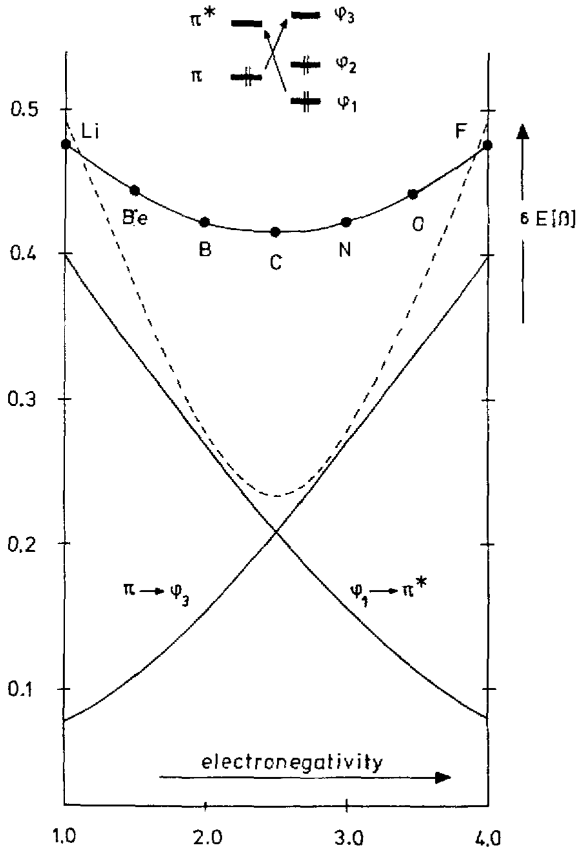


Figure 2.



In Hückel theory[3] the MO's φ_1 to φ_3 and their coefficients depend on the overlap integral ß ($ß=k_{CX}ß_o$) and on the coulomb integral α ($\alpha=\alpha_c+h_Xß_o$), where the latter can be related to the Pauling electronegativity of X. For a given olefine (ethylene) the interaction energies are the sum of two hyperbolic functions (Figure 2, solid lines). The following rules emerge:

(1) Providing overlap between C and X is the same, the interaction energy (δE in ß units) and hence the electrophilic reactivity of a singlet carbene is strongest if X is most electronegative[4].

(2) A change in the electronegativity of X affects the electrophilic reactivity more if X belongs to the second row of the periodic table rather than the first row (decreased overlap integral ß; the computed interaction energies for $ß=0.5ß_o$ are represented by the dashed line in Figure 2). This corresponds to a decrease in the internal mesomeric stabilization[5] of the singlet carbene (less favourable 2p-3p versus 2p-2p π-type overlap).

(B) The σ-orbital for the type II interaction is a hybrid of the s- and p-AO at the carbon and the symmetric combination φ of p-orbitals at X (Figure 3). The resulting bonding combination σ points out of the plane spanned by the atoms XCX, while the corresponding antibonding combination σ^* points into the plane. On this basis the orbital overlap of σ^* with π (of the olefine) is unfavourable for an electrophilic attack. The levelling of σ and hence its nucleophilicity is determined by two opposing factors: the interaction between s and φ raises while the interaction between p and φ lowers its energy. A change in the orbital energy of σ (and hence its nucleophilicity) is given by a first order perturbation[3] of the interacting orbitals, in (2)

(2) $$\delta E_\sigma = \delta E_\sigma(p,X) + \delta E_\sigma(s,X) + \delta E_\sigma(X)$$

On this basis, the following additional rules hold:

(3) Given the same overlap between the participating orbitals φ, p and s the energy of σ raises with decreasing electronegativity of X ($\delta E(p,X)=\delta E(s,X)=0$)

(4) As the electronegativity of X increases, the overlap between the orbitals s and φ dies off more rapidly than the overlap between p and φ[6]; this effect is even more pronounced in the 3p valence shell (second row of the periodic table) than in the 2p valence shell (first row of the periodic table).

Both tendencies exert an additive effect.

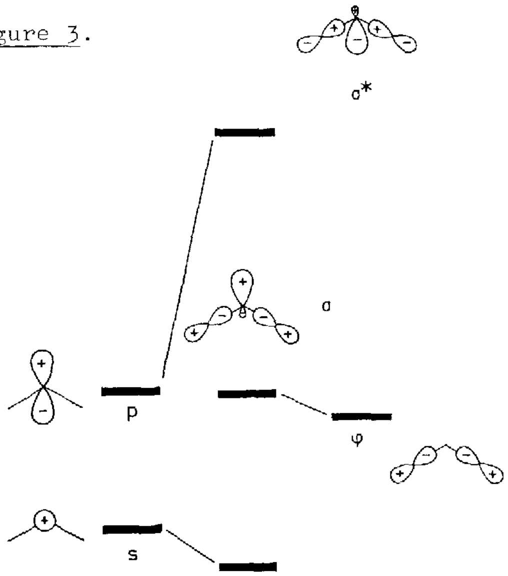
The trends in the Hückel energies for φ_1 to φ_3 and σ are supported by optimized ab initio calculations at a STO-3G level (Table 1, orbital energies in eV). They reveal that the $:C(SCH_3)_2$ carbene should possess the most nucleophilic σ-orbital. Although F is more electronegative than Cl, the σ-orbital in $:CF_2$ obtained is higher in energy than in $:CCl_2$. This is a consequence of decreasing destabilizing interaction between s and φ (case B4).

Table 1.

X in $:CX_2$	$\varepsilon(\varphi_1)$	$\varepsilon(\varphi_2)$	$\varepsilon(\varphi_3)$	$\varepsilon(\sigma)$
X=NH_2	-12.2	-8.8	10.3	-7.1
OH^a	-13.9	-10.8	8.3	-7.7
F	-16.5	-13.8	6.5	-9.3
Cl	-13.3	-11.9	3.2	-9.9
SH^a	-9.8	-7.6	7.0	-6.7
$SCH_3{}^a$	-9.2	-7.0	7.2	-6.4
$OCH_3{}^a$	-12.1	-9.7	8.2	-7.6

^{a}all-trans conformation

Figure 3.



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(4) For the computation of the interaction energies in Figure 2 the following Hückel parameters were assumed: (a) solid lines, $\beta=\beta_o$, (b) broken line $\beta=0.5\beta_o$; h_X defined by the Pauling electronegativity.

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