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SUBSTITUENT EFFECTS IN PHOTOCYCLOADDITION REACTIONS

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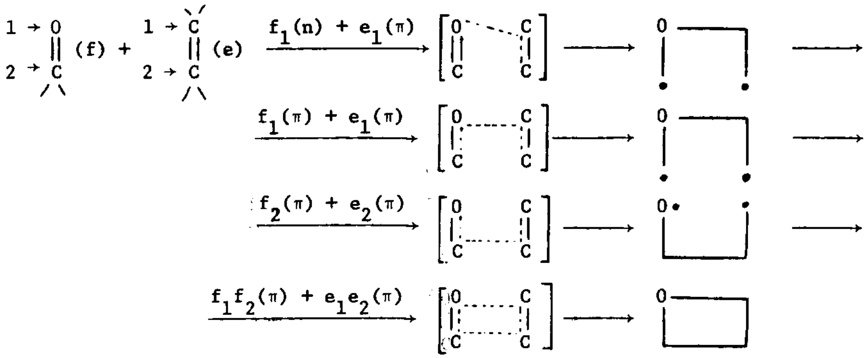
In this paper, I will attempt to show how a very simple theoretical approach can lead to accurate correlations of molecular structure with experimental results. The perturbational MO method will be applied to the photocycloaddition of carbonyl compounds to olefins, a reaction which yields an oxetane (Paterno-Büchi reaction[1]). The addition of the n,π^* excited formaldehyde species to the simplest olefin, ethylene, is the prototype reaction with substituents to be introduced later in the discussion. Regardless of the respective geometries of the two reactants during the initial step of the reaction, one can enumerate four distinct types of transition states leading to bond formation, eqs. 1-4. Eq. 1 depicts the attack of the radical nonbonding electron of oxygen upon the olefin to yield a biradical intermediate, while eq. 4 represents a concerted $[_{\pi}2 + {}_{\pi}2]$ addition. In unrefined outline, these are the cited mechanisms for Paterno-Büchi reactions.[2]



(1)

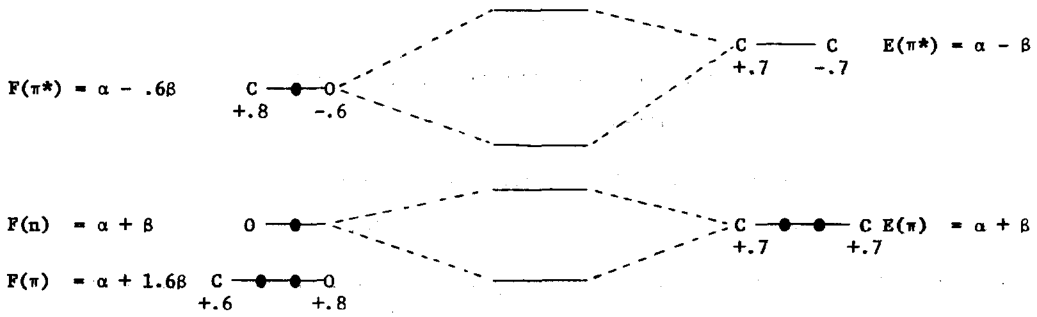
(2)

(3)

(4)

MO diagrams are given below for formaldehyde and ethylene, and the electron occupancy for our purpose is indicated. The formation of each transition state, eqs. 1-4, can be treated as an intermolecular perturbation of the MO's of the reactants.[3] The most important stabilizing level combinations and splittings are shown by dashed lines in the MO diagram. The perturbation energies are calculated using eq. 5 and 6, first and second-order perturbation energies respectively.[3] The formulas are easily interpreted. The transition states are assumed to

Hückel MO's for Formaldehyde and Ethylene



have a partial bond between orbitals f of molecule F and orbitals e of molecule E. The

$$E_1 = c_f c_e \ \gamma \qquad (5) \qquad\qquad E_2 = \frac{(c_f c_e)^2}{(E_F - E_E)} \ \gamma^2 \qquad (6)$$

closer in energy, the interacting molecular levels are, the more the transition state is stabilized. The amount of stabilization is also a function of the electron density in the more occupied orbital, and of the density of the vacancy in the orbital with which it is interacting, accounting for the MO coefficients in eqs. 5 and 6. γ is the atomic orbital perturbation exchange integral, and if one assumes that bonds are half-formed in the transition state, then $\gamma = 1/2\beta$ and the units of second-order energies are $\gamma^2/\beta = 1/4\beta$.

The four assumed reaction pathways give calculated perturbation energies as follows: (1) 0.83γ, (2) 0.60γ, (3) 0.73γ, and (4) 1.01γ. The concerted mode of addition (4) is favored, and the biradical mechanism (1) could be a competing process. The most important energy level interactions are easily identified as the degenerate or nearly degenerate interactions, E(π) → F(n) for mode (1), and F(π*) → E(π*) for mode (4).

The effects of substituents can be deduced by tracing the molecular energy level variations and orbital coefficient changes which are induced by the substituents. Substituents can be broadly grouped into electron donating, electron attracting, and conjugative categories. Electron donating substituents raise the molecular energy levels, antibonding more than bonding. Electron-attracting substituents lower all energy levels, bonding more than antibonding. F(n) is changed only by a second-order inductive effect. In general, conjugative substituents lead to a spreading of π energy levels, with the highest occupied π level raised, and the lowest vacant level lowered in energy. In addition a much lower electronic density will be found at the reactive sites in either π or π* orbital.

Deduced substituent effects are summarized in the table. Comparisons with some well-studied reactions will illustrate the utility of the theory. The addition of acetone to 1,2-dicyanoethylene proceeds with retention of configuration in the olefin and a $[_{\pi}2 + _{\pi}2]$ concerted mechanism has been deduced.[2b] The table shows that the substitution pattern doubly favors a concerted mechanism.

Substituent Effects in Photoformation of Oxetanes

Substituent / Mechanism	$CH_2 = O$			$CH_2 = CH_2$		
	Attracting	Donating	Conjugating	Attracting	Donating	Conjugating
biradical	0	-	0	-	0	-
$[_{\pi}2 + _{\pi}2]$	- -	+ +	-	+ +	- -	+

Benzaldehyde gives a mixture of isomeric oxetanes when photolyzed with trimethylethylene, and diradical intermediates generated after attack of non-bonding oxygen electron on the olefin have been postulated.[4] The present theoretical approach confirms the proposal. The orientation selectivity observed[4] is also correctly predicted. The overriding level interaction is $E(\pi) \rightarrow F(n)$. In $E(\pi)$ the wave-function coefficient is largest at the p-orbital with one methyl substituent, since the ground state of the olefin is polarized $(CH_3)_2C^{\oplus}—^{\ominus}CHCH_3$. Therefore attack by non-bonding oxygen electron on the least-substituted carbon generates a more stable transition state (larger perturbation energy, cf. eq. 5) than would result from attack at the more substituted carbon atom. This argument based on the relative stabilities of transition states, leads to the same result as that which is based upon the deduced relative stability of biradical intermediates.

An interesting stereochemical result is obtained when acetone and acrylonitrile, are allowed to react. The only product,[5] 4-cyano-2,2-dimethyloxetane, is not predicted on the basis of the most stable biradical intermediate. First, one observes that the substituent effect table indicates the predominance of a concerted reaction. Second, one can deduce or calculate that the pertinent orbital coefficients in levels $F(\pi^*)$ of acetone and $E(\pi^*)$ of acrylonitrile are very unequal, carbon larger than oxygen, and terminal carbon in acrylonitrile larger than second carbon. Hence, stabilization energies for concerted transition states would be much larger for the observed mode of reaction than for the one with inverted stereochemistry.

The different mechanistic tendency of carbonyl $^3n,\pi^*$ states and $^1n,\pi^*$ states should be mentioned.[2] In this very approximate treatment the reactivity difference cannot be discussed in detail. However, since triplet carbonyls are lower in energy than singlet carbonyls, the energy gap F(π*) → E(π*) would be larger for triplet carbonyl and lead to a lower tendency to undergo a concerted reaction. Lastly, on the basis of the present theory, one can gain a partial understanding of the non-reactivity of those conjugated carbonyl compounds with lowest π-π* excited states.[6] The energy gap F(π*) → E(π*) is large, and there is a decreased electronic density at the carbonyl group in level F(π*). A concerted reaction is therefore inhibited,and the biradical alternative does not occur since no half-vacant non-bonding oxygen orbitals are present.

Specific cases may be treated by reference to molecular diagrams of the particular molecules which are undergoing a reaction. Then an appropriately chosen value for the perturbation integral will allow more quantitative deductions to be made. Studies of this type are in progress.[7]

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