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PERTURBATIONAL ANALYSIS OF 1,3-DIPOLAR CYCLOADDITION REACTIONS OF DIAZOMETHANE

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Perturbational molecular orbital methods have furnished a clue to the problems of reactivity and regioselectivity in 1,3-dipolar cycloadditions.[1] Within the framework of frontier molecular orbital theory [2] semiquantitative correlations of rate data with orbital energy separations were obtained. In order to check the validity and limitations of the simple perturbation treatment, we have now applied a more sophisticated procedure [3,4] to cycloaddition reactions of diazomethane.[5] This treatment based on CNDO/2 wavefunctions allows interpretations similar to independent electron models.

Using experimental geometries or standard bond lengths and bond angles, the CNDO/2 wave functions of diazomethane and a number of olefins were evaluated. To perform the all valence electron perturbation calculation,the reacting molecules were placed above each other symmetrically with respect to the reacting atoms at a distance of 2.5 Å between the two planes. According to ab initio calculations for the reaction of diazomethane and ethylene [6] the transition state has not been reached at this separation. Furthermore,the ground state geometries can still be used, this being a prerequisite for a meaningful perturbation calculation.

In Figure 1 the olefins are arranged according to the experimental orientation and in Table I to increasing reactivity. Methyl vinyl ether serves as a substitute for n-butyl vinyl ether and propene as a substitute for 1-hexene. The sum of first and second order perturbation energies is negative (stabilizing) and increases from top to bottom of Table I. Although this result parallels qualitatively the experimental observations, the numbers should be positive as the transition state should not have been reached yet. It is characteristic of CNDO/2 not to produce activation barriers for cycloaddition reactions [3,7]. However, the strength of the perturbation treatment consists in a comparative analysis of individual energy components as is shown in columns 4-7 of Table I.

Diazomethane belongs to type I of the classification of 1,3-dipoles, i.e., the reactivity is mainly determined by the interaction of HOMO(diazomethane) - LUMO(olefin).[8] This is borne out by the calculations as can be deduced from a comparison of column 5 with columns 6 and 7. The second HOMO - LUMO interaction contributes only a little to the overall stabilization and can therefore be omitted from our discussion.

As expected for the frontier electron model, the HOMO(diazomethane) - LUMO(olefin) excitation energies decrease with increasing reactivity. The inverse behavior is observed for the corresponding stabilization energies. These latter values should correlate linearly with the log k_2 values if the frontier electron theory is a valid approximation. A corresponding plot, however, shows a lot of scattering. In particular the stabilization energies for conjugated olefins are much smaller than expected on the basis of the rate data. In fact the correlation of the inverse HOMO(diazomethane) - LUMO(olefin) excitation energies, a plot similar to that in the preceding communication [5], shows better linearity even though it corresponds to a cruder approximation.

However, the calculations and the experimental results can be reconciled if one includes the charge transfer interactions of HOMO(diazomethane) with higher unoccupied π-MO's of the conjugated olefins (column 6 and Fig. 1). Conjugated olefins fit now as well as the other dipolarophiles (correlation coefficient 0.92). These stabilization energies amount to almost all of the π-charge transfer stabilizations (last column) demonstrating once more the importance of HOMO(diazomethane) for the reactivity.

Thus, the calculations point to a breakdown of frontier electron theory for molecules with conjugated double bonds. The reason is clear : the contributions of individual atomic orbitals in π-MO's of conjugated molecules are smaller, but the number of π-MO's with their compressed energy separations increases. Therefore, further CT-interactions must be included.

A more detailed discussion of these and other perturbation calculations on 1,3-dipolar cycloaddition reactions will be given in the full paper.

Table 1. Perturbation Energies for Cycloaddition Reactions of Diazomethane

	$8 + \log k_2$	1.+ 2. Order (kcal/mol)	HO_D - LU_{01}		$HO_D - \Sigma\pi^*_{01}$ Stabilization (kcal/mol)	total π-CT Stabilization (kcal/mol)
			Excitation (eV)	Stabilization (kcal/mol)		
Methyl vinyl ether	1.0 [a]	-7.11	11.47	-8.11	-8.11	-8.19
Propene	2.643 [b]	-7.22	11.08	-8.52	-8.52	-8.58
Butadiene	4.330	-7.38	10.11	-6.91	-8.97	-9.17
trans-Piperylene	3.386	-7.00	10.14	-6.13	-8.74	-8.93
trans-1-Methoxybutadiene	3.127	-6.83	10.19	-6.43	-8.79	-9.34
Ethylene	4.602	-8.46	11.31	-9.47	-9.47	-9.66
Styrene	4.648	-6.88	10.08	-5.17	-8.94	-9.12
Methyl crotonate	5.806	-5.07	8.96	-8.50	-9.64	-10.42
Methyl methacrylate	6.713	-8.88	9.01	-9.34	-10.60	-10.83
Methyl acrylate	8.049	-10.65	8.90	-10.93	-12.22	-12.37

[a] $\log k_2$ of butyl vinyl ether ; [b] $\log k_2$ of 1-hexene ; [c] Rate constant was divided by a statistical factor of two for the plot of Fig. 1.

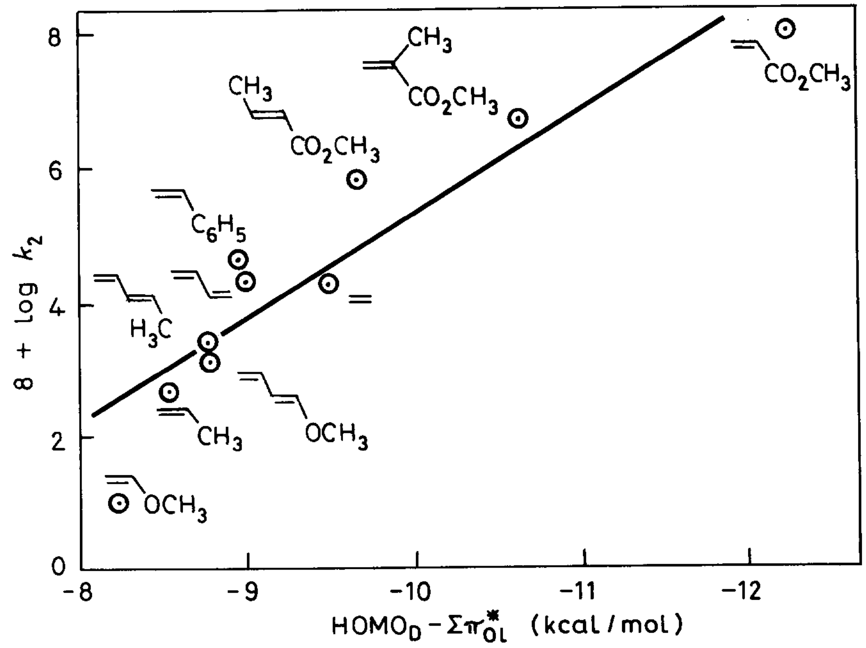

Figure 1. Correlation of $\log k_2$ for the cycloaddition of diazomethane to olefinic dipolarophiles with the calculated interaction energy of HO(diazomethane) with all unoccupied π-MO's of the dipolarophile

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