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KINETICS OF 1,3-DIPOLAR CYCLOADDITION REACTIONS OF DIAZOMETHANE; A CORRELATION WITH HOMO-LUMO ENERGIES

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The early transition states of concerted cycloadditions allow the application of MO perturbation theory (PMO) which is based on orbital energies and eigenvector coefficients of reactants. Recently PMO provided at least qualitative answers to many vexing problems of reactivity sequences and of regioselectivity.[1] Orbital energies and coefficients calculated by CNDO/2 have been used,[2,3] sometimes after calibration with experimental energy values.

Many 1,3-dipolar cycloadditions receive contributions from both HO-LU interactions to a comparable extent.[4] They show a characteristic structure-rate correlation : electron-releasing as well as electron-attracting substituents increase the reactivity of the dipolarophile.[1] A paraboloid curve resulted from plotting log k_2 of phenyl azide cycloadditions vs. the ionization potentials (IP) of twenty olefinic and acetylenic dipolarophiles in accordance with a drastically simplified second order perturbation equation.[5] More and better quantitative correlations are desirable.

Cycloadditions of diazomethane are predominantly HO(1,3-dipole) - LU(dipolarophile) controlled as shown by a general consideration of orbital energies of 1,3-dipoles,[4] by calculations of the hypersurface of the reaction diazomethane + ethylene[6] as well as by the fact that diazomethane cycloadditions are only accelerated by electron-attracting substituents in the dipolarophile.[1]

We have supplemented earlier kinetic data[7] by a large bulk of cycloaddition rate constants of diazomethane, phenyl- and diphenyldiazomethane.[8] The kinetic methods and results as well as the adducts will be described elsewhere. We wished to check the validity of the PMO approach to the dipolarophile activity scale on the basis of experimental data. Therefore, the second order perturbation equation was simplified : a. Restriction to HO-LU interactions, i.e., to the term with HO(diazomethane) - LU(dipolarophile) ; b. Numerators are set equal for all dipolarophiles (eq 1) ;

$$\Delta E = \frac{k\beta^2}{E_{\text{HO(diazomethane)}} - E_{\text{LU(dipolarophile)}}} \qquad (1)$$

c. IP of diazomethane (9.03 eV)[9] is taken as a measure of HO(diazomethane) ; d. The EA's of dipolarophiles were approximated by subtracting the energies of the $\pi\rightarrow\pi^*$ transition from the IP's. The quantity defined in eq 2 stands for the reciprocal HO-LU distance D; it should be proportional to the energy gain from HO-LU overlap in the transition state and thus be a linear function of log k_2.

$$1/D = \left[IP_{\text{diazomethane}} - (IP - E_{\pi\rightarrow\pi^*})_{\text{dipolarophile}}\right]^{-1} \qquad (2)$$

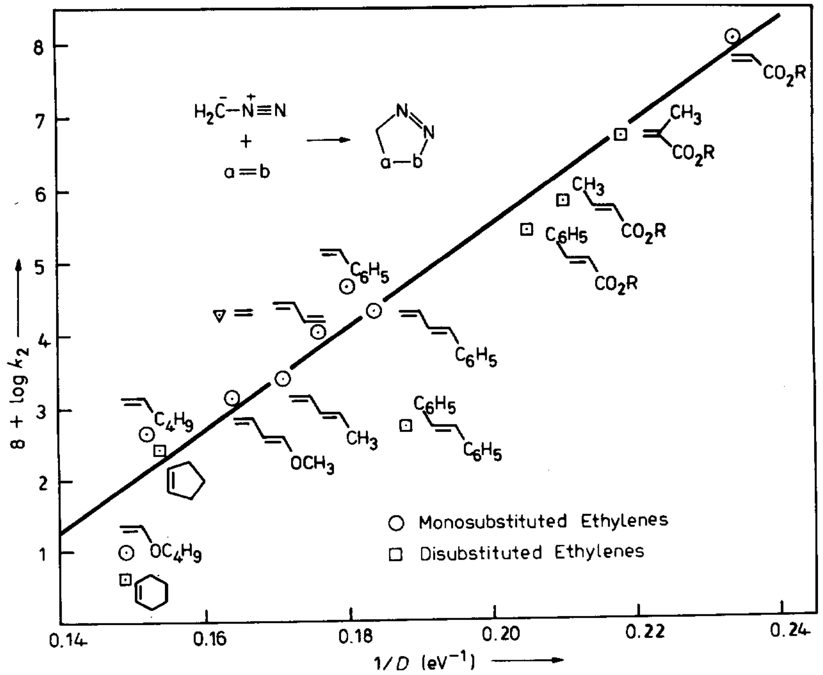

Figure 1. log k_2 as a function of 1/D which is an empirical measure of the reciprocal energy distance HO(diazomethane) - LU(dipolarophile).

Table 1. Rate Constants of Diazomethane Cycloadditions and Energy Values which Correspond to Orbital Energies

	10^5k_2 in DMF, 25° ($l \cdot mol^{-1} sec^{-1}$)	IP (eV)	$\pi \rightarrow \pi^*$ (eV)	D (eV)
A. <u>Compounds with CC double bonds</u>				
Ethyl acrylate	112 000	10.72	5.97	4.28
Methyl methacrylate	5 170	10.28	5.83	4.58
Methyl crotonate	641	10.11	5.85	4.77
Methyl cinnamate	264	8.63	4.48	4.88
Styrene	44.5	8.48	5.00	5.55
Ethylene [a]	40	10.51	7.66	6.18
Butadiene [a]	21.4	9.08	5.72	5.67
trans-1-Phenylbutadiene	21	8.16	4.58	5.45
trans-Piperylene	2.43	8.78	5.59	5.84
trans-1-Methoxybutadiene	1.34	8.21	5.28	6.10
trans-Stilbene [a,b]	1.01	7.90	4.19	5.32
1-Hexene	0.44	9.45	7.01	6.59
Cyclopentene	0.27	9.18	6.64	6.49
Butyl vinyl ether	0.01	8.80	6.46	6.69
Cyclohexene	0.004	9.13	6.82	6.72
B. <u>Compounds with CC Triple Bonds</u>				
Methyl propiolate	49 700	11.68	6.20	3.55
Ethyl phenylpropiolate	397	8.93	4.81	4.91
Methyl tetrolate	175	11.10	6.02	3.95
trans-Pent-2-en-4-yne	4.6	9.04	5.58	5.57
Phenylacetylene	2.7	8.82	5.07	5.28
1-Hexyne	0.14	10.18	7.22	6.07

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[a] The cycloadditions are regioselective. The rate constants of symmetrical dipolarophiles were divided by a statistical factor of 2 for the plot of Fig. 1.

[b] Assignment of IP uncertain, therefore not used for least square treatment of straight line.

For the dipolarophiles of Table I the IP's[10] and the uv absorptions were available. Considering the crudity of the approximation, the linearity of the function in Fig. 1 (slope 70.8, correlation coefficient r = 0.947) is fair. Separate linear functions for mono- and disubstituted ethylenes are of better quality. Ethylene and trans-stilbene deviate the most ; in the latter case the band assignment of the photoelectron spectrum is problematic. The analogous plot for the six acetylenic dipolarophiles produces a straight line (r = 0.910) with a smaller slope (39.1). The rate ratio of correspondingly substituted olefinic and acetylenic dipolarophiles amounts to 0.53 - 16.

Thus, the rate constants obey the sequence expected for reactant orbital control in accordance with the early transition states of concerted cycloadditions. There is no resemblance with the activity series anticipated for the late transition states of diradical formation from 1,3-dipole and dipolarophile.[1,11]

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