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REACTIVITY SEQUENCES OF DIPOLAROPHILES TOWARDS DIAZOCARBONYL COMPOUNDS - MO PERTURBATION TREATMENT

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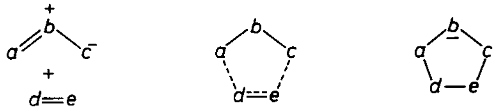
Summary Whereas diazomethane cycloadditions are only accelerated by electron-attracting substituents in the olefinic or acetylenic dipolarophile, the cycloadditions of diazoacetic, diazomalonic and diazo(phenylsulfonyl)acetic ester show in accordance with the PMO treatment U-shaped activity functions when log k_2 is plotted versus the lowest IP of the dipolarophiles.

The puzzling problem of reactivity scales in concerted additions (Diels-Alder reaction, 1,3-dipolar cycloaddition)[1,2] found an elegant solution in the MO perturbation treatment (PMO) by Sustmann.[3,4] The dipolarophile activity sequences are 1,3-dipole-specific and depend on the energy separations of the frontier orbitals; these energy distances show up in the denominators of the second order terms of the perturbation equation (1).



Transition State

$$\Delta E = \frac{\left[c_a c'_d \beta_{ad} + c_c c'_e \beta_{ce}\right]^2}{E_I} + \frac{\left[c'_a c_d \beta_{ad} + c'_c c_e \beta_{ce}\right]^2}{E_{II}} = \Delta E_I + \Delta E_{II} \qquad (1)$$

$E_I = E_{\psi_2} - E_{\psi_B}$ = HO(1,3-Dipole) - LU(Dipolarophile)
$E_{II} = E_{\psi_A} - E_{\psi_3}$ = HO(Dipolarophile) - LU(1,3-Dipole)
Atomic orbital coefficients of HO : c_a, c_d, etc.
LU : c'_a, c'_d, etc.

β_{ad}: Resonance integral of new σ bond a—d, etc.

Diazomethane turned out to be a 1,3-dipole of type I in Sustmann's classification.[5] Its cycloadditions are HO(1,3-dipole) - LU(dipolarophile) controlled (Fig. 1,2); in accordance with the known influence of substituents on the LU energy of ethylene,[6] only electron-attracting groups increase the dipolarophilic activity. Ethyl acrylate adds diazomethane at 25°C 10^7 times faster than butyl vinyl ether, whereas enamines are inert.[5] Electron-releasing substituents in the diazomethane should likewise accelerate the cycloaddition as demonstrated for aryldiazomethanes.[7] The introduction of a methoxycarbonyl group into diazomethane lowers the HO energy and should diminish the cycloaddition rate by an increase of E_I. Would the lowering of the LU energy in diazoacetic ester be sufficient to give weight to the LU(1,3-dipole) - HO(dipolarophile) interaction corresponding to ΔE_{II} in eq (1) ?

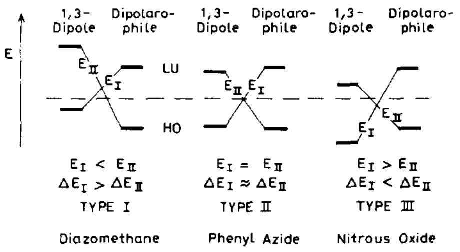


Figure 1. Classification of 1,3-dipoles by their frontier orbitals energies

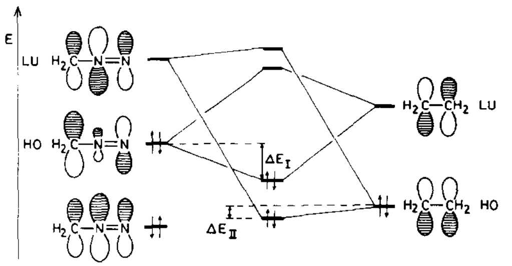
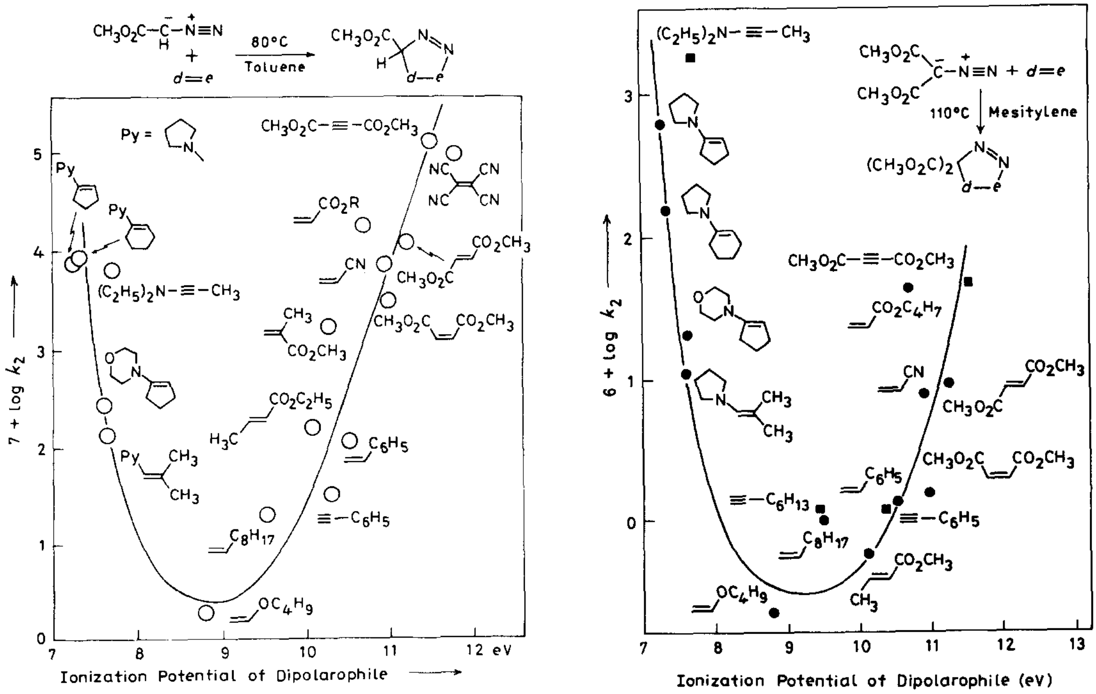


Figure 2. Frontier orbital interaction for the reaction diazomethane + ethylene

The rates of the cycloadditions of methyl diazoacetate in toluene at 80°C were measured by the extinction decrease of the IR absorption at 2100 cm^{-1}. Second order rate constants were evaluated via pseudo first order constants in the presence of a large excess of dipolarophile.

The log k_2 values which stretch over five powers of ten are plotted in Fig. 3A versus the ionization potential (IP) as a measure of the electron density of the dipolarophilic π bond. They show an enlightening departure from the linear function ^{5} which log k_2 of diazomethane entertains with the inverse energy difference E_I of the first term of eq (1). Beginning with the dipolarophiles which are equipped with several electron-



A. Methyl diazoacetate B. Dimethyl diazomalonate

Figure 3. Cycloaddition rate constants as a function of IP of dipolarophiles.

attracting substituents, one observes a diminution of the rate constants with sinking IP. After passing 9 eV, however, the curve turns upwards and reaches high activities for four enamines and one ynamine; the products will be described elsewhere. Diazomethane does not react with enamines and ynamines.

The U shape function of Fig. 3A characterizes methyl diazoacetate as a 1,3-dipole of the Sustmann type II. Both frontier orbital interactions contribute to a comparable extent. In the right branch of the U curve the interaction HO(1,3-dipole) - LU(dipolarophile) predominates, whereas the high activity of the enamines and an ynamine reveal a greater importance of the second term of eq (1) which deals with LU(1,3-dipole) - HO(dipolarophile). The equally spaced HO - LU separations produce the smallest energy gain in eq (1); the vinyl ether minimum in Fig. 3A might come close to $\Delta E_{I} = \Delta E_{II}$.

The second ester group in dimethyl diazomalonate generates a further orbital energy decrease. Kinetic measurements were based on the diminution of the IR diazo band at 2129 cm^{-1}. The rate constant of self-decomposition, $k_{dec} = 5.2\ 10^{-6}\ sec^{-1}$, had to be subtracted from the $k_{\psi 1}$ values of "slow" dipolarophiles.

The U shape for the function of the diazomalonic ester in Fig. 3B is lopsided. Electron-rich dipolarophiles exceed the activity of electron-deficient systems; e.g., diethylaminopropyne reacts with diazomalonate 40 times faster than dimethyl acetylenedicarboxylate which is still the record dipolarophile towards diazoacetate. We deduce an increasing weight of ΔE_{II} in eq (1) from the comparison of Fig. 3A and 3B.

A phenylsulfonyl group triggers an even stronger decrease of orbital energies than the ester function. Again the IR diazo band (2123 cm^{-1}) was used to measure the concentration of diazo(phenylsulfonyl) acetic ester. All k_2 values except those for enamines and ynamines required correction for the self-decomposition of

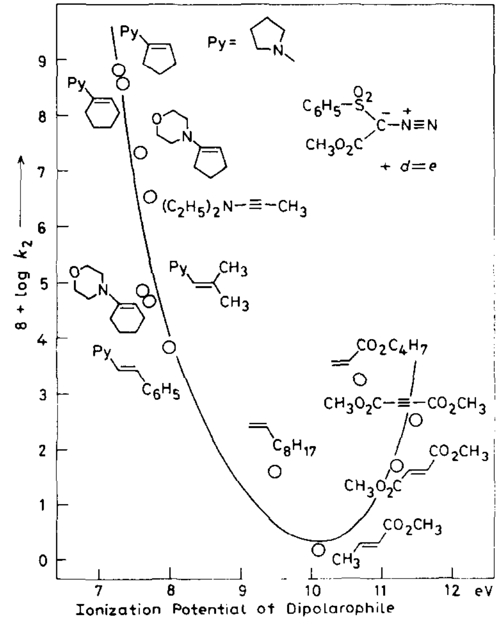


Figure 4. Rate constants (log k_2) for the cycloadditions of diazo(phenylsulfonyl)acetate to ethylenic and acetylenic dipolarophiles in toluene at 80°C plotted versus the ionization potential of the dipolarophile.

the diazo compound; $k_{dec} = 1.7\ 10^{-6}\ sec^{-1}$ contributes more than half to $k_{exp} = 2.7\ 10^{-6}\ sec^{-1}$ in the presence of 10 equiv butyl acrylate. The rate constant of ethyl crotonate is uncertain, because $k_{\psi 1}$ in the presence of 5.5 M dipolarophile is only by 5 % greater than k_{dec}.

The highly deformed U shape in Fig. 4 places methyl diazo(phenylsulfonyl)acetate in the transition between type II and type III (Fig. 1) with a strong preponderance of the LU(diazo compound) - HO(dipolarophile) interaction. The minimum has shifted to 10 eV; 1-decene exceeds crotonic ester ~20fold. Pyrrolidinocyclopentene reacts 10^5 times faster than acrylic ester and diethylaminopropyne surpasses acetylenedicarboxylic ester 10^4 fold in rate.

Complaints about the poor quality with which log k_2 fit the curves in Fig. 3 and 4 are certainly justified. We are dealing with qualitative relationships, because the way to these plots is paved with simplifying assumptions. Diazomethane cycloadditions are determined by only one HO-LU interaction, namely ΔE_I in eq (1). A good linear correlation with $1/E_I$ was achieved,[5] when all the numerators which contain the functions of the atomic orbital coefficients were set equal.[8] Can the data reported here be correlated with ΔE according to eq (2) ?

$$\Delta E = \Delta E_I + \Delta E_{II} = \text{Const}\left(\frac{1}{E_I} + \frac{1}{E_{II}}\right) \qquad (2)$$

This is indeed possible, but the straight lines are not of the same quality as the one obtained for diazomethane.[5] E.g., the data for diazo(phenylsulfonyl)acetic ester fit a linear relation with $r = 0.877$. The HO energies were based on the IP's, whereas the LU energies rest on comparisons with few experimental values of electron affinities.[9,10]

Replacement of the diazomethane carbon atom by atoms of higher electronegativity effects a stepwise decrease of orbital energies. Diazomethane, organic azides and nitrous oxide represent the types I - III in Sustmann's classification (Fig. 1). We have demonstrated here that the introduction of acceptor substituents into diazomethane also shifts the 1,3-dipole to type II in methyl diazoacetate and further towards type III for dimethyl diazomalonate and methyl diazo(phenylsulfonyl)acetate.

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