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SOLVENT DEPENDENCE OF CYCLOADDITION RATES OF PHENYLDIAZOMETHANE AND ACTIVATION PARAMETERS

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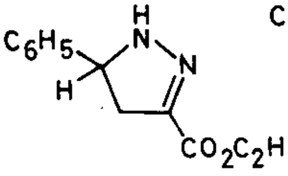
Dedicated to Tetsuo Nozoe on the Occasion of His Seventy-seventh Birthday

The small influence of solvent polarity on the rate constants of phenyldiazomethane additions to ethyl acrylate and norbornene as well as the Eyring activation parameters of diazoalkane cycloadditions are interpreted as evidence for early transition states of these concerted reactions.

Inequality of the two frontier orbital interactions in a concerted cycloaddition necessarily involves some charge transfer in the transition state. If in the reaction of diazomethane and ethylene the interaction HO (diazomethane) – LU(ethylene) is stronger than LU(diazomethane) – HO (ethylene), then this is tantamount to the statement that diazomethane loses more electronic charge via its HOMO than it gains through its LUMO (see Fig. 1 of the preceding communication). How does solvation energy change during the activation process of cycloaddition ?

The methods described in the preceding communication [1] were applied to determine the rate constants of the formation of 1 and 2 in various solvents. The cycloaddition of phenyldiazomethane to acrylic ester is accelerated 5.3 times on increasing the solvent polarity, i.e., on changing from cyclohexane to methanol (Table 1), whereas the k_2 values for phenyldiazomethane + norbornene reveal only some scatter. The interpretation of small rate differences is problematic. Nevertheless, the rate data of ethyl acrylate fulfil a tolerably linear relation when plotted versus the empirical parameter of solvent polarity, [2]

E_T (Fig. 1).



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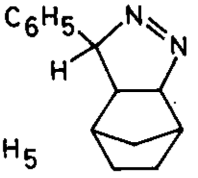

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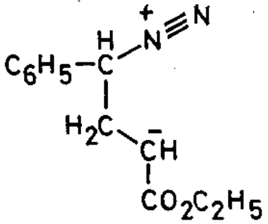

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Table 1. Influence of Solvent Polarity on the Rate Constants of Phenyldiazomethane Cycloadditions to Ethyl Acrylate and Norbornene at 25°C

Solvent	E_T (kcal mol^{-1})	Ethyl Acrylate $10^2 k_2$ ($l\ mol^{-1} sec^{-1}$)	Norbornene $10^5 k_2$ ($l\ mol^{-1} sec^{-1}$)
Cyclohexane	31.2	4.14	9.52
Carbon Tetrachloride	32.5	3.80	7.11
Benzene	34.5	6.42	8.33
Dioxane	36.0	6.12	7.83
Ethyl acetate	38.1	5.00	6.47
Pyridine	40.2	9.91	8.34
Benzonitrile	42.0	10.9	10.1
Dimethylformamide	43.8	13.1	8.94
Acetonitrile	46.0	10.0	8.38
Butanol	50.2	23.2	10.7
N-Methylformamide	54.1	20.5	11.8
Methanol	55.5	22.1	9.33

The small solvent dependence of the rate constants is in harmony with little charge transfer in the early transition state of a concerted cycloaddition. Leroy and Sana [3] calculated transition state properties by a LCAO-SCF-MO method and obtained the transfer of 10 % of an electronic charge in the system diazomethane + acrylonitrile, and 6 % for diazomethane + propene. According to these calculations, the transition states are so early on the reaction coordinate that the bond lengths of the reactants have not changed; only the

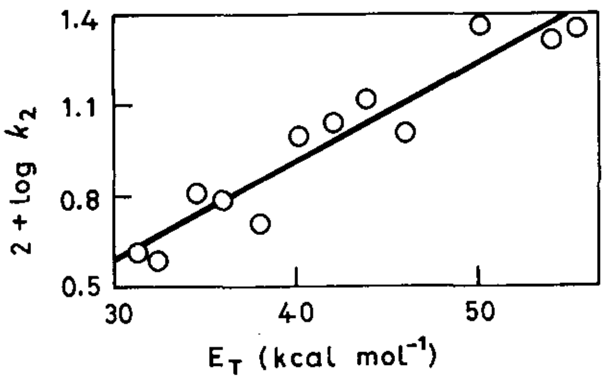

Figure 1

angles are shifted. The data are not compatible with a transition state which is structurally related to the zwitterionic intermediate 3. Big effects of solvent polarity on rate were observed for the formation of zwitterions as high-energy intermediates; the 2+2 cycloadditions of tetracyanoethylene to isobutenyl ethyl ether or anethole occur 10 800 or 29 000 times faster in acetonitrile than in cyclohexane.[4]

Table 2. Eyring Parameters for the 1,3-Dipolar Cycloadditions of Diazoalkanes to Ethyl Acrylate (EA), Norbornene (N), and 1-Phenylbutadiene (PB) in Dimethylformamide

System	10^5k_2 at 40°C ($l\ mol^{-1}\ sec^{-1}$)	ΔH‡ (kcal mol^{-1})	ΔS‡ (e.u.)
EA + Diazomethane	216 000	7.5 ± 0.6	- 33 ± 2
EA + Phenyldiazomethane	27 300	9.3 ± 0.7	- 31 ± 2
EA + Diphenyldiazomethane	812	10.8 ± 0.6	- 34 ± 2
EA + Methyl diazoacetate	26		
N + Diazomethane	66	13.2 ± 0.9	- 31 ± 3
N + Phenyldiazomethane	31	14.4 ± 0.9	- 28 ± 3
N + Diphenyldiazomethane	3.8	14.3 ± 1.0	- 33 ± 3
N + Methyl diazoacetate	0.34	16.0 ± 1.0	- 33 ± 3
N + Dimethyl diazomalonate	0.009	19.7 ± 1.0	- 28 ± 3
PB + Diazomethane	68	13.8 ± 0.8	- 29 ± 3
PB + Diphenyldiazomethane	0.58	16.1 ± 0.8	- 31 ± 3

The early transition states of diazoalkane cycloadditions find confirmation in the Eyring activation parameters which are based on kinetic measurements at five temperatures. Moderate activation enthalpies and large negative activation entropies are typical for concerted cycloadditions of the Diels-Alder [5] or the 1,3-dipolar type.[6] Although the rate constants in Table 2 spread over 10^8, the $\Delta S^{\ddagger}$ values show with -28 to -34 e.u. a remarkable constancy. The range of the rate constants is mainly determined by the differences of $\Delta H^{\ddagger}$.

The large negative $\Delta S^{\ddagger}$ values are the result of

a. making one molecule out of two ;
b. the highly ordered transition state.

The term $T\Delta S^{\ddagger}$ constitutes 58 % and 42 % of the activation free energy for diazomethane additions to ethyl acrylate and norbornene, respectively. The entropy encrease must be defrayed very early on the reaction coordinate, i.e., in the formation of the "orientation complex" of the reactants. The moderate $\Delta H^{\ddagger}$ values suggest that rehybridization has not progressed very far in the transition state.

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