Kinetics and Mechanism of the 2 + 2 Cycloaddition of Tetracyanoethylene to 2,5-Dimethyl-2,4-Hexadiene

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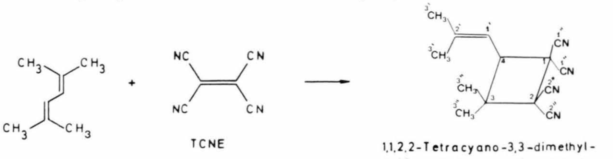
The kinetics of the 2 + 2 cycloaddition reaction between tetracyanoethylene and 2,5-dimethyl-2,4-hexadiene in different solvents has been studied by following the disappearance of the intermediate EDA-complex spectrophotometrically. It is concluded that the EDA-complex is transformed through a concerted cyclicpolar transition state to give the vinyl cyclobutane derivative (III). The effects of various solvents on the reaction rates have been analysed using a multiparameter approach. The thermodynamic parameters (ΔH^0 and ΔS^0), of EDA-complex formation and the activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) of the cycloaddition have been discussed.

Introduction

Concerted $[{}_{\pi}2_s + {}_{\pi}2_s]$ thermal cycloaddition reactions are symmetry forbidden [1]. However, 2 + 2 thermal reactions are allowed via biradicals [2] or zwitterions [3], as well as by a concerted process $[{}_{\pi}2_a + {}_{\pi}2_s]$ [1]. Epiotis [4] suggested that polar 2 + 2 cycloadditions between olefins with small energy gap between HOMO (highest occupied molecular orbital) of the donor olefin and LUMO (lowest unoccupied molecular orbital) of the acceptor olefin are allowed if the "charge-transfer" configuration is lowest in energy. Similarly, Fukui et al. [5], have proposed the concept of "pseudoexcitation" for good donor-acceptor pairs. In this concept the transition state is stabilized through third-order interaction between the ground state, a mono-transferred, and a mono-excited configuration.

Trans-fixed 1,3-dienes undergo 2 + 2 cycloaddition with tetracyanoethylene (TCNE) [6]; similarly, 1,1-disubstituted-1,3-dienes are known to react with TCNE preferentially in a 2 + 2 manner [7]. This is most probably due to steric effect and/or the transoid conformation of the diene make the 2 + 4 cycloaddition difficult, or impossible.

2,5-Dimethyl-2,4-hexadiene (DMH), inspite of its low ionisation potential ($I_p = 7.84$ eV) [8], does not react with maleic anhydride or its derivatives ($1.2 > E_A > 0.6$ eV) [9]. However, a more potent acceptor TCNE ($E_A = 2.5$ eV) [10] reacts by 2 + 2 cycloaddition, in all solvents investigated, to give only the vinyl cyclobutane derivative (**III**).



DMH I

TCNE II

1,1,2,2-Tetracyano-3,3-dimethyl-4-(2-methylpropenyl)cyclobutane III

The aim of the present work was to study the mechanism of this reaction. Thus, the kinetics of the product, as well as the formation of the EDA-complex, were studied in different solvents. Various possible mechanisms were discussed on the basis of different solvents and thermodynamic parameters.

Experimental

Materials

Commercial tetracyanoethylene (Fluka) was crystallized from 1,2-dichloroethane, followed by three times sublimation under vacuum at 50 °C in the presence of active carbon, m.p. 201 °C [11]. 2,5-Dimethyl-2,4-hexadiene (Fluka) was refluxed for four hours over lithium aluminium hydride and distilled before use, b.p. 134 °C [8]. The solvents, chloroform and dichloromethane (Merck. spectrograde reagents) were used without further purification, and the other solvents were purified by usual methods [12]. The cycloadduct (**III**) was prepared by stirring 3.5 g

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(0.027 M) of TCNE and 4.2 g (0.038 M) of DMH in 200 ml of chloroform until the blue colour faded at 25 °C. Chloroform was evaporated under vacuum and the remaining solid was crystallized from cyclohexane, m.p. 119 °C, $C_{14}H_{14}N_4$ requires: C, 70.95%; H, 5.88%; N, 23.53%. Found: C, 70.66%; H, 5.9%; N, 23.37%. IR: 3030 (CH), 2220 (CN) and 1225 cm^{-1} (c = c); UV (cyclohexane): $\lambda_{max} = 210$ nm $\log \varepsilon = 4.17$; ^1H-NMR ($CDCl_3$): $\delta = 1.6$ (d, 6H, CH_3), 1.9 (d, 6H, CH), 3.8 (d, H, CH, $J = 10.8$) and 5.3 (d, H, CH=, $J = 10.8$). ^{13}C-NMR ($CDCl_3$): $\delta = 146.5$ (C2′), 112.8 (Cl′), 110.7, 109.6 (Cl″), 109.8, 108.4 (C2″), 50.1 (C4), 49.9 (C3), 43.3 (C2), 38.9 (C1), 27.4, 26.2 (C3′), 21.5, 19.1 (C3″); MS: m/e 132 $[(CH_3)_2\ C{=}CH{-}CH{=}C(CN)_2]^+$, 110 $(DMH)^+$, 105 $[(CH_3)_2\ C{=}CH{-}C{\equiv}C{-}CN]^+$, 95, 78, 77, 65, 64, 55 and 41.

Kinetic measurements

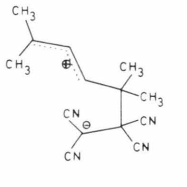
The equilibrium constant (K 1 mol^{-1}) of EDA-complex formation between TCNE and DMH, and the rate of cyclo-addition were determined spectrophotometrically by observing the absorbance of the band maximum (Table 1) of EDA-complex. Hewlett Packard 8450 A UV/VIS, and Perkin Elmer 555 spectrophotometers were used. Constant temperature was obtained by circulating water to a 10 mm quartz cell (Hellma 160 QS) from a constant temperature circulating bath. The temperature was measured in the cell by using a platinium resistance thermometer which had previously been calibrated by using a Hewlett-Packard 280 A quartz thermometer. The temperature maintained was constant within 0.02 °C. The concentration ratios of [DMH]/[TCNE] were in the range 20–40, thus providing the pseudo-first-order rate constants from which the second order rate constants were evaluated by dividing by [DMH]. The absorbance at λ_{max} were extrapolated to $t = 0$, by using the absorbance A_0 at $t = 0$; the equilibrium constants for EDA-complex formation were determined from Benesi-Hildebrand equation [13];

$$[\mathrm{TCNE}]/A_0 = 1/\varepsilon l + (1/K \varepsilon l)(1/[\mathrm{DMH}]), \quad (1)$$

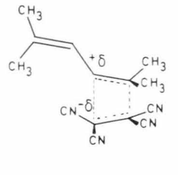
where [TCNE] is the initial concentration of tetracyanoethylene, [DMH] the concentration of 2,5-dimethyl-2,4-hexadiene, ε the molar absorption coefficient of the EDA-complex and l the optical path length.

Results and Discussion

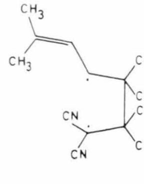
The reaction between 2,5-dimethyl-2,4-hexadiene and tetracyanoethylene in the investigated solvents is a second-order reaction. The intermediate EDA-complex is formed immediately after mixing the reactants, its absorption band maximum lies in the visible region far from the absorption of the reactants. In order to get a clearer picture of the reaction mechanism of the cycloaddition, we have tried to answer the question, whether the 2 + 2 thermal cycloaddition proceeds through transition state **IV** (zwitterion), **VI** (biradical), or through a concerted cyclic transition state **V**; the latter being described as a polar transition state facilitated by pseudo-excitation via a CT-like configuration.



IV



V



VI

Table 1. The observed rate constants[a] of 2 + 2 cycloaddition of DMH with TCNE in several solvents and λ_{max} of the EDA-complex.

Solvent	[TCNE], $M \cdot 10^3$	λ_{max} nm	k_{obs}, 1 M^{-1} sec^{-1} $\times 10^3$ (temp, °C)			
1. Chloroform	2.97[b]	652	1.07 (22.10)	1.47 (32.79)	1.88 (40.88)	2.39 (51.46)
2. Dichloromethane	4.06[b]	648	0.631 (13.06)	0.830 (22.72)	1.03 (31.35)	1.23 (37.97)
3. Acetonitrile	16.78	606	0.188 (23.23)	0.292 (31.01)	0.498 (40.13)	0.799 (49.35)
4. Ethylacetate	16.23	590	0.055 (23.72)	0.104 (30.98)	0.193 (41.44)	0.331 (49.43)
5. Benzene	7.96	630	0.106 (22.10)	0.289 (35.85)	0.471 (43.19)	0.845 (52.67)
6. Tetrahydrofurane	12.18	585	0.124 (31.32)	0.236 (40.57)	0.542 (48.89)	1.02 (58.49)
7. 1,4-Dioxane	13.74	605	–	0.164 (39.43)	0.327 (49.68)	0.581 (58.49)

[a] At least three runs were used to obtain each rate constant, [b] [DMH] ≈ 40 [TCNE]. Otherwise [DMH] ≈ 20 [TCNE].

In order to throw light on the above problem, the kinetics of the reaction were studied in different solvents. Unfortunately, many solvents had to be eliminated due to either solvolysis of TCNE in several solvents (e.g., nitromethane, dimethylformamide, and protic solvents), or its very low solubility in other solvents (e.g., cyclohexane, carbon tetrachloride and tetrachlorethylene). However, the few common solvents left gave valuable information about general solvent effects on the present reaction. The reaction was found to obey a pseudo-first-order kinetic equation when $[\mathrm{DMH}] \geq 20\,[\mathrm{TCNE}]$. The observed second-order rate constants were obtained by dividing by the concentration of 2,5-dimethyl-2,4-hexadiene, [DMH]. The values of k_{obs} in different solvents and various temperatures are collected in Table 1.

Reactions proceeding through a zwitterion intermediate in the rate determining step generally show a strong influence of solvent polarity on the rate constants [3]. The k_{obs} values in Table 1 show, however, relatively small variation with solvent, and the greater values were found for chloroform, and not for the more polar solvent acetonitrile. These results, as well as the unsuccessful trapping of a zwitterion intermediate by either methanol or p-toluenethiol led us to exclude the idea of a zwitterion intermediate in the rate determining step. A biradical intermediate, represented by **VI**, is even more unlikely since such an intermediate ought to be almost completely solvent independent [2]. Further, radical initiators as benzyl peroxide, or radical inhibitors as hydroquinone, have no effect on the rate. Accordingly, a biradical intermediate is very unlikely.

Correlations of $\log k_{\mathrm{obs}}$ of the present reaction with the microscopic dielectric constant, ε^{-1}, or with Kirkwood function [14], $(\varepsilon - 1)/(2\varepsilon + 1)$, are very poor, and a plot of $\log k_{\mathrm{obs}}$ against $E_T(30)$ (transition energy for the long wave length band of 2,4,6,3′,5′-pentaphenyl-1,4′-hydroxyphenyl-pyridiniumbetaine) [15] shows very wide scattering. However, the more recently introduced acceptor-number (AN) [16] of solvents give better correlation, Figure 1. The corresponding linear equation obtained from least squares treatment is represented by equation (2).

$$\log k_{\mathrm{obs}} = 0.074\,\mathrm{AN} - 4.77 \quad (r = 0.80). \tag{2}$$

The acceptor number, AN, for the acceptor properties of solvent, is defined by Gutmann et al. [16], as the ^{31}p-NMR chemical shift values of triethylphosphine oxide relative to those of the 1:1 adduct $\mathrm{Et_3PO\text{-}SbCl_5}$ dissolved in 1,2-dichloroethane, arbitrarily taken as 100.

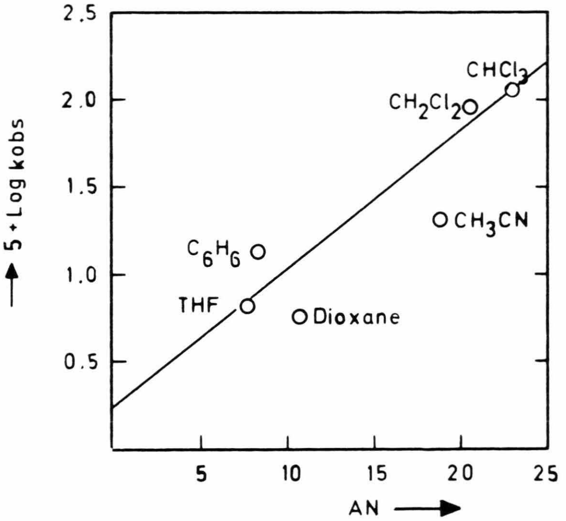


Fig. 1. Observed rate constants, k_{obs}, for [2 + 2] cycloaddition of TCNE and DMH at 25° in various solvents plotted against the Acceptor-number (AN)

The poor correlation factor ($r = 0.80$) shows, however, that the solvent effect in the present reaction is more complicated than (2) can express. In order to take into account other aspects of the reaction medium, as polarisability expressed by $(n^2 - 1)/(n^2 + 2)$ [17] [3f] and inherent polarity expressed by $(\varepsilon - 1)/(2\varepsilon + 1)$ [18], have been introduced into a multiparameter equation of the form:

$$\begin{aligned}\log k_{\mathrm{obs}} = {} & \log (k_{\mathrm{obs}})_0 + \alpha (n^2 - 1)/(n^2 + 2) \\ & + \beta (\varepsilon - 1)/(2\varepsilon + 1) + \gamma\,\mathrm{AN},\end{aligned} \tag{3}$$

where $\log (k_{\mathrm{obs}})_0$ is a statistical factor corresponding to the value of $\log k_{\mathrm{obs}}$ in the gas phase, or in a completely inert solvent, α, β and γ are regression coefficients describing the sensitivity of $\log k_{\mathrm{obs}}$ of the different solvent-solute interaction parameters. A computer regression-statistical treatment [19] gave the following equation for the present reaction:

$$\begin{aligned}\log k_{\mathrm{obs}} = {} & -9.1 + 13.9 (n^2 - 1)/(n^2 + 2) \\ & + 2.28 (\varepsilon - 1)/(2\varepsilon + 1) \\ & + 0.073\,\mathrm{AN} \quad (r = 0.99).\end{aligned} \tag{4}$$

The above equation gives a high correlation factor for the observed solvent effects, but it might be argued that by using a sufficient number of variable parame-

Table 2. The physical parameters[a] of the solvents used in present work.

Solvent	ε at 25 °C	$\mu \cdot 10^3$ (Cm)	n_D^{20}	E_T^b Kcal mol^{-1}	DN^c Kcal mol^{-1}	AN^d
1. Chloroform	4.81	3.84	1.4429	39.1	–	23.1
2. Dichloromethane	9.93	5.17	1.4242	41.1	1.1	20.4
3. Acetonitrile	37.5	11.48	1.3441	46.0	14.1	18.9
4. Ethylacetate	6.02	6.27	1.3724	38.1	17.1	11.5
5. Benzene	2.28	0.0	1.5011	34.5	0.1	8.2
6. Tetrahydrofurane	7.58	5.84	1.4072	37.4	20.0	8.0
7. 1,4-Dioxane	2.21	1.50	1.4224	36.0	14.8	10.8

[a] The values of dielectric constant (ε), dipole moment (μ) and refractive index (n) were taken from fer. 12. [b] The empirical solvent polarity parameter E_T^{15}. [c] Donor-number of solvents DN^{16}. [d] Acceptor-number of solvents AN^{16}.

Table 3. A comparison of the observed rate constants and the calculated rate constants from (4) at 25 °C in several solvents.

Solvent	k_{obs} 1 mol^{-1} sec^{-1}	k_{calc} 1 mol^{-1} sec^{-1}
1. Chloroform	1.17×10^{-3}	1.26×10^{-3}
2. Dichloromethane	8.85×10^{-4}	8.02×10^{-4}
3. Acetonitrile	2.09×10^{-4}	2.13×10^{-4}
4. Ethylacetate	6.10×10^{-5}	6.14×10^{-5}
5. Benzene	1.33×10^{-4}	1.35×10^{-4}
6. Tetrahydrofurane	6.80×10^{-5}	6.96×10^{-5}
7. 1,4-Dioxane	5.64×10^{-5}	5.55×10^{-5}

ters good correlation can always be found without necessarily expressing a physical meaning. However, a comparison between the present work and previous works of similar reactions where the mechanisms have already been established, ought to give further information about the usability of (4). Thus, a statistical treatment for the data given by Kiselev and Miller [20], for the reaction between 9,10-dimethylanthracene and TCNE has been analysed in a similar way. The resulting equations, (5) and (6), have nearly the same weight coefficients:

$$\log k_{obs} = 3.67 + 0.068\ \mathrm{AN} \quad (r = 0.89)\,, \tag{5}$$

$$\log k_{obs} = -\,0.28 + 10.1\,(n^2 - 1)/(n^2 + 2) + 1.7(\varepsilon - 1)/(2\,\varepsilon + 1) + 0.105\ \mathrm{AN} \quad (r = 0.99)\,. \tag{6}$$

Table 2 represents the different physical parameters of the solvents used in the present work. The good agreement between the observed rate constants and those reproduced by (4) is shown in Table 3, indicating the excellent fitting of (4) to our experimental data.

The overall thermodynamic parameters of activation enthalpy, ($\Delta H^{\neq}$), and entropy ($\Delta S^{\neq}$) of activation, for the reaction in different solvents are collected in Table 4. The $\Delta H^{\neq}$ values are of the same magnitude for all the investigated solvents, except for chloroform and dichloromethane, where the values are approximately the halves of the others. The large negative entropies of activation are in agreement with a concerted polar cyclic, but non-synchronous one-step mechanism [21]. The $\Delta S^{\neq}$ values for the reaction in chloroform and dichloromethane are also less negative. It is suggested that the character, and the role of the EDA-complex as an intermediate in the reaction path may be the main reason for the observed differences of the activation parameters of chloroform and dichloromethane. The following scheme represents the assumed reaction steps:

$$\mathrm{DMH} + \mathrm{TCNE} \overset{K}{\rightleftarrows} \text{EDA-complex} \xrightarrow{k_1} (\mathbf{III}),$$

(Scheme 1)

where K (1 mol^{-1}) is the equilibrium constant of EDA-complex and k_1 (sec^{-1}) is the first-order rate constant of formation of the vinyl cyclobutane derivative (**III**). The equilibrium constant K measured independently by extrapolation of the absorbance to $t = 0$, using the Benesi-Hildebrand equation (1) [13], are represented in Table 4 for different solvents. It is seen that the K values are very small in electron-donor solvents, whereas the values in chloroform and dichloromethane are comparable with other solvent systems studied [22].

The effect of the EDA-complex formation, as represented in Scheme 1, was treated according to the method of Andrews and Keefer [24, 25]. It was found that the observed rate constant, k_{obs} is related to k_1 and K as follows:

$$k_{obs} = k_1\,K/(1 + K\,[\mathrm{DMH}]) \tag{6}$$

Table 4. Equilibrium constant of EDA-complex formation, observed rate constant at 25 °C[a], observed enthalpy and entropy of activation of the reaction in several solvents.

Solvent	K 1 mol^{-1}	k_{obs} 1 mol^{-1} sec^{-1}	$\varDelta H^{\neq}_{obs}$ kJ mol^{-1}	$-\varDelta S^{\neq}_{obs}$ J mol^{-1} deg^{-1}
1. Chloroform	0.90 ± 0.05	1.17×10^{-3}	20.0 ± 2	36.0 ± 2
2. Dichloromethane	1.35 ± 0.07	8.85×10^{-4}	17.0 ± 2	48.0 ± 3
3. Acetonitrile	~ 0.05	2.09×10^{-4}	43.0 ± 3.5	170.0 ± 4
4. Ethylacetate	–	6.10×10^{-5}	52.0 ± 3	150.0 ± 4
5. Benzene	$0.27^{b} \pm 0.02$	1.33×10^{-4}	51.0 ± 3	146.0 ± 4
6. Tetrahydrofurane	$\sim 10^{-3}$	6.80×10^{-5}	64.0 ± 4	110.0 ± 4
7. 1,4-Dioxane	$\sim 10^{-3}$	5.64×10^{-5}	54.0 ± 4	143.0 ± 4

[a] Calculated by interpolation of the kinetic data in Table 1.
[b] Corrected by taking in consideration the K value between Benzene and TCNE[28].

Table 5. The observed and calculated equilibrium constants for the EDA-complex formation, calculated rate constant of the adduct formation (**III**) and some thermodynamic parameters in chloroform and dichloromethane.

Solvent	t °C	$K_{obs} \pm 0.1$ 1 mol^{-1}	K_{calc} 1 mol^{-1}	$k_1 \times 10^3$ sec^{-1}	$\varDelta H^{\neq}_1$ kJ mol^{-1}	$\varDelta S^{\neq}_1$ J mol^{-1} deg^{-1}	$\varDelta H_0 \pm 2.0$ kJ mol^{-1}	$\varDelta S_0 \pm 4.0$ J mol^{-1} deg^{-1}
Chloroform	15.43	1.28	1.26	0.814	37.61	−173.2	−20.8	−70.0
	25.06	0.90	0.89	1.50				
	35.36	0.73	0.72	2.46				
Dichloromethane	15.43	1.70	1.68	0.510	30.35	−202.4	−16.2	−51.8
	25.06	1.35	1.34	0.821				
	35.36	1.09	1.07	1.26				

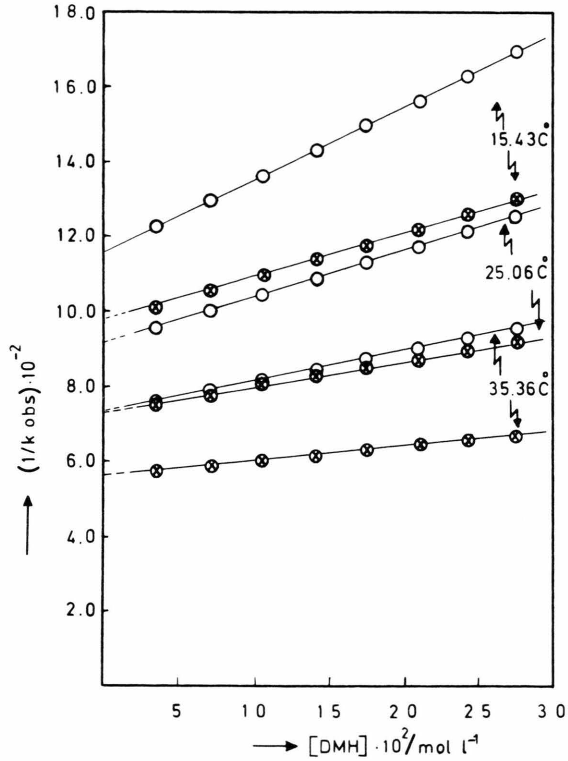


Fig. 2. Dependence of the observed rate constants, k_{obs}, on the DMH concentration for the reaction between TCNE and DMH in ⊗ chloroform and ○ dichloromethane.

or

$$1/k_{obs} = 1/k_1 K + [\mathrm{DMH}]/k_1 \qquad (7)$$

in which the [DMH] ≫ [TCNE].

The values of K and k_1 were calculated by measuring the kinetics of the reaction at different concentrations of DMH using (7). These values, and the values of K_{obs} (1 mol^{-1}) using the method of Benesi-Hildebrand, are shown in Table 5 for the reaction in chloroform and dichloromethane. Figure 2 represents the corresponding values at different temperatures fitted to (7). The agreement between the observed and calculated equilibrium constants is very good, strongly indicating that the EDA-complex takes place as an intermediate during the reaction. Unfortunately, these observations alone cannot distinguish whether Scheme 1 is correct, or the EDA-complex is formed in a dead-end equilibrium reaction*. However, the values of the observed enthalpy of activation ($\varDelta H^{\neq}_{obs}$) are much lower for reactions represented by Scheme 1 than those expected for the dead-end equilibrium reactions where $\varDelta H^{\neq}_{obs}$ will be independent on the enthalpy of complex formation ($\varDelta H^0$), but dependent

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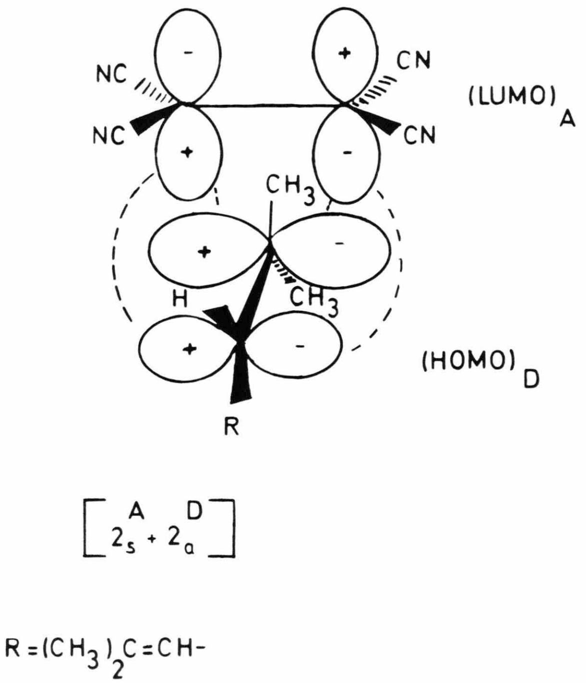
* EDA-complex $\overset{K}{\rightleftharpoons}$ DMH + TCNE $\xrightarrow{k_2}$ (**III**), and the observed rate constant, k_{obs} is related to k_2 and K as follows [23, 24], $k_{obs} = k_2/(1 + K\,[\mathrm{DMH}])$.



on ΔH^0 in Scheme 1:

$$\Delta H^{\neq}_{\text{obs}} = \Delta H^{\neq}_1 + \Delta H^0 \tag{8}$$

where $\Delta H^{\neq}_1$ is the enthalpy of activation for conversion of complex into vinyl cyclobutane (**III**). The negative values of ΔH^0 will decrease the observed enthalpy of activation. Sufficiently negative ΔH^0 might also give rise to negative $\Delta H^{\neq}_{\text{obs}}$ [20]. ΔH^0 and $\Delta H^{\neq}_1$ values for the present reaction in chloroform and dichloromethane are tabulated in Table 5. It is seen that the $\Delta H^{\neq}_{\text{obs}}$ values are nearly equal to the sum of $\Delta H^{\neq}_1$ and ΔH^0. The low enthalpy of EDA-complex formation in the other solvents is expected due to the competition of these solvents as electron-donor with DMH, leading to $\Delta H^{\neq}_{\text{obs}} \approx \Delta H^{\neq}_1$. This effect, and the large negative entropy of activation (Table 5), as well as the solvent dependent rates of the reaction, led us to conclude that the reaction probably proceeds through an EDA-complex via a cyclic polar-transition state similar to that postulated for Wittig reaction [25, 26], where the rates of the reaction in carbon tetrachloride, chloroform and cyclohexane are greater than in acetonitrile and dimethylformamide.

The proposed mechanism of the present reaction is in accordance with the frontier molecular orbital theory proposed by Epiotis, [4] and Fukui et al. [5]. Although it is true that a concerted-electron transfer process cannot be excluded in the present reaction, since $I_p - E_A - 4$ is only 1.34 eV, a concerted cycloaddition of the type $[2_s^A + 2_a^D]$ is however, more likely for good donor-acceptor pairs [27], which is the case in the present reaction.

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