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Experimental Proof That the Diels–Alder Reaction of Tetracyanoethylene with 9,10-Dimethylanthracene Passes through Formation of a Complex between the Reactants

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Abstract: Up to the present, it has been considered impossible to determine kinetically whether the complex often formed between diene and dienophile is a true intermediate in the Diels–Alder reaction. A method based on the effect of temperature on the reaction rates has been tested and found successful in proving that the complex formed by tetracyanoethylene and 9,10-dimethylanthracene is indeed a true intermediate in the Diels–Alder reaction of those molecules.

For nearly 50 years, the Diels–Alder reaction (DAR) has been employed as an important method of synthesis of carbocyclic and heterocyclic compounds. In the last 2 decades, the mechanism of the reaction has been given considerable attention.[2-5] The influence of substituents both in the diene and in the dienophile[6] and the nature of the effects of solvents,[7,8] pressure,[9] catalysts,[3,4] and other factors have been investigated.

Experiment and theory indicate that the transition state in the DAR comes about by a closely concerted and symmetric interaction of the π-electron systems of the reactants.[2-5] Nevertheless, the interpretations of the experimental kinetic parameters are often complicated by remarkably strong interactions between the reactants and the solvent, the transition state and the solvent, and even between the reactants themselves. The latter interaction often results in an electron donor–acceptor molecular complex (MC) as shown by a charge-transfer band in the ultraviolet spectrum[10] before reaction.

The effect of such complex formation on the DAR was first treated by Andrews and Keefer.[11-13] For the two possible pathways from reactants A and B to adduct P:

$$A + B \rightleftharpoons MC \xrightarrow{k_1} P \tag{1}$$

$$MC \rightleftharpoons A + B \xrightarrow{k_2} P \tag{2}$$
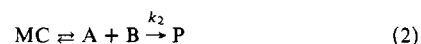
it was shown that the experimental rate constant, k_{exp}, is related to k_1 and k_2 as follows:

$$k_{exp} = k_1 K/(1 + K[B]) \tag{3}$$

$$k_{exp} = k_2/(1 + K[B]) \tag{4}$$

where K is the equilibrium constant for the formation of MC and $[B] \gg [A]$. The observed decrease of k_{exp} with increase of $[B]$ in the DAR of anthracene and 9,10-dimethylanthracene with maleic anhydride and some of its derivatives was in agreement with eq 3 and 4. Furthermore, the value of K for the complex formed by 9,10-dimethylanthracene and maleic anhydride obtained by those equations from the rate data agreed well with the value obtained directly from the zero-time optical densities by the usual spectroscopic procedure. Although their data could not distinguish between pathways 1 and 2, they showed that the principal effect of the concentration change of the reactants

was due to the complex formation rather than to change in the activity coefficients. Their analysis has been confirmed by work with other DAR.[14]

Although eq 3 and 4 indicate that pathways 1 and 2 are kinetically indistinguishable at constant temperature, they also suggest that the pathways might be distinguishable by the effect of temperature on the k_{exp} values via the dependence of K on temperature. By suitable choice of K and $K[B]$ values, we have found that this is true as is shown below.

The reactants chosen for the demonstration were 9,10-dimethylanthracene (DMA) and tetracyanoethylene (TCNE). Not only did this choice provide suitable magnitudes of K and k_{exp}, but it also avoided complications due to cis-trans diene equilibria, endo-exo forms of adduct, polymerization reactions, and reversibility of adduct formation. The rates of reaction were very high in most of the solvents used but were conveniently measured by the stopped-flow technique.

The results show that pathway 1 is followed, i.e., that the complex is a true intermediate, lying on the reaction coordinate, and does not enter merely through a side reaction of the free donor and acceptor molecules.

Experimental Section

Materials. 9,10-Dimethylanthracene (K & K Laboratories, Plainview, N.Y.) was recrystallized from benzene-n-hexane (1:2) and was then put through an Al_2O_3 column, mp 182–183° (lit.[15] 183.5–184.5°). Spectral purity of this DMA was confirmed by the lack of absorption in the range 350–400 nm by its solution to which a slight excess of maleic anhydride had been added. TCNE (Eastman Organic Chemicals) was sublimed twice in vacuo (4–5 Torr) [snow-white needles, mp 198–200° in sealed tube (lit.[16] 198–200°)] and was stored in the dark under nitrogen.

Acetonitrile was purified by the method of Brown and Cookson.[17] The other solvents were purified by the usual methods.[18] Absence of hydrolysis of TCNE in the aromatic solvents was verified in all cases by spectrophotometric observation of the whole CT band of the complex formed with the solvent. In the nonaromatic solvents, a few drops of an aromatic solvent was added to the TCNE to form a complex. In all solvents, the CT bands (maxima, 420–450 nm) remained unchanged over a period of 10–20 hr.

Kinetic Measurements. A Durrum-Gibson Model D-108 stopped-flow apparatus was used for the rate measurements. Improvements were made in its thermostating devices. The water was circulated directly from the thermostat rather than by the heat-exchanger system, and separate jackets were constructed for the reservoir syringes.

For thermostat temperatures different from ambient by ±10–20°, a small temperature gradient is apt to occur between the observation cuvette and the drive syringes.[19] In addition to the uncertainty it causes in the temperature of the cuvette, this thermal gradient gives rise to density gradients in the system in the cuvette with the result that the absorbance measurements fluctuate. We found that the temperature gradient and its effects were removed by driving four to five fillings of the reaction system through the cuvette immediately before making the measurements.

The mixing was tested before and after the kinetic runs by measuring the change in the optical density at 400 nm of a DMA solution on mixing with pure solvent in the apparatus. Within the experimental error of less than ±2%, the changes obeyed Beer's law and were independent of which syringe was used for solvent and which for solution.

For measurements in nonaromatic solvents, a large excess of TCNE was used to give pseudo-first-order rates by the equation, $k_{exp} = (2.303/t[TCNE]) \log (d_0/d_t)$, where d_0 and d_t are the optical density at zero time and time t, respectively. This was especially useful because of the high rates (half-lives were 10–20 msec) and the resultant large effect that would be produced by the dead time (2–5 msec) for second-order conditions. Figure 1 shows a typical set of measurements made by this procedure. The wavelengths used always lay in the range 400 ± 5 nm, where the DMA has a high extinction coefficient in the nonaromatic solvents.
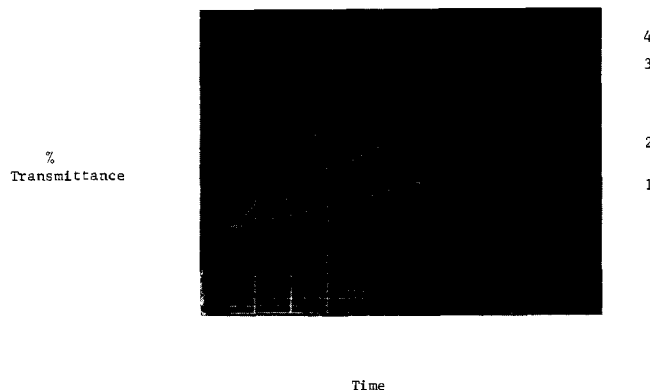

Time

Figure 1. Oscillogram of Diels-Alder reaction of TCNE with 9,10-dimethylanthracene (DMA) in acetonitrile at 40.4°. Full ordinate scale, 0–100%; time scales, 1,2,5,10 msec per large division; $[TCNE]_0 = 8.78 \times 10^{-4} M$; $[DMA]_0 = 4.85 \times 10^{-5} M$. $k_1 = 4.20 \times 10^4$, $k_2 = 4.27 \times 10^4$, $k_3 = 4.26 \times 10^4 M^{-1} sec^{-1}$. Average k for six such determinations = $4.25 (\pm 0.04) \times 10^4 M^{-1} sec^{-1}$ (see Table I).

In the aromatic solvents, equal concentrations of reactants were used because of the convenience in following the reaction by the decrease in absorbance of the complex of TCNE with solvent. Here, the rates were low enough to render negligible the effect of dead-time uncertainty. The rate constants were calculated by the equation, $k_{exp} = (\epsilon l/t)[(1/d_t) - (1/d_0)]$, where ϵ is the molar absorptivity, l the path length, and d_t and d_0 are as before. The effective ϵ values were obtained by separate measurements of TCNE solutions. With the aromatic solvents, the wavelength was kept constant somewhere in the neighborhood of the maximum of the CT band of the solvent-TCNE complex, i.e., 430–440 nm.

The same stock solutions were used at all temperatures for each system in order to minimize the effect of variation of the low concentrations of the reactants expected according to eq 3 and 4. As shown by the observed rate constants (Table I) for the dichloroethane and chloroform systems, the concentration effect was not large and did not obscure the effect of temperature.

Results and Discussion

Earlier work has produced evidence favoring pathway 1, in which the product is formed directly from the MC rather than from the free reactants. For example, the structures and behaviors of the MC have been found so closely similar to those of the transition state in several DAR as to indicate that pathway 1 rather than pathway 2 is followed.[5,11,17,20] In one case, the MC has been isolated and, after purification, has, in the neat condition, spontaneously formed the adduct.[21]

Despite the attractiveness of the earlier evidence, none of it has excluded pathway 2. We have found a more certain method of determining which path is followed. The method is based on eq 3 and 4 which show that, if $K[B] \ll 1$ then, for pathway 1, $k_{exp} = k_1 K$ whereas, for the other route, $k_{exp} = k_2$. Under those conditions, $\Delta H^{\ddagger}_{exp} = \Delta H^{\ddagger}_1 + \Delta H^{\circ}_{MC}$ for pathway 1, where $\Delta H^{\ddagger}_{exp}$ is the observed enthalpy of activation, $\Delta H^{\ddagger}_1$ is the enthalpy of activation for the passage of the MC to the transition state, and ΔH°_{MC} is the enthalpy of formation of the complex from the free reactants. For the other pathway, $\Delta H^{\ddagger}_{exp}$ is independent of ΔH°_{MC}.
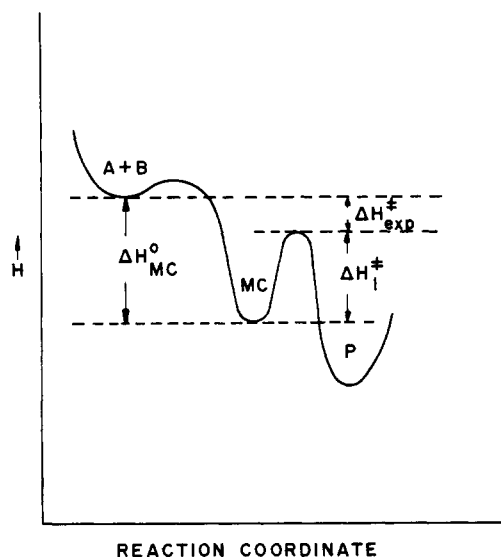
Figure 2 shows the enthalpy profile for pathway 1 and the interrelation of the three enthalpy changes defined above. As the figure shows, if the complex is so strongly bound that ΔH°_{MC} is of greater magnitude than $\Delta H^{\ddagger}_1$, the observed enthalpy of activation, $\Delta H^{\ddagger}_{exp}$, will be negative, a result that is impossible for pathway 2 according to eq 4.

The choice of reactants, TCNE and DMA, was made to provide both the large K and the low $K[B]$ product needed without producing rates that were inconveniently low.

Table I. Rate Constants[a] and Activation Parameters of the Diels–Alder Reaction of 9,10-Dimethylanthracene with Tetracyanoethylene in Several Solvents

Solvent	$[TCNE]$, $M \times 10^4$	k_{exp}, M^{-1} sec^{-1} × 10^{-3} (temp, °C)				$\Delta H^{\ddagger}_{exp}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{exp}$, e.u.
1. o-Xylene	10.55[b]	0.790 (13.5)	0.816 (14.7)	1.050 (25.0)	1.605 (40.2)	4.38	−30
2. Toluene	8.44[b]	2.29 (13.5)	2.81 (25.0)	3.79 (39.4)	3.81 (40.2)	2.85	−33
3. Benzene	6.56[b]	7.60 (13.5)	8.48 (25.0)	10.8 (39.4)	10.4 (40.2)	1.73	−35
4. Acetonitrile	8.78	46.5 (12.0)	43.5 (25.1)	42.5 (40.4)		−1.19	−41
5. Dichloromethane	6.53	150 (12.0)	136 (25.3)			−1.79	−41
6. 1,2-Dichloroethane	4.67	111 (11.8)	110 (24.9)	89.5 (40.4)		−1.93	−42
	8.75	102 (12.9)	92.7 (24.9)	83.0 (36.1)		−2.07	−43
	8.90	96.0 (12.4)	89.0 (24.9)	83.6 (36.1)	81.3 (43.1)	−1.64	−41
7. Chloroform	3.94	290 (14.0)	260 (24.6)	216 (39.4)		−2.67	−43
	4.20	278 (12.0)	214 (25.1)	185 (40.4)		−3.12	−44.5
	4.70	263 (11.1)	226 (24.8)	190 (42.8)		−2.43	−42
8. CCl$_4$	3.34		40.16 (25.0)				
9. n-Hexane	0.805		14.35 (25.0)				

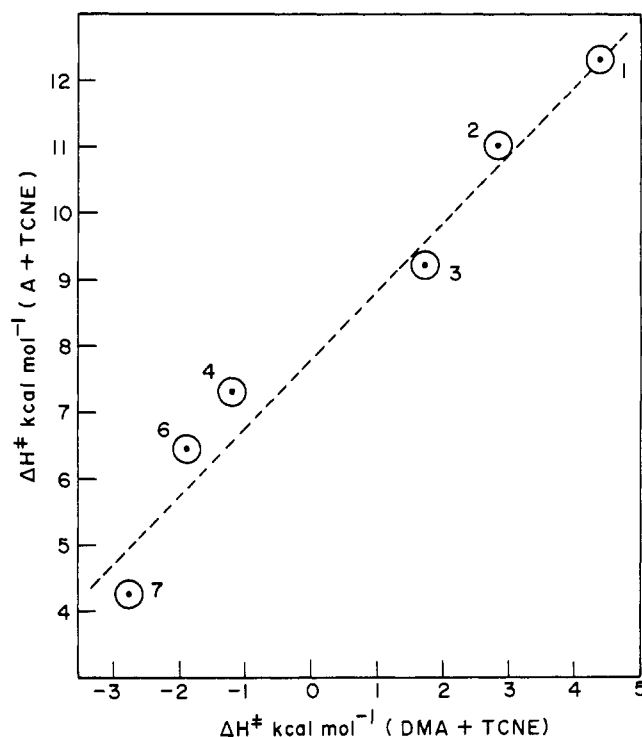[a] At least five runs were used to obtain each rate constant. [b] [TCNE] equals [DMA]. Otherwise [TCNE] ~ 20[DMA].

Figure 2. The enthalpy profile for pathway 1 in which the complex (MC) is a true intermediate.

Figure 3. Correlation of $\Delta H^{\ddagger}_{exp}$ values as functions of solvent for the anthracene-TCNE and 9,10-dimethylanthracene-TCNE reactions.

Using the ionization potential value, 7.04 eV, found for DMA by Konovalov and Kiselev,[22] we estimated a value of K at 25° equal to 150 M^{-1} in CH$_2$Cl$_2$ on the assumption that the MC obeys the same dependence on ionization potential as found for the methylbenzenes.[23] Accordingly, extremely low [B] values were used to approximate the K[B] requirement. As the results in Table I show, the choice was satisfactory and resulted in negative values of $\Delta H^{\ddagger}_{exp}$ in the nonaromatic and more polar solvents, where smaller $\Delta H^{\ddagger}_1$ values probably occur.[14] This constitutes the first experimental proof that a DAR follows pathway 1 rather than pathway 2.

Thompson and Holder[14] studied both the MC and the rates of the DAR of TCNE with benz[a]anthracene and 9-bromoanthracene in CCl$_4$, chloroform, and benzene at two different temperatures in each solvent. From the values of K obtained, they evaluated k_1 and k_2 from k_{exp}. Although their systems were such that $\Delta H^{\ddagger}_{exp}$ was never negative, their results showed the large differences between $\Delta H^{\ddagger}_1$ and $\Delta H^{\ddagger}_2$ produced by ΔH°_{MC} as explained above. Their $\Delta S^{\ddagger}_{exp}$ values, like those we obtained (Table I), were large and negative and, although of slightly lower magnitude in the aromatic solvent benzene, were relatively less affected by the solvent than the $\Delta H^{\ddagger}_{exp}$ values.

Brown and Cookson[17] measured $\Delta H^{\ddagger}_{exp}$ and $\Delta S^{\ddagger}_{exp}$ for the reaction of TCNE with anthracene in 16 different solvents, including nearly all of the solvents used in our experiments. Their $\Delta H^{\ddagger}_{exp}$ values showed a solvent dependence nearly identical with that which we observed. Figure 3 shows that correlation and indicates that the DAR of TCNE with anthracene also follows pathway 1. The plot suggests that the TCNE-anthracene reaction would exhibit a negative $\Delta H^{\ddagger}_{exp}$ value in a solvent that would stabilize the slightly polar transition state more than chloroform does. The $\Delta S^{\ddagger}_{exp}$ values obtained by Brown and Cookson also show a variation with solvent similar to our values. They showed that their data were consistent with the direct conversion of the complex into the adduct.

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Solvolysis of 1-Quadricyclylcarbinyl 3,5-Dinitrobenzoate

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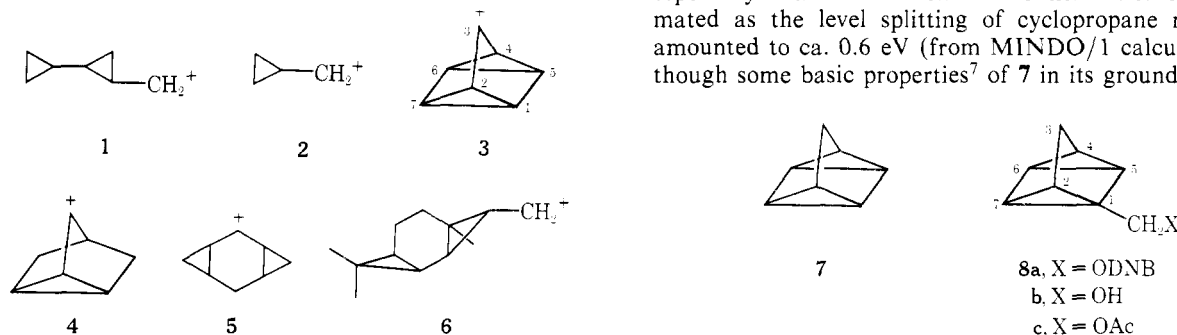
Abstract: 1-Quadricyclylcarbinol (**8b**) was synthesized from 2-norbornadienylcarbinyl acetate (**9c**), and 3,5-dinitrobenzoate of **8b** was solvolyzed in 60% aqueous acetone at 25° to yield three isomeric alcohols, **9b, 10b, 11b**, and three isomeric dinitrobenzoates, **9a, 10a, 11a**. 1-Quadricyclylcarbinyl 3,5-dinitrobenzoate (**8a**) solvolyzed 120 million times faster than cyclopropylcarbinyl 3,5-dinitrobenzoate. The extremely great stabilization of 1-quadricyclylcarbinyl cation was explained by the strain relief (70–75%) and the cyclopropyl–cyclopropyl interaction (25–30%). The charge delocalized form **15** derived from the cyclopropyl–cyclopropyl interaction (characterized by MO calculations) satisfactorily explained the product distribution.

The remarkable facility of cyclopropane rings to stabilize carbonium ions has attracted much attention of organic chemists.[1] Experimental and theoretical approaches have clarified that the great stabilization is attained by a conjugation between the vacant p orbital at the carbinyl carbon and $sp^{4.12}$ hybrid orbital in the plane of cyclopropane.[1b]

However, little attention has been given to systems endowed with a possibility of cyclopropyl–cyclopropyl interaction[2] despite its great theoretical interest and the extensive structural variations possible. An extra stabilization, if any, of a generalized ionic system (**1**) compared with cyclopropylcarbinyl cation (**2**) is attributable to the assumed cyclopropyl–cyclopropyl interaction. Thus, 3-quadricyclyl *p*-bromobenzenesulfonate (**3**-OBs) solvolyzes only 15 times faster

1   2   3

4   5   6

than the corresponding nortricyclyl derivative (**4**-OBs).[3] However, that **3**-OBs is only two to three times more reactive than cyclopropylcarbinyl-OBs[4] implies that no significant assistance is attained by the introduction of cyclopropyl of inappropriate arrangement in **3**, in contrast to the energetically additive effect observed for cyclopropyl rings in bis(cyclopropyl)carbinyl systems such as **5**.[5] No or little extra stabilization was observed for the system **6**.[4b] The cyclopropyl–cyclopropyl interaction, therefore, has no significant contribution to the stabilization of **3**, **5**, or **6**. From their theoretical approaches, Wilcox et al.[6] discussed poor transmission of substituent effect of the cyclopropyl rings on stabilization (or destabilization) of **2**.

The regiospecificity and stereospecificity of the cycloaddition reaction of quadricyclane (**7**)[2a] with dienophiles, however, are best interpreted by an unusually effective cyclopropyl–cyclopropyl interaction in quadricyclane (**7**) especially in a transition state. The interaction energy estimated as the level splitting of cyclopropane ring bonds amounted to ca. 0.6 eV (from MINDO/1 calculation), although some basic properties[7] of **7** in its ground electronic

7   8a, X = ODNB
           b, X = OH
           c, X = OAc

state have the value of normal cyclopropane. It seems quite likely that only the arrangement of the two cyclopropane rings in nearly parallel and in close proximity afforded such