Are Charge-Transfer Complexes Intermediates in Diels-Alder Reactions? A Case Study of the Reaction of 1,2-Dimethylenecyclopentane with Tetracyanoethylene

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The Diels-Alder reaction of 1,2-dimethylenecyclopentane (**1**) and tetracyanoethylene (TCNE) is kinetically studied by conventional and stopped-flow UV/Vis absorption-spectroscopic techniques. A transient charge-transfer (CT) absorption band with λ_{max} = 490 nm (half-life at 20°C ca. 3.4×10^{-2} s) is detected in dichloromethane solution. For the molar extinction coefficient a value of $\varepsilon_{490} = 310\ \text{M}^{-1}\ \text{cm}^{-1}$ has been determined from measurements of the optical density at zero time as a function of excess diene concentration. With the aid of computer simulation the combined kinetic analysis of the disappearance of reactants and CT complex reveals that the data obtained from experiments at equimolar concentration and at a single temperature (20°C) can be interpreted equally well by both the model where the CT complex is an intermediate on the reaction path and where it is in a nonreactive side equilibrium with the reactants. Activation parameters have been determined for the disappearance of the starting compounds and of the CT complex. Contrary to what is expected for a CT complex being an intermediate in a concerted Diels-Alder reaction a more negative activation entropy for the decay of the CT complex than for the disappearance of the reactants is found. This suggests that the CT complex is unlikely to exhibit a transition-state-like structure as is required for a concerted cycloaddition. Experiments under pseudo-first-order conditions have led to an extension of the reaction scheme by a second-order reaction of the CT complex with the excess diene, the rate constant of which is virtually identical to that for the direct bimolecular cycloaddition. The conclusion is drawn for our case that there are more arguments against than arguments for the CT complex being a preorientation complex in the [4+2] cycloaddition.

Soon after the discovery of the general principle of the Diels-Alder cycloaddition in 1928[1], Kuhn and Wagner-Jauregg[2] reported the observation of transient colors during the course of these reactions. This phenomenon has been observed many times in later years and its significance for the mechanism of the Diels-Alder reaction has been under discussion ever since[3]. Mulliken's theory of charge-transfer (CT) complexes[4] provided an explanation for the origin of the new absorption band which occurred on mixing solutions of an electron donor diene and an electron acceptor olefin. It did not, however, provide any information about the role of these species in the cycloaddition.

The questions asked centered around the problem whether the CT complex is an intermediate [eq. (1)] or whether it is in a non-reactive side equilibrium with the reactants [eq. (2)]. An implication of eq. (1) has been that the intermediate complex constitutes a preorientation of the reactants similar to the transition state for a concerted cycloaddition[3], in particular since the rules of conservation of orbital symmetry implicated a structure of the transition state for [4 + 2] cycloadditions.

$$\text{A} + \text{B} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \text{AB}_{\text{CT}} \xrightarrow{k_1} \text{P} \qquad (1)$$

$$\text{AB}_{\text{CT}} \underset{k_+}{\overset{k_-}{\rightleftharpoons}} \text{A} + \text{B} \xrightarrow{k_2} \text{P} \qquad (2)$$

Andrews and Keefer[5] pointed out that no decision concerning the reaction course, eq. (1) or eq. (2), can be made from rate measurements for the disappearance of the starting compounds at a single temperature. On the other hand, activation parameters may provide more definite information. Kiselev and Miller[6] postulated that the negative activation enthalpy they determined for the cycloaddition reaction of 9,10-dimethylanthracene with tetracyanoethylene (TCNE) in some solvents is evidence for a CT complex as an intermediate. However, a negative activation enthalpy only demonstrates that an intermediate is involved in the reaction. The nature of the intermediate remains an assumption, a CT complex being one possibility. More recently, Fukuzumi and Kochi[7,8] analyzed cycloaddition reactions of substituted anthracenes with tetracyanoethylene, where CT complexes were observed, and advanced the idea that the activated complex in these cycloadditions resembles the excited state of a CT complex, namely a radical-ion pair. This conclusion was derived from correlations of CT excitation energies with rate data and their analogy with some organometallic reactions where electron transfer actually had been observed. However, it might be questioned if these observations can be related to the significance of ground-state CT complexes in thermal Diels-Alder reactions.

In continuation of our interest in partial or complete electron transfer in the course of Diels-Alder reactions[9-11] we here present a paper in which we have studied the role of the CT complex in a more appropriate model reaction.

The majority of the published studies in this area involve aromatic compounds as diene component. Aromatic com-

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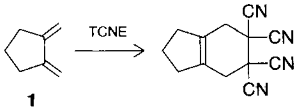
pounds in general are prone to form CT complexes[3,12]. Therefore, we selected the nonaromatic 1,2-dimethylenecyclopentane (**1**) as diene component. The reaction of **1** with TCNE produces the cycloadduct **2** in high yield[13]. If a CT complex between **1** and electron-acceptor olefins can be detected, its significance should be closer related to the cycloaddition than in the case where such a complex results from an aromatic "diene".



1 **2**

Results

Rapid-Scan Measurements: A variable-temperature stopped-flow spectrophotometer[14] was used to detect transient absorptions. The spectrometer is equipped with a rapid-scan unit which allows the recording of a spectrum within ca. 5 ms. When 0.1 – 0.2 M solutions of the reactants in dichloromethane were mixed at 20 °C a transient absorption with λ_{max} = 490 nm was recorded (Figure 1). This absorption disappeared completely within ca. 100 ms. Spectra were recorded at various times after mixing (see Figure 1). Approximate isosbestic points are present close to both ends of the absorption band. This indicated the formation of a new absorbing species during the decay of the CT absorption. This phenomenon will be discussed in more detail below.

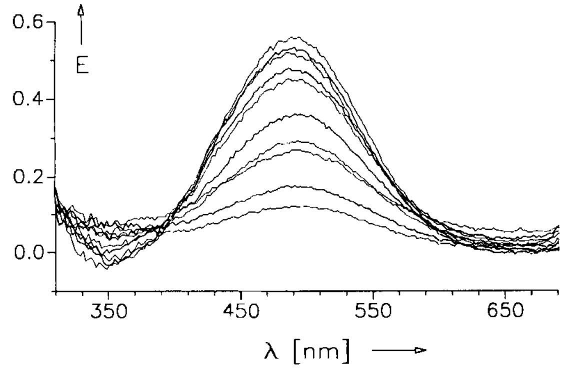


Figure 1. Transient absorption spectrum of the CT complex formed from **1** (*c* = 0.05 M) and TCNE (*c* = 0.05 M) in CH_2Cl_2 at 20°C; age times [s]: 0.003, 0.004, 0.006, 0.009, 0.013, 0.023, 0.035, 0.048, 0.066, 0.093

The equilibrium constant for complex formation was determined from time-resolved measurements of the optical density as a function of excess diene concentration, extrapolated to time zero. The nonlinear regression of $E_{t=0}$ vs. diene concentration (up to a 50-fold excess) yielded an equilibrium constant K = 1.3 ± 0.2 M^{-1} and $\varepsilon(\lambda_{max})$ = 301 ± 19 $M^{-1}cm^{-1}$ at 20°C. The small value of K corresponds to a small percentage of CT complex being in equilibrium with the reactants. The molar extinction coefficient is in general accordance with the expected values for CT complexes[12].

Kinetic Measurements: Both the decay of the starting material and of the CT complex were followed spectrophotometrically by the stopped-flow method at 20°C. The combined data were subjected to a curve-fitting program, based on numerical integration of the differential equations for the kinetic scheme under consideration[15]. Both reaction models [eq. (1) and eq. (2)] could be fitted with equal accuracy to the experimental concentration/time (*c/t*) profiles. The rate constants were determined as k_1 = 189 s^{-1} and k_2 = 298 $l\ mol^{-1}s^{-1}$ for model (1) and model (2), respectively. The fitting procedure provided no absolute values for k_+ and k_-. Lower limits for these rate constants were estimated from the fact that no buildup of the CT complex could be detected after the "dead time" (mixing time) of 2 ms of the stopped-flow device, i.e. the equilibrium is established within 2 ms. Thus, k_+ must be $\geq 10^4\ l mol^{-1}s^{-1}$. Since the equilibrium is established very fast we can safely assume that k_1 or k_2 are significantly smaller than k_+ and k_-. The quality of the fit depends on the ratio k_+/k_-, i.e. the equilibrium constant K. It is rewarding to see (and may be regarded as a support of the analysis) that the calculated equilibrium constants $K_{calcd.}$ = 1.58 and 1.65 M^{-1} for the fit on eq. (1) or eq. (2), respectively, are very close to the experimental value of K = 1.3 ± 0.2. The rate constants k_1 and k_2 for the two kinetic schemes are related by $k_2 = k_1K$[5], which is confirmed by the evaluated numbers. The basic result of these measurements is that the combined analysis of the *c/t* curves for the decay of the starting compounds and the CT complex at a single temperature does not allow a differentiation between the two schemes, i.e. it leads to the same conclusion as if only the decay of the starting compounds is analyzed[5].

Activation Parameters: As mentioned in the introduction, activation parameters constitute a separate body of information, which, in principle, may allow a discrimination between the two models as was shown by Kiselev and Miller[6] for a special case. In Table 1 we have collected the activation parameters which result from temperature-dependent measurements of k_1 and k_2 between 0 °C and 20 °C. Also included are values which were obtained from *c/t* curves for the disappearance of the starting diene, neglecting the presence of a CT complex, i.e. which are based on the conventional interpretation of the Diels-Alder reaction as a simple bi-

Table 1. Activation parameters for the cycloaddition reaction of **1** with TCNE according to different reaction schemes

Activation parameters	2nd order[a)]	CT-complex as Side reaction	CT-complex as Intermediate
E_a [kcal mol^{-1}]	4.1 ± 0.1	4.1 ± 0.2	2.5 ± 0.3
lg A	5.5 ± 0.1	5.5 ± 0.1	4.2 ± 0.3
$\Delta H^{\ddagger}$ [kcal mol^{-1}]	3.5 ± 0.2	3.6 ± 0.2	2.0 ± 0.3
$\Delta S^{\ddagger}$ [cal mol^{-1} K^{-1}]	−35.1 ± 0.6	−35.0 ± 0.7	−41.3 ± 1.2
$\Delta G^{\ddagger}$ [kcal mol^{-1}]	14.0 ± 0.01	14.0 ± 0.01	14.3 ± 0.02

[a)] Assuming no CT-complex formation.

molecular process. The latter values are almost identical to those where eq. (2) underlies the kinetic analysis. They are in line with many other kinetic measurements for Diels-Alder reactions where high negative activation entropies and moderately high activation enthalpies have been observed[16]. However, on application of eq. (1) a different picture results. A smaller activation enthalpy and a more negative activation entropy are obtained than for the scheme of eq. (2). In our opinion this observation contradicts the presumption that a CT complex resembles the activated complex in structure. Preorientation similar to the activated complex should correspond to a decrease in entropy and, therefore, the activation entropy for the second, monomolecular step – represented by the temperature dependence of k_1 – should be more positive than for a direct bimolecular cycloaddition. Thus, we conclude from the comparison of the activation parameters for the two reaction schemes that the CT complex is not, if at all, an intermediate which resembles the transition state of the cycloaddition. If the CT complex is indeed an intermediate then its structure is unlikely to be related to the transition state of the product-forming step.

Pseudo-First-Order Kinetics: A further set of kinetic experiments was carried out under pseudo-first-order conditions. On the assumption (which has been verified experimentally, see above) that the equilibrium between the CT complex and the reactants is established very fast and that a great excess of one of the reactants is applied, the kinetic equation for the disappearence of the total concentration $[A]_t$ of the minor component, uncomplexed and complexed, can be written as $-d[A]_t/dt = k_{exp}\,[A]_t$. The meaning of k_{exp} is different for the two models as can be seen from eq. (3) and eq. (4), where eq. (3) is related to the reaction scheme of eq. (1) and eq. (4) to that of eq. (2). For the decay of the CT complex identical expressions for k_{exp} were obtained. Simple inspection of the two equations reveals that at a very high excess of B the rate constant k_{exp} approaches the value of k_1 [eq. (3)] or of k_2/K [eq. (4)].

$$k_{exp} = \frac{k_1 K[B]_0}{1 + K[B]_0} \tag{3}$$

$$k_{exp} = \frac{k_2[B]_0}{1 + K[B]_0} \tag{4}$$

The values of k_1, k_2, and K, determined from measurements at equimolar concentrations of the reactants by application of the above described fitting procedure[15], were used to calculate "pseudo-experimental" concentration/time curves as a function of excess [B] (**1**). The "pseudo-experimental" rate constants k_{exp}^{pseudo}, obtained from these $[A]/t$ curves by a fit to a simple exponential, were plotted against $[B]_0$ (Figure 2, trace 1). Another, equivalent set of „experimental" rate constants k_{exp}^{pseudo} was calculated by insertion of k_1, k_2, and K into eq. (3), giving identical results.

The experimental decay traces of $[A]_t$ and $[AB]_{CT}$ from the "excess" measurements could be fitted perfectly to simple exponentials. The rate constants obtained from both the decay of $[A]_t$ and $[AB]_{CT}$ are slightly different, but within the accuracy of the technique identical. The plot of the experimental pseudo-first-order rate constants k_{exp} as a function of exess $[B]_0$ is shown in Figure 2. Obviously, k_{exp} increases approximately linearly with $[B]_0$ and does not converge towards the limiting values expected for the models represented by eq. (1) and eq. (2). Consequently, it has to be concluded that both models do not describe the experimental behavior correctly. A solution to the foregoing discrepancy was achieved by an extension of the kinetic scheme (Scheme 1).

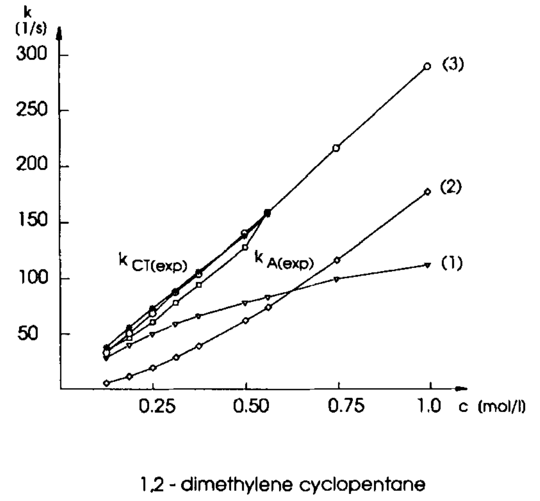
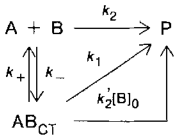


Figure 2. Experimental and calculated pseudo-first-order rate constants as a function of the excess diene concentration (c_{TCNE} = 0.0125 M, c_{diene} = 0.0125 – 0.600 M); see text for explanation

Scheme 1



An optimum solution was found when we included a pseudo-first-order process which describes a bimolecular reaction of the CT complex with the excess component B (**1**). The experimental rate constant k_{exp} for pseudo-first-order conditions now can be written as eq. (5).

$$k_{exp} = \frac{k_1 K[B]_0}{1 + K[B]_0} + \frac{k_2' K[B]_0^2}{1 + K[B]_0} \tag{5}$$

Since besides k_2' all constants in this equation had been determined from measurements at equimolar concentrations of the reactants, k_2' could be calculated from eq. (5). An average second-order rate constant of 300 l mol^{-1}s^{-1} was obtained. The magnitude of this constant is very similar to that of k_2 derived from the kinetic scheme of eq. (2). Taking the value for k_2' as starting point we recalculated all rate constants in the extended scheme with the aid of the above-mentioned optimization program, assuming that no direct product formation from the CT complex had occurred, i. e. eq. (2) has been supplemented by the additional bimolecular reaction of the CT complex with B. However, the analysis showed no differences in the calculated values of k_2' whether this approach is taken, whether eq. (1) is extended by the additional bimolecular reaction, or whether a combination of the two equations is used. The calculated equilibrium constant remained unchanged during reoptimization. The rate constants $k_2 = 284$ l mol^{-1}s^{-1}, and $k_2' = 297$ l mol^{-1}s^{-1} appear to be identical within the experimental error. Using these constants, we then calculated $k_{\text{exp}}^{\text{pseudo}}$ values from the synthetic *c/t* profiles for the "excess" measurements. Now, a linear relationship between $k_{\text{exp}}^{\text{pseudo}}$ and the concentration $[B]_0$ was obtained (see Figure 2, trace 3). Calculation of k_{exp} by insertion of the foregoing values into eq. (5) gave identical results. It can easily be seen that a strictly linear relationship, namely $k_{\text{exp}} = k_2[B]_0$ results from eq. (5) if k_1K becomes *numerically* equal to k_2'. Fortunately, this situation is fulfilled in our system (see above). Thus, the linear k_{exp} vs. $[B]_0$ relationship results from a compensating superposition of the second, quadratic term in eq. (5) (Figure 2, trace 2) with that of the first term (Fig. 2, trace 1) as a function of $[B]_0$.

The necessity to complement the schemes of eq. (1) or eq. (2) by a bimolecular reaction of the CT complex with the excess component in order to reproduce the observed linear dependence of k_{exp} on $[B]_0$ raises doubts whether model (1), in which the CT complex acts as an intermediate, is realized. If preorientation is a prerequisite for product formation then it does not seem to be reasonable that the preoriented complex further undergoes a bimolecular reaction to form the cycloadduct.

A similar bimolecular reaction of a CT complex, formed from *N,N*-dimethylaniline and TCNE, with excess *N,N*-dimethylaniline, has been postulated by Rappoport[17] and has been recently proposed for the [2+2] cycloaddition reaction of *N*-vinylcarbazole with dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate[18].

The Quasi-Isosbestic Points: The situation is slightly more complicated than described so far. The transient UV spectra (Figure 1) and the decay traces (Figure 3) of the CT complex showed after an initial fast disappearance of the CT band a residual absorption which "grew in" during the decay of the CT band. The decay of this secondary absorption was slower ($\tau_{1/2}$ = 1.9 s) than that of the primary CT complex ($\tau_{1/2} = 3.4 \times 10^{-2}$ s).

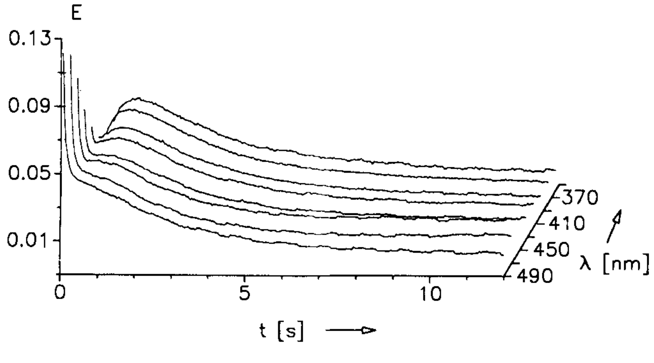


Figure 3. Decay of the absorption of the CT complex from **1** (c = 0.025 M) and TCNE (c = 0.025 M) in CH_2Cl_2 at 20°C as a function of time and wavelength, showing the formation and subsequent decay of a new absorbing species

Thus, a new species is formed which absorbs in the 300−600-nm range of the spectrum. The nature of this species is unknown so far. The molecule which comes to mind in this context is the radical anion of TCNE which indeed absorbs in this region of the spectrum[18,19]. The TCNE radical anion shows a characteristic, broad absorption at λ = 350−500 nm with numerous vibrational maxima of molar extinctions in the range of $\varepsilon = 4-7 \times 10^3$ M^{-1} cm^{-1}. Attempts to identify the TCNE radical anion by EPR spectroscopy were unsuccessful so far. Due to the transient nature of the additional absorption a stopped-flow equipment might be necessary for the EPR spectroscopic detection. Not knowing what the absorption spectrum of a zwitterion deriving from starting compounds A and B would look like, we cannot rule out such an intermediate. Trapping experiments with a variety of trapping agents (methanol, ethanol, *p*-nitrophenol, picric acid) were unsuccessful, however, making the zwitterion hypothesis rather unlikely. The buildup of the new species followed a first-order rate law with a rate constant of $k = 3.7 \pm 0.2$ s^{-1} at 20°C. This value is not equivalent to the experimental first-order rate constant ($k_{\text{exp}}^{298} = 20.3 \pm 0.7$ s^{-1}) obtained for the decay of the CT band from measurements at equimolar concentrations (5.0×10^{-2} M) of the starting compounds. This means that the formation of the secondary species is not directly related to the decay of the CT complex, i.e. it must originate form an undetected third intermediate which is formed during the disappearance of the CT complex. This is also the reason for the fact that no good isosbestic points habe been observed.

As shown below, we calculate the contribution of the reaction which produces the secondary absorption to be only of the order of about 2% of the total conversion of the substrates. The postulate of the formation of TCNE$^{\bullet-}$ would be in line with the measured optical density. If all starting material had been converted into TCNE$^{\bullet-}$ the optical density should have been much greater than that of the initial CT complex. When the kinetic scheme (Scheme 1) is supplemented by the additional reaction and again reoptimized no changes of the rate constants, $k_2 = 284$ l mol^{-1} s^{-1} and $k_1 = 297$ l mol^{-1} s^{-1}, are found, The rate constant for the additional first-order process is calculated to $k = 3.8$ s^{-1}, in good agreement with the experimental value. Even though the latter process participates only to the extent of a few percent it might be of general significance. It could indicate that the CT complex has the possibility to convert into radical ions, and it should be of interest to follow the fate of these radical ions, in particular to answer the question of whether they form the cycloadduct. In this respect a case has to be found where this additional process contributes more than just a few percent. One possibility seems to be an increase of the electron-donor capability of the diene. A kinetic analysis of examples where we observe thermal electron transfer from diene to dienophile[9,10] is in progress.

The above-mentioned rate constants allowed the calculation of the contribution of individual pathways to the decay of the reactants. For our models we calculated for equimolar concentrations of the reactants that 96% disappear via the CT complex [extended eq. (1)], or the direct cycloaddition of the substrates [extended eq. (2)], 2% by the bimolecular reaction of the CT complex with a reactant, and 2% by the additional, unidentified pathway. The latter process is thus insignificant in this case. Whether it also leads to the cycloadduct cannot be decided. A minor side product might have escaped detection by NMR spectroscopy. Due to the small equilibrium constant for formation the direct reaction of the CT complex with the diene substrate also contributes only to a very small extent. However, when the reaction is carried out in the presence of a fiftyfold excess of one reactant, i. e. about 50% of the minor component is present in complexed form, the contribution from this pathway increases to about 50% and now competes successfully with the direct cycloaddition (49%). This can easily be deduced from Figure 2.

Discussion

The problem of charge-transfer complexes in Diels-Alder reactions has been attracting attention for a long time. Weak interactions, and CT complexes have to be classified as such, may be important in determining the course of a reaction. The CT complex has been viewed as some kind of arrangement of diene and dienophile reflecting the structure of the transition state for a concerted cycloaddition. The transition structure of a concerted cycloaddition derives qualitatively from the rules of conservation of orbital symmetry and quantitatively from ab initio calculations[20] (in the latter case mainly for butadiene and ethylene). It is interesting to note that no theoretical calculation has given evidence for a CT complex prior to the transition state so far. The analogy between transition-state structure and CT complex structure may not be a good one since this suggests a static picture of the CT complex even though it is held together only by weak forces, i. e. there must be a lot of flexibility in such a complex.

Most of the quantitative work in this area has been carried out on aromatic compounds as diene component, in particular by using anthracene and its derivatives[5-7,21-23]. For the latter cases the presently accepted view is that the CT complex is an intermediate on the route to product formation. Such interpretations trace back mainly to the results of Kiselev and Miller[6] who reported a negative activation enthalpy for the reaction of 9,10-dimethylanthracene with TCNE, a fact which is indeed strong evidence for the intermediacy of a CT complex. Kiselev and Miller also cited earlier work by Brown and Cookson[20] and by Thomson and Holder[21] to be in agreement with their conclusions. The last-mentioned authors analyzed the rate and activation data for the cycloaddition reaction of benz[*a*]anthracene and 9-bromoanthracene with TCNE in terms of both the model in which the CT complex is an intermediate and in which it exists in a nonreactive side equilibrium. Thomson and Holder reached no conclusion as to which mechanism is followed, because not only the rate data but also the activation parameters appeared to be in agreement with both mechanisms. Later, Lofti and Roberts[22] assumed on the basis of Kiselev and Miller's results that the CT complex is an intermediate. They suggested that the solvent effects they observed in cycloaddition reactions of anthracene derivatives with TCNE are supporting the CT complex to be an intermediate. The more important results of these studies were the determination of thermodynamic properties of the CT complexes. Thus, the association constant of complex formation for anthracene and TCNE is small and rather strongly solvent-dependent (K_c (25°C) = 3.11 and 1.02 M^{-1} in CCl_4 and CH_2Cl_2, respectively). The enthalpy and entropy of formation ($\Delta H^\circ = -3.20 \pm 0.4$ and -2.70 ± 0.3 kcal mol^{-1}, $\Delta S^\circ = -8.6 \pm 1.2$ and -8.7 ± 0.8 cal $\text{K}^{-1}\,\text{mol}^{-1}$ in CCl_4 and CH_2Cl_2, respectively) are in agreement with those for CT complexes between chloranil and anthracene derivatives[20]. Kochi and co-workers[7,8] were also influenced by Kiselev and Miller. They provided analogies between correlations of rate data for cycloaddition with CT excitation energies and for rates of electron transfer for organometallic compounds with CT excitation energies, from which they derived an electron-transfer model for the transition state of the Diels-Alder reaction. Basically, their results do not show directly that the ground-state CT complex has to be an intermediate but they suggested that the excited state of the CT complex resembles the transition state.

Our study was initiated by several aspects: (i) It seemed not justified to us to extrapolate data for aromatic "dienes" to the whole area of normal Diels-Alder reactions. Therefore, we deliberately selected the aliphatic diene **1** as more typical of the majority of dienes which serve as cycloaddition substrates. Due to its synperiplanar structure any CT complex which might have been formed must include the active conformation of the molecule, thus eliminating any ambiguities arising from uncertain conformational situations. (ii) The possibility to carry out detailed kinetic measurements, including CT complex formation and disappearance, by using a variable-temperature stopped-flow equipment. (iii) The application of as many approaches as possible to obtain information from kinetic measurements, i. e. determination of rate constants at a single temperature, determination of activation parameters, measurements at eqimolar concentrations of the reactants, and measurements under pseudo-first-order conditions. (iv) The application of computer simulation programs to test various reaction models on the kinetic data.

Our principal results are: (a) TCNE and **1** form a transient CT complex with an association constant of $K = 1.3 \pm 0.2$ l mol^{-1} at 20°C. The molar extinction of the absorption maximum at $\lambda_{max} = 490$ nm is $\varepsilon = 301 \pm 19$ $\text{M}^{-1}\,\text{cm}^{-1}$. (b) The combined kinetic analysis of the *c*/*t* curves for both disappearance of the reactants and disappearance of the CT complex at a single temperature provides no information which goes beyond the kinetic analysis of the decay of the starting compounds. The data can be interpreted with the same accuracy by both models, i. e. no distinction is possible between the CT complex being a reaction intermediate or existing in a non reactive side equilibrium. (c) While the ΔG^{+} values are identical for both models (1) and (2) within experimental error, the activation enthalpies and entropies are different. The lower activation enthalpy would favor the CT complex as an intermediate for product formation. However, a more negative activation entropy is observed for the model where the CT complex is an intermediate. This is contrary to what is expected for the situation where the CT complex is a preoriented intermediate in the cycloaddition. Complex formation should be accompanied by a decrease in entropy, for instance, of ca. -8 cal $K^{-1}mol^{-1}$ for the system investigated by Lofti and Roberts[22]. Therefore, we would have expected a less negative value for the activation entropy than for the activation entropy for a direct cycloaddition of the starting compounds. Since our data reveal the loss of more activation entropy in going from the CT complex to the transition state for cycloaddition than starting from the free reactants, it seems unlikely that the CT complex is the assumed intermediate in this cycloaddition. (d) The kinetic measurements under pseudo-first-order conditions suggest that the reaction models are not complete. In order to reconcile the simulations with the experimental data an additional channel for product formation has to be included, which involves a bimolecular reaction of the CT complex with the excess diene component. Conceptually, this is also not in line with the picture of the CT complex as the intermediate which then forms the product in a monomolecular reaction. (e) Approximately 2% of the CT complex decays to a transient species which absorbs in the visible region of the spectrum. This process is tentatively interpreted as formation of the TCNE radical anion. As mentioned above, a zwitterion might be another possibility. Since no other product than the cycloadduct could be found it is assumed that this intermediate also forms the cycloadduct.

During the preparation of this manuscript a closely related study by Hall and co-workers[18] appeared in which the [2+2] cycloaddition reaction of N-vinylcarbazole with dimethyl 2,2-dicyanoethylene-1,1-dicarboxylate was investigated. A reaction scheme was proposed in which the CT complex is an intermediate. The case where the CT complex is in a nonreactive equilibrium was not considered. Our experience shows that it is impossible to distinguish between the two models, since the experimental decay of the CT complex is well simulated as a first-order process also under equimolar conditions. We believe that the data in ref.[18] would also fit the process where the formation of the CT complex constitutes a non reactive pathway. In agreement with our results Hall et al. observed an additional bimolecular reaction of the CT complex with the excess component.

Conclusion

The results of the above analysis of the cycloaddition reaction of **1**, as a typical aliphatic diene, with TCNE do not support the assumption that the CT complex is an intermediate which resembles the transition structure for cycloaddition. However, this does not mean that CT interactions are not important in determining the overall reactivity in the cycloadditions. They are the consequence of the perturbational reactivity model where the wave function of the transition state is approximated as a linear combination of ground-state and CT-excited-state wave functions. It does not require the formation of a ground-state CT complex. In view of the results of Kiselev and Miller[6] which can be interpreted as showing that a CT complex is an intermediate in that cycloaddition it does not seem to be appropriate to extrapolate our findings to the whole area of normal Diels-Alder additions and vice versa.

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Experimental

The cycloaddition reaction of **1** with TCNE has been described before[24]. The cycloadduct is formed in >90% isolated yield, and no other product could be detected by ^{1}H-NMR spectroscopy of the crude reaction mixture. All reactions and kinetic measurements were carried out in purified dichloromethane.

Stopped-Flow Measurements: The experiments were carried out with a Cryostopped-Flow spectrofluorimeter from HI-TECH Scientific[14]. The spectrometer is equipped with a Spectrascan MG-3000 unit which allows scans from 200 to 850 nm within ca. 7 ms. The apparatus can be thermostated from -100°C to $+60$°C with an accuracy of ±0.1°C. The spectrometer is connected to a Hewlett-Packard 300 desktop computer and uses the DataPro software suite of HI-TECH Scientific for acquisition, presentation, and analysis of kinetic data.

Kinetic Measurements: The disappearance of the reactants at λ = 270 nm was followed with a conventional spectrometer (Cary 219) at equimolar concentrations (5.0×10^{-5} M of the reactants in dichloromethane. The cell which was connected by optical wave guides to the spectrometer was introduced in a thermostated bath (±0.5°C) for measurements at low and ambient temperatures. The signal was directly recorded by a small dedicated computer which allowed the transfer of the data to a floppy disk. The stopped-flow kinetic measurements had to be carried out at higher concentrations, usually equimolar solutions of 5.0×10^{-2} M, in order to obtain a sufficient signal-to-noise ratio. Depending on the decay being followed, scan times ranged from < 1 s to ca. 20 s.

Evaluation of the Kinetic Data: A combined analysis of the *c/t* curves for the decay of reagents and CT complex was carried out with a MicroVAX GPX II and a FORTRAN program based on numerical integration[15]. The procedure was as follows: The decay curves for reactants were analyzed with a personal computer in terms of a second-order reaction taking into account possible absorbances of both reactants at the wavelength of measurements. The fits generally showed correlation coefficients >0.999. With the second-order rate constants obtained by this procedure decay curves were calculated at the same concentration where the CT complex kinetics had been carried out. The combined data sets were analyzed by a Simplex program[15] which enabled the test of different reaction schemes by adjusting the differential equations to the desired scheme. Numerical integration and a Simplex optimization process gave a set of rate constants from which decay curves could be calculated and compared with the experimental ones. The measurements were carried out at least twice, normally more than three times, with fresh samples. The reproducibility of the stopped-flow measurements was ca. ±5%, although a single data set could be fitted with higher accuracy. Systematic errors resulting from sample preparation, temperature measurements, etc. were also considered.

On this basis we estimated an accuracy of the rate and equilibrium constants of ca. ±5%.

CAS Registry Numbers

1: 20968-70-1 / **1** · TCNE: 135774-43-5 / TCNE: 670-54-2

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