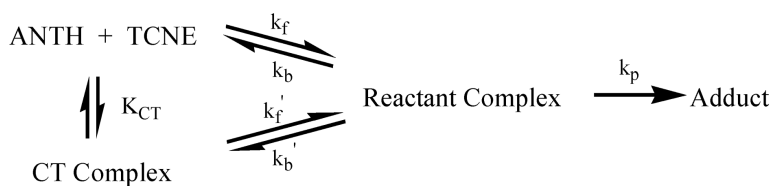


Resolution of the Non-Steady-State Kinetics of the Two-Step Mechanism for the Diels–Alder Reaction between Anthracene and Tetracyanoethylene in Acetonitrile

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Resolution of the Non-Steady-State Kinetics of the Two-Step Mechanism for the Diels–Alder Reaction between Anthracene and Tetracyanoethylene in Acetonitrile

Kishan L. Handoo, Yun Lu, and Vernon D. Parker*

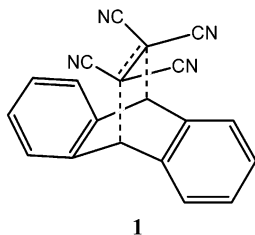
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Abstract: The Diels–Alder reaction between anthracene and tetracyanoethylene in acetonitrile does not reach a steady-state during the first half-life. The reaction follows the reversible consecutive second-order mechanism accompanied by the formation of a kinetically significant intermediate. The experimental observations consistent with this mechanism include extent of reaction–time profiles which deviate markedly from those expected for the irreversible second-order mechanism and initial pseudo first-order rate constants which differ significantly from those measured at longer times. It is concluded that the reaction intermediate giving rise to these deviations cannot be the charge-transfer (CT) complex, which is formed during the time of mixing, but rather a more intimate complex with a geometry favorable to the formation of the Diels–Alder adduct. The kinetics of the reaction were resolved into the microscopic rate constants for the individual steps. The rate constants, as shown in equation 1, at 293 K were observed to be $5.46 \text{ M}^{-1} \text{ s}^{-1}$ (k_i), 14.8 s^{-1} (k_b), and 12.4 s^{-1} (k_p). Concentration profiles calculated under all conditions show that intermediate concentrations increase to maximum values early in the reaction and then continually decay during the first half-life. It is concluded that the charge-transfer complex may be an intermediate preceding the formation of the reactant complex, but due to its rapid formation and dissociation it is not detected by the kinetic measurements.

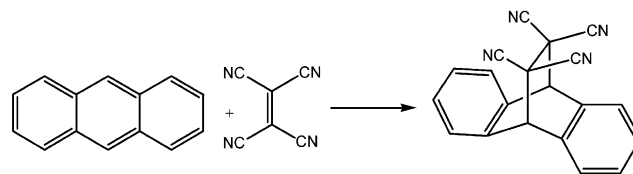
Introduction

The reaction between anthracene (ANTH) and tetracyanoethylene (TCNE) is a classic example of the Diels–Alder reaction (Scheme 1). An early¹ kinetic investigation by Brown and Cookson provided a wealth of information concerning the general characteristics of the reaction. The rate of the reaction is strongly influenced by whether TCNE interacts with the solvent. In aromatic solvents, reaction rates are moderated due to the formation of charge-transfer (CT) complexes between TCNE and the aromatic solvent. A number of possible intermediates or transition states were discussed, and it was concluded that a symmetrical transition state (**1**) lies on the reaction coordinate arising from either the CT complex or the uncomplexed reactants.



The role of CT complexes in the Diels–Alder reactions of anthracenes with TCNE and other dienophiles has been debated

Scheme 1



over the years.^{2–7} Thompson and Holder³ favored a mechanism in which the CT complex is an intermediate in the reactions between anthracenes and TCNE. However, they pointed out the earlier work by Andrews and Keefe⁴ who showed that the latter mechanism cannot be distinguished from one in which the CT complex is formed in a nonproductive side-equilibrium. Kiselev and Miller concluded, on the basis of the observation of a negative Arrhenius activation energy, that the CT complex between 9,10-dimethylantracene and TCNE is an intermediate in the reaction leading to the Diels–Alder adduct in acetonitrile.⁵ A recent theoretical study by Wise and Wheeler⁷ led to their conclusion that their calculations unambiguously establish that the CT complex is an intermediate during the reaction between ANTH and TCNE in chloroform.

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We have recently shown that several organic reactions, previously believed to follow simple second-order kinetics, pass through kinetically significant intermediates and that the reactions do not achieve the steady-state before late in the first half-life.^{8–15} These include the proton-transfer reactions between methylarene radical cations and pyridines,^{8,10–12} the proton-transfer reaction between a nitroalkane and hydroxide ion,⁹ a hydride-transfer reaction between NAD⁺ and NADH model compounds,¹³ the S_N2 reaction between methyl iodide and *p*-nitrophenoxide ion,¹⁴ and the classical E2 elimination reaction between 2-(*p*-nitrophenyl)ethyl bromide and alkoxide ions.¹⁵

The non-steady-state treatment allows for the resolution of the kinetics into the microscopic rate constants for the reversible consecutive second-order mechanism 1. The feature of the



kinetic data which makes this possible is that the rate constants (k_f , k_b , and k_p) affect the overall rate of the reaction to different extents during the pre-steady-state time period than under steady-state conditions. We initiated our study of the reaction between ANTH and TCNE in acetonitrile to attempt to resolve the kinetics of the two-step mechanism and provide experimental details of the reaction mechanism.

Results and Discussion

Mechanism Analysis. The primary feature of the reversible consecutive second-order mechanism 1 in the time period before steady-state is achieved which makes it readily distinguishable from the irreversible second-order mechanism 2 is that under



these conditions the increase in the product concentration lags behind the corresponding decrease in reactant concentration during the early stages of the reaction, giving rise to deviations in the extent of reaction–time profile from that expected for mechanism 2. The extent of reaction–time profiles then depend on whether increase in product concentration or decrease in reactant concentration is monitored. Under pseudo first-order conditions, it is convenient to compare the initial rate constant (k_{init}) with the corresponding pseudo first-order rate constant (k_{pfo}) measured at longer times. If reactant concentration is monitored, $k_{\text{init}}/k_{\text{pfo}}$ can be considerably greater than unity, and when product concentration is monitored, the ratio can be significantly less than unity. The qualifier, “can be”, is used to take into account the fact that $k_{\text{init}}/k_{\text{pfo}}$ equal to unity is the limiting response for mechanism 1 and under limiting conditions the two mechanisms are kinetically indistinguishable.

In this work, we chose to define k_{init} as the pseudo first-order rate constant for the extent of reaction ranging from 0 to 0.05,

Table 1. Rate Constant and Time Ratios for the Reactions of Anthracene with Tetracyanoethylene in Acetonitrile at 293 K

[TCNE], mM	λ , nm	$k_{\text{init}}/k_{\text{pfo}}^a$	$t_{0.50}/t_{0.05}^b$
20	380	1.02(0.03)	13.7(0.4)
40	380	1.09(0.05)	14.7(0.6)
80	380	1.21(0.10)	16.1(1.2)
160	380	1.50(0.14)	19.6(1.6)
20	320	0.98(0.05)	13.2(0.6)
40	320	0.95(0.03)	12.9(0.3)
80	320	0.91(0.03)	12.4(0.4)
160	320	0.81(0.05)	11.1(0.5)

^a Rate constant ratio is defined in the text. Numbers in parentheses are standard deviations for data derived from 40–60 absorbance–time curves.

^b Time ratio is defined in the text. Numbers in parentheses are standard deviations for data derived from 40–60 absorbance–time curves.

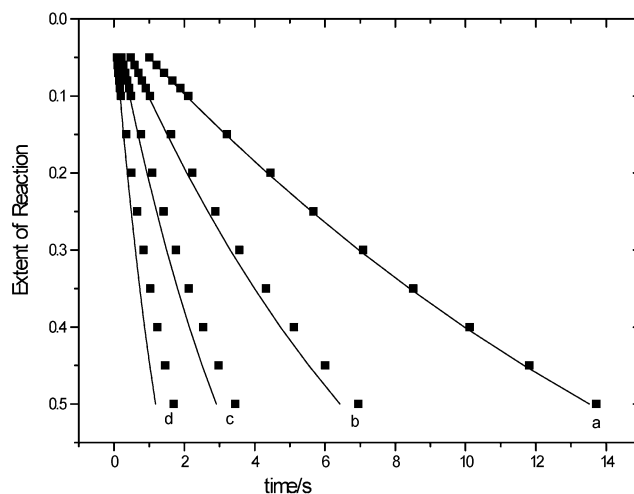


Figure 1. Extent of reaction–time profiles for the reaction of anthracene (0.0002 M) with tetracyanoethylene (20 (a), 40 (b), 80 (c), and 160 (d) mM) in acetonitrile at 293.2 K. Experimental data are represented by solid squares, and the solid lines define the expected response to the irreversible second-order mechanism 2.

and k_{pfo} was defined as the pseudo first-order rate constant for the extent of reaction ranging from 0.05 to 0.50. The time ratios ($t_{0.50}/t_{0.05}$) are the ratios of times necessary to reach the extent of reactions equal to 0.50 and 0.05, respectively. The data in Table 1 summarize the rate and time ratios observed for the reaction of ANTH (0.0002 M) with TCNE (0.02–0.16 M) in acetonitrile at 293.2 K. Anthracene in acetonitrile exhibits several absorbance maxima in the wavelength range 320–380 nm. The feature of most interest is the wavelength dependence of both $k_{\text{init}}/k_{\text{pfo}}$ and $t_{0.50}/t_{0.05}$ that is explained in the following paragraph. The rate constant ratios measured at 380 nm are greater than 1.00 (the expected value for mechanism 2), while those obtained at 320 nm are significantly less than 1.00. Also, the time ratios evaluated at 380 nm are greater than 13.5 (the mechanism 2 value), while those found at 320 nm are consistently less than the simple mechanism value. The deviations of both of the ratios from those expected for mechanism 2 are dependent on [TCNE]₀, small at 20 mM and becoming increasingly larger as the [TCNE]₀ is varied up to 160 mM. The latter point is clearly demonstrated by the large deviations of the extent of reaction–time profiles (Figure 1) generated from absorbance–time data gathered for the reactions at 380 nm as compared to the theoretical profiles for mechanism 2. The latter were adjusted to the experimental times by normalization to $t_{\text{mechanism2}} = t_{\text{experimental}}$ at the extent of reaction equal to 0.05.

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The analysis of theoretical data for mechanism 1 reveals relationships 3 and 4 that give the qualitative dependence of the ratios on whether the reactant or product is monitored. In the latter case, relationship 5 shows that the instantaneous product concentration is equal to the initial limiting reactant

$$k_{\text{init}}/k_{\text{pfo}} \geq 1.00; \quad t_{0.50}/t_{0.05} \geq 13.5 \quad (\text{reactant is monitored}) \quad (3)$$

$$k_{\text{init}}/k_{\text{pfo}} \leq 1.00; \quad t_{0.50}/t_{0.05} \leq 13.5 \quad (\text{product is monitored}) \quad (4)$$

$$[\text{product}] = [A]_0 - [A] - [I] \quad (5)$$

concentration ($[A]_0$) minus the instantaneous concentrations of the reactant ($[A]$) and the intermediate ($[I]$). Our interpretation of the origin of the absorbance at 380 nm is that it is due to reactant (ANTH) only, while that at 320 nm is due to both ANTH and the intermediate.

Each data line in Table 1 was derived from 40–60 absorbance–time profiles obtained at either 380 or 320 nm. The values in parentheses are the standard deviations in the ratios for all of the measurements. The observed ratios are clearly inconsistent with the irreversible second-order mechanism 2 and are qualitatively consistent with those expected for the reversible consecutive second-order mechanism 1.

The rate constant ratio ($k_{\text{init}}/k_{\text{pfo}}$) for mechanism 2 is 1.00. This follows from the fact that the rate of decay of reactant concentration is exactly equal to the rate of increase in product concentration according to this mechanism. As stated earlier, the deviations from unity predicted for mechanism 1 are due to the fact that product formation lags behind decay of reactant concentration. The ratio of times necessary to reach the extent of reaction equal to 0.50 and that to reach the extent of reaction equal to 0.05 ($t_{0.50}/t_{0.05}$) gives a direct measure of the deviation between experimental data and 13.5, the value expected for mechanism 2. The latter is also the lower limit for that quantity for mechanism 1 when the extent of reaction is defined in terms of the decrease in reactant concentration or the upper limit when it is defined in terms of increase in product concentration. The final column in Table 1 summarizes the experimentally observed values of $t_{0.50}/t_{0.05}$. Only the value for the reaction at the lowest $[\text{TCNE}]_0$ is reasonably close to 13.5, the value of the ratio for the irreversible second-order mechanism 2. All other values of the ratio differ significantly from the limiting value.

In view of the recent proposal¹ that the mechanism of the Diels–Alder reaction between ANTH and TCNE in chloroform involves the intermediate formation of the CT complex according to eq 6, we will first evaluate whether this mechanism is



consistent with the data in Table 1. Because the equilibrium between the reactants and the CT complex is assumed to be very rapid,^{5,7} the rate law expected for mechanism 6 is eq 7 in which K_{CT} is the equilibrium constant for formation and dissociation of the CT complex and k_a is the rate constant for

$$-d[\text{ANTH}]/dt = d[\text{adduct}]/dt = k_a K_{\text{CT}} [\text{ANTH}] [\text{TCNE}] \quad (7)$$

the product forming step. Obviously, this rate law differs from that for the irreversible second-order mechanism 2 only in the

definition of the apparent rate constant ($k_{\text{app}} = k_a K_{\text{CT}}$) and is thus indistinguishable from the single-step mechanism as has previously been pointed out.^{5,7} If formation of the CT complex is a nonproductive equilibrium, calculations have recently been presented to show that the side-equilibrium will not cause deviations of $k_{\text{init}}/k_{\text{pfo}}$ and $t_{0.50}/t_{0.05}$ from values predicted for simple second-order kinetics if the side-equilibrium is established rapidly as compared to the rate of the product forming reaction.¹³

The experimental data summarized in Table 1 are consistent with the reversible consecutive second-order mechanism 1. What this requires is that the intermediate (I) in (1) is formed at rates comparable to the overall rate of the reaction, that is, considerably more slowly than the formation of the CT complex. Thus, the CT complex is not I in eq 1. If the CT complex lies on the reaction coordinate between the reactants and product, a second intermediate is required to account for the kinetics. The kinetics do not distinguish between this possibility and the case where there is a single intermediate which is not the CT complex.

The overall conclusion is that the experimental data are inconsistent with those expected for mechanism 2. This implicates the reversible second-order consecutive mechanism 1 as a likely possibility for the Diels–Alder reaction between ANTH and TCNE in acetonitrile.

Estimation of the Equilibrium Constant for the Diels–Alder Reaction between Anthracene and Tetracyanoethylene in Acetonitrile. Absorbance measurements at 380 nm ($T = 293.2$ K) of solutions of ANTH (0.2 mM) and TCNE (1.0, 2.0, 4.0, and 8.0 mM) indicated that in all cases anthracene, within experimental error, was completely converted to the Diels–Alder adduct. Furthermore, reaction of ANTH (1.0 mM) and TCNE (1.1 mM) in acetonitrile was observed to be at least 90% complete at 293 K. For reaction 8 with $[\text{ANTH}]_0$ equal to 0.2 mM and $[\text{TCNE}]_0$ equal to 1.0 mM, assuming an equilibrium constant (K_{eq}) of 10^5 M^{-1} , ANTH is expected to be 98.8% converted to the adduct. We therefore conclude that $K_{\text{eq}} \geq 10^5$



M^{-1} in acetonitrile at 293.2 K. The minimum $[\text{TCNE}]_0$ used in the kinetic studies was 20 mM. Thus, under the kinetic conditions, the Diels–Alder reaction between ANTH and TCNE can be considered to be essentially irreversible. The significance of this fact is that reverse reaction 8 can be neglected in fitting experimental data to theoretical data for mechanism 1.

Fitting Experimental Data for the Reaction of Anthracene with Tetracyanoethylene to Theoretical Data for the Reversible Consecutive Second-Order Mechanism 1. Under pseudo first-order conditions, with $[B]_0$ in large excess over $[A]_0$, eqs 9–11, where $\lambda_1 \lambda_2 = k_f k_p$ and $(\lambda_1 + \lambda_2) = k_f + k_b + k_p$, give the instantaneous values of $[A]$, $[I]$, and $[\text{product}]$ for the

$$[A] = [A]_0 (\lambda_2 - \lambda_1)^{-1} \{ (k_b + k_p - \lambda_1) \exp(-\lambda_1 t) - (k_b + k_p - \lambda_2) \exp(-\lambda_2 t) \} \quad (9)$$

$$[I] = [A]_0 k_f (\lambda_2 - \lambda_1)^{-1} \{ \exp(-\lambda_1 t) - \exp(-\lambda_2 t) \} \quad (10)$$

$$[\text{product}] = [A]_0 \{ 1 + k_f k_p (\lambda_1 - \lambda_2)^{-1} \exp(-\lambda_1 t) + k_f k_p [\lambda_2 (\lambda_2 - \lambda_1)]^{-1} \exp(-\lambda_2 t) \} \quad (11)$$

reversible consecutive mechanism 1.^{16,17} Equation 9 is applicable for the calculation of extent of reaction–time profiles based on the decay of [A].

To generate the extent of reaction–time profiles, calculations were carried out with reaction times changing incrementally between calculations so that about 50 000 calculations were necessary to reach an extent of reaction equal to 0.50. For example, if the half-life of the reaction is 5 s, the first calculation was at $t = 0.0001$ s. The reaction time was then incremented by 0.0001 s ($t = 0.0002$ s) for the second calculation, and calculations are repeated until the extent of reaction for the last calculation was >0.50 . The times for the extent of reaction equal to 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, and 0.50 were then determined from the data, and a data file consisting of 14 extent of reaction/time points was constructed. The 14 data points for analysis correspond to those we use in experimental studies. The data file was then compared to an appropriate experimental file during the procedure to find the best fit between experimental and theoretical data.

The protocol we have used for the fitting of experimental to theoretical data in this paper involves concurrently fitting the extent of reaction–time data for three [TCNE]₀ (20, 40, and 80 mM). A number of k_f values over the entire applicable range (k_f ranging from $(k_{app})_{s.s.}$ to about 10 $(k_{app})_{s.s.}$) were selected, and at each k_f , k_p was varied while adjusting the other rate constant (k_b) to conform to eq 12 where $(k_{app})_{s.s.}$ is the apparent pseudo first-order rate constant obtained by treating the kinetic data in the customary manner. The latter resulted in an array of

$$(k_{app})_{s.s.}/k_f = (k_p/k_b)/(1 + k_p/k_b) \quad (12)$$

extent of reaction–time profiles, one for each k_p value at each k_f value. For example, calculations for 25 k_f with 50 k_p at each k_f for the first iteration of the fitting procedure resulted in 1250 extent of reaction–time profiles. Because 50 000 calculations were involved in each extent of reaction–time profile, an enormous number of calculations were carried out just in the first iteration. However, the calculations do not require excessive computer time; the $25k_f \times 50k_p$ extent of reaction–time profile array only requires about 25 s using a 850 MHz Pentium III processor.

After the theoretical extent of reaction–time profiles were generated, the best fit of the calculated data to the input data file involved the determination of the deviation between the calculated extent of reaction–time points and those in the experimental data input file. The output for comparison is the total deviations Λ_{total} , defined in eqs 13 and 14, between the three sets of data arrays (input and calculated). The terms

$$\Lambda_C = 100 \sum_{i=1}^{14} (t_{calc}^{E.R.} - t_{file}^{E.R.})/t_{file}^{E.R.}/14 \quad (13)$$

$$\Lambda_{total} = \Lambda_{C=20mM} + \Lambda_{C=40mM} + \Lambda_{C=80mM} \quad (14)$$

$t_{calc}^{E.R.}$ and $t_{file}^{E.R.}$ are the times to reach a given extent of reaction (E.R.) in the calculated profile and in the input profile, respectively. The summation in (13) is over the 14 time points calculated for each extent of reaction–time profile. The best

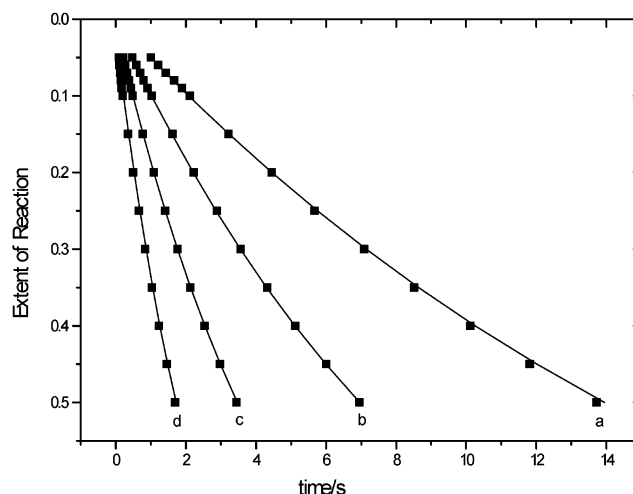


Figure 2. Extent of reaction–time profiles for the reaction of anthracene (0.0002 M) with tetracyanoethylene (20 (a), 40 (b), 80 (c), and 160 (d) mM) in acetonitrile at 293.2 K. Experimental data are represented by solid squares, and the solid lines are the best-fit theoretical data for the reversible consecutive second-order mechanism 1.

fit of experimental to theoretical data was taken to be the set of rate constants which gave rise to the minimum value of Λ_{total} defined by eq 14.

The results of the fitting procedure for the reactions of ANTH with TCNE in acetonitrile at 293 K are illustrated in Figure 2a–d. The extent of reaction–time profiles correspond to data for [TCNE]₀ equal to 20, 40, 80, and 160 mM, respectively. The experimental data are represented by solid squares, and the best-fit theoretical data are represented by solid lines. In all cases, excellent correspondence of the experimental and theoretical data was observed.

Rate Constants for the Reactions between ANTH and TCNE in Acetonitrile. The best-fit rate constants (Figure 2a–d) for the reaction between ANTH and TCNE in acetonitrile at 293 K are $5.46 \text{ M}^{-1} \text{ s}^{-1}$ (k_f), 14.8 s^{-1} (k_b), and 12.4 s^{-1} (k_p). The parameters refer to the reversible consecutive mechanism that in this specific case is shown in eq 15. In (15), the intermediate is written as an association complex



(ANTH/TCNE) without any structural detail.

Calculated Concentration Profiles for the Intermediate Complex in the Reaction between ANTH and TCNE. The concentration profiles of the intermediate complex (I) in all of the reactions were calculated using eq 10, and the rate constants were summarized in the previous section. The results of the calculations are illustrated in Figure 3 for reactions in which [TCNE]₀ was equal to 20 (a), 40 (b), 80 (c), and 160 (d) mM. The time scale ($t/t_{0.5}$) is the real time divided by the experimental half-life ($t_{0.5}$). Use of this time scale allows data for all of the [TCNE]₀ to be displayed in the same range. Depending upon [TCNE]₀, at 293 K, [I] increased from 0 to about 0.0008 (20 mM), 0.0016 (40 mM), 0.0031 (80 mM), and 0.0059 (160 mM) before beginning to decay. The maximum value of [I] calculated (160 mM) corresponds to about 3% of [ANTH]₀. Aside from the magnitudes of [I], the other feature of most interest in Figure 3 is the fact that after reaching the maximum values, [I] steadily

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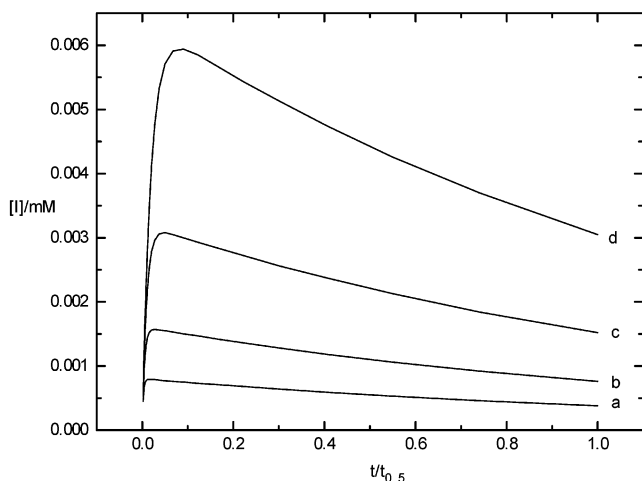


Figure 3. Calculated concentration profiles for the intermediate complex in the reversible consecutive mechanism 1 for the reaction between anthracene (0.0002 M) and tetracyanoethylene (20 (a), 40 (b), 80 (c), and 160 (d) mM) in acetonitrile at 293.2 K.

Table 2. Experimental and Theoretical Time and Rate Constant Ratios for the Reactions of ANTH with TCNE at 293.2 K^a

[TCNE] ₀ , mM	λ, nm	(t _{0.50} /t _{0.05})		(k _{final} /k _{pt0})	
		observed ^b	theory ^c	observed ^b	theory ^c
20	380	13.7	14.1	1.02	1.05
40	380	14.7	14.7	1.09	1.09
80	380	16.1	16.1	1.21	1.21
160	380	19.6	19.3	1.50	1.46
20	320	13.2	13.2	0.98	0.97
40	320	12.9	12.9	0.95	0.93
80	320	12.4	12.3	0.91	0.88
160	320	11.1	10.8	0.81	0.78

^a Extent of reaction = 1 - ([ANTH] + [intermediate])/[ANTH]₀ = [adduct]/[ANTH]₀, assuming the extinction coefficient at 320 nm is the same for the intermediate as for anthracene. ^b Data from Table 1. ^c Theoretical data for the reversible consecutive second-order mechanism with $k_f = 5.46 \text{ M}^{-1} \text{ s}^{-1}$, $k_b = 14.8 \text{ s}^{-1}$, and $k_p = 12.4 \text{ s}^{-1}$.

declines throughout the first half-life and a steady-state is not achieved at all during this time period.

Spectral Evidence for the Presence of the Intermediate Complex during the Reaction between ANTH and TCNE in Acetonitrile.

We considered it to be likely that the intermediate complex has absorbance bands in the same region as the reactant, anthracene. However, in view of the very low concentrations of the intermediate, the absorbance due to the transient is expected to be obscured by that due to the substrate. Because ANTH has absorbance bands ranging from about 320 to 380 nm, we assumed that absorbance at the higher wavelengths (λ) would be more likely to be free from intermediate absorbance that might be expected at lower λ. If the latter assumption is correct, absorbance at the low end of this range would likely be derived from both ANTH and ANTH/TCNE. Making a further assumption, that is, that the extinction coefficients of ANTH and ANTH/TCNE do not differ significantly, would allow the extent of reaction–time profile based on formation of product (Adduct) to be estimated taking advantage of eq 16. The bottom four lines in Table 2 are a comparison of predicted (based on the rate constants derived

$$[\text{adduct}] = [\text{ANTH}]_0 - [\text{ANTH}] - [\text{ANTH/TCNE}] \quad (16)$$

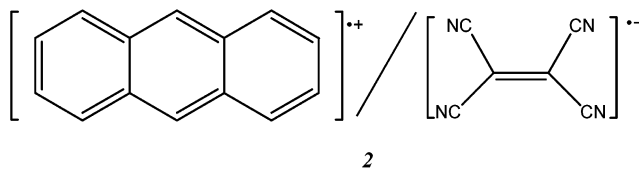
from the experimental to theoretical data fit of absorbance–

time data gathered at 380 nm) values of $(t_{0.50}/t_{0.05})_{\text{product}}$ and those observed at 320 nm. The theoretical data are derived for the increase in [adduct], and excellent correspondence was found between the predicted and the observed time ratios. The assumption of equal extinction coefficients of ANTH and ANTH/TCNE at 320 nm is certainly an approximation and most likely only gives reasonable results because of the fact that the [ANTH/TCNE] is very low in comparison to [ANTH].

Diode-array acquisition of spectra (300–450 nm) during the first half-life of the reaction between ANTH (1.0 mM) and TCNE (160 mM) in acetonitrile at 293 K failed to show the presence of new absorbance bands in addition to those present in the anthracene spectrum. However, the quantitative single wavelength measurements, discussed in the previous paragraph, show that the absorbance–time profiles observed at 320 nm are significantly different from those obtained at 380 nm and conform to expectations for the absorbance at the lower wavelength to include both that due to ANTH and that due to ANTH/TCNE as described in the previous paragraph.

We find an absorbance maximum for the CT complex at 657 nm, at a slightly lower wavelength than previously observed in other solvents,¹⁸ which is not expected to interfere with measurements at 320 and 380 nm. The rate of formation of the CT complex is expected to be at or near diffusion control as was demonstrated for the formation of the benzene–iodine complex in hexane at 300 K.¹⁹ Our stopped-flow studies show that the reaction in acetonitrile giving rise to the CT complex is complete during the time of mixing. The rapid equilibrium between reactants and CT complex is not expected to affect the extent of reaction–time profiles.¹³

The Structure of the Reaction Intermediate. There are a number of conceivable structures for the kinetically significant intermediate during the Diels–Alder reaction between anthracene and tetracyanoethylene. Of these, the radical ion-pair **2** depends on an initial electron transfer between the two reactants (eq 17). The equilibrium constant for electron transfer



(K_{17}) in acetonitrile can be estimated to be equal to 10^{-19} from Ebersson's tabulated standard electrode potentials.²⁰ Using an analysis²¹ which assumes that k_{-17} , the rate constant for reverse reaction 17, is equal to the diffusion-controlled value in acetonitrile ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$) leads to an estimate of the maximum possible value for k_{17} of about $10^{-9} \text{ M}^{-1} \text{ s}^{-1}$. The rate constant for the formation of the reaction intermediate in this study was found to be equal to $5.46 \text{ M}^{-1} \text{ s}^{-1}$, nearly 10 orders of magnitude greater than the predicted maximum possible value of k_{17} . This analysis rules out **2** for the structure of the kinetically significant intermediate.

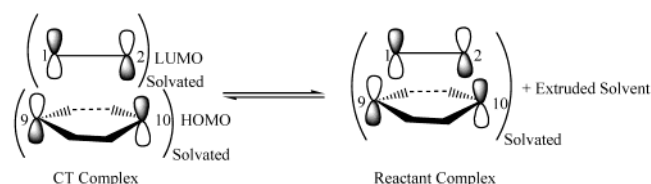
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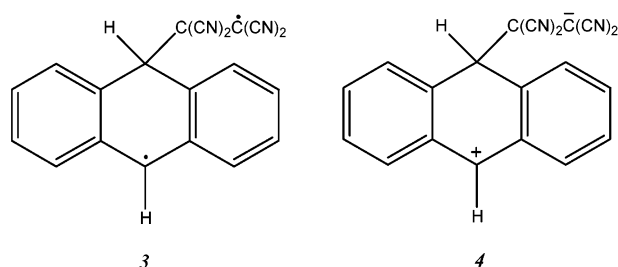
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Scheme 2



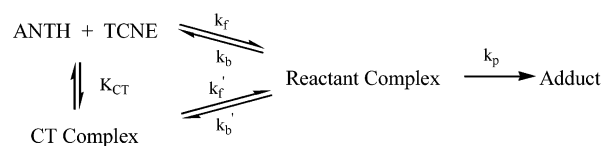
Stepwise mechanisms, involving the formation of diradical intermediates, have been discussed.^{22,23} For the Diels–Alder reaction of ANTH and TCNE, the latter corresponds to structure **3**. If **3** is considered as a possible intermediate, it is also necessary to consider the zwitterion **4** because internal electron transfer in **3** to give **4** is likely to be a very facile process. We find a value of 12.4 s^{-1} for k_p , the rate constant for the product forming reaction of ANTH and TCNE at 293 K in acetonitrile. In our opinion, it is inconceivable that either the intramolecular



diradical (for **3**) or the zwitterionic (**4**) ring closure reaction takes place with a rate constant as low as 12.4 s^{-1} . It should be pointed out the distances between reactive centers in **3** and **4** are much shorter than is implied by the flat drawings. We believe that we are justified in ruling out structures **3** and **4** as possibilities for the intermediate in the reaction between ANTH and TCNE under our conditions.

Because it is well known^{1,7} that charge-transfer complexes exist in solutions of ANTH and TCNE, it is likely, but not necessary, that the CT complex is an intermediate on the way to reactant complex formation. The structure of the CT complex is most likely one which provides a favorable interaction between the TCNE LUMO and the ANTH HOMO. The CT complex is expected to be rather loose with a considerable interplanar distance between the ANTH and TCNE planes. For example, Kochi²⁴ has found interplanar distances of the order of 3.2 \AA for Br_2 -methyl benzene CT complexes in the solid state. Density function calculations suggest an interplanar distance of 3.40 \AA for the ANTH-TCNE CT complex in the gas phase.²⁵ We suggest that the conversion of the CT complex to the reactant complex requires the extrusion of solvent from the former to give the latter which has a significantly shorter interplanar distance as illustrated in Scheme 2. In Scheme 2, the orientations of the ANTH and TCNE moieties are those reported in the gas phase, and our representation shows the LUMO orbital of TCNE and the 9,10-position contributions to the HOMO of ANTH. Only the central ring of ANTH is shown in Scheme 2 for the sake of clarity.

Scheme 3



The fact that the CT complex is formed at a near diffusion-controlled rate, that is, a process with a very small barrier, implies that the reactants at least partially retain their solvation shells. On the other hand, we propose that the formation of the reactant complex from either reactants or from the CT complex involves a considerably larger barrier because solvent is extruded. The latter accounts for the much longer time scale during which the reactant complex is kinetically observable. We therefore propose that the reactant complex shown on the right in Scheme 2 provides a reasonable representation of the kinetically significant intermediate required by the kinetic studies.

Conclusions

Our primary conclusion is that kinetic data for the reaction between anthracene and tetracyanoethylene in acetonitrile at 293 K correspond very closely to theoretical data generated for the reversible consecutive second-order mechanism (15). Very large deviations were observed between experimental data and theoretical data calculated assuming the irreversible second-order mechanism 2. The kinetically significant intermediate complex in eq 15 is not the CT complex that is formed on a much shorter time scale than our kinetic measurements and is in rapid equilibrium with the reactants. In view of the theoretical study for this reaction in chloroform,⁷ it is likely that in acetonitrile the CT complex lies on the reaction coordinate between reactants and the reactant complex. Without any direct evidence for the participation of the CT complex, we propose the mechanism illustrated in Scheme 3 in which the CT complex may, or may not, be an intermediate.

Although our kinetic data do not provide evidence for the structure of the kinetically significant intermediate, we have ruled out a number of potential structures including (i) the CT complex, (ii) a radical cation–radical anion pair (**2**), (iii) a diradical (**3**) generated from a stepwise reaction, and (iv) the corresponding zwitterion (**4**). We propose that the structure of the reactant complex is one that can be envisioned to arise from extrusion of solvent from either reactants or the CT complex (Scheme 2). The observed intermediate may have CT properties, even though it is not the CT complex that we observe to have an absorbance maximum equal to 657 nm in acetonitrile.

Experimental Section

Materials. Anthracene was a commercial sample of the highest purity available. Tetracyanoethylene was recrystallized two times from dry chlorobenzene before use. Acetonitrile (Aldrich, HPLC Grade) was distilled twice (collecting the middle fraction) after refluxing over P_2O_5 for 24 h.

Data Collection. The kinetic measurements were carried out on a Hi-Tech Scientific SF-60 stopped-flow spectrophotometer with a Techne Flow Cooler FC-200 thermostat to control the temperature of the cell block within $\pm 0.2 \text{ }^\circ\text{C}$. Data, 2000 points over the first half-life, were collected under pseudo first-order conditions for the reaction of ANTH (0.2 M) with TCNE (20–160 mM) in acetonitrile at 293.2 K.

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Data Manipulation. The 2000 data points for each kinetic run were smoothed by the least squares procedure of Savitzky and Golay.²⁶ The background absorbance was then subtracted, and the absorbance–time data were converted to extent of reaction–time data ($(1 - [\text{ANTH}]/[\text{ANTH}]_0)$ or $[\text{adduct}]/[\text{ANTH}]_0$ vs t), and the times necessary for the ratio to equal 0.05–0.50 (at 0.05 intervals) were determined. The latter were collected in data files for import into the program for fitting of experimental to theoretical data.

Data Fitting Procedure. The procedure for fitting experimental extent of reaction–time profiles to theoretical data is described in detail in a previous section. Further details on the protocol for the concurrent fitting of extent of reaction–time profiles can be found in a recent publication.¹²

Spectral Measurements during the Reaction. Spectra (300–450 nm) were obtained with an HP8452A Diode Array spectrometer housed in a glovebox ($[\text{O}_2] < 1$ ppm) immediately after mixing a solution containing ANTH (1.0 mM) and TCNE (160 mM) in acetonitrile at 293 K. The first spectrum was obtained after approximately 25% of the ANTH had been consumed. The half-life of the reaction under these

conditions is about 1.75 s. No new absorbance bands were observed in the three spectra recorded in succession.

A spectrum (HP8452A Diode Array spectrometer) was recorded in the wavelength range from 500 to 800 nm immediately after mixing a solution containing ANTH (4.8 mM) and TCNE (160 mM) in acetonitrile at 293 K. A single absorbance band ($\lambda_{\text{max}} = 657$ nm) was observed which decayed rapidly with time. Stopped-flow experiments were carried out with the same anthracene solution and TCNE solutions (160, 80, 40 mM). The maximum absorbance was observed at the first time point in all cases, indicating that formation of the CT complex was complete during the time of mixing (about 4 ms). The absorbance–time profiles were extrapolated to zero time, and the Benesi–Hildebrand equation²⁷ was used to estimate the values of the charge-transfer association constant, K_{CT} ($0.35 \pm 0.05 \text{ M}^{-1}$), and the extinction coefficient of the CT complex at 657 nm, ϵ_{657} ($1950 \pm 270 \text{ M}^{-1} \text{ cm}^{-1}$).

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