Molecular Complexes. Part II.[1] Kinetic Studies of Reactions of Tetracyanoethylene with Benz[*a*]anthracene and 9-Bromo- and 9,10-Dibromoanthracene

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Solvent effects on reactions of tetracyanoethylene with aromatic donors have been investigated. Increasing solvent polarity results in smaller association constants for initial molecular complex formation, but in turn, enhances the rate of subsequent Diels–Alder reactions. Corrections for competitive solvent–solute complexation are considered. The kinetic measurements are in accord with a slightly polar transition state leading to the final Diels–Alder adduct.

Soon after the initial preparation of tetracyanoethylene (TCNE), it was discovered that the compound can function as an active dienophile in Diels–Alder reactions.[2,3] In chloroform the reaction of TCNE with anthracene to give a Diels–Alder adduct occurs *ca.* 10^5 times faster than the corresponding reaction with maleic anhydride.[4] Upon mixing TCNE with an aromatic ' diene ' an intensely coloured solution is formed almost instantaneously. This colour, which fades as the reaction proceeds, is attributable to the rapid initial formation of an electron donor–acceptor complex. It has not been established whether the complex is a true intermediate in the Diels–Alder reaction, or merely an unstable co-existing species without mechanistic importance.[3,5] In either event, a gradual decrease in the absorption band characteristic of the complex provides a convenient method for following the rate of the overall reaction.

The present work is part of a continuing study of the effects of polar and non-polar solvents on interactions involving molecular complexes. Here we report solvent effects on formation constants, rate constants, and associated thermodynamic and kinetic parameters for reactions of TCNE with benz[*a*]anthracene and 9-bromo- and 9,10-dibromo-anthracene in carbon tetrachloride, in chloroform, and in benzene.

EXPERIMENTAL

Instrumentation.—Absorbance measurements were carried out with a Beckman DU-2 or a Cary 14 spectrophotometer. Spectral data were collected at 288, 298, and 313 ± 0·2 K by use of matched 0·01 m quartz cells with pure solvent as the reference. At all three temperatures absorbance values were easily reproducible to within 0·003 absorbance units.

Materials.—All solid materials were Eastman reagent grade. Tetracyanoethylene was recrystallized from benzene and twice sublimed at 398 K and a pressure of 133·3 N m^{-2}; m.p. 470·5—471·0 K. Benz[*a*]anthracene, m.p. 434·0—434·8 K, and 9-bromoanthracene, m.p. 369·0—370·0 K, were recrystallized from 95% ethanol. 9,10-Dibromoanthracene, m.p. 497·0—497·5 K was recrystallized twice from chloroform. Fisher spectrograde benzene and carbon tetrachloride were purged with oxygen-free nitrogen (dew point <213 K) immediately before use. Chloroform (Fisher spectrograde) was treated as described previously[6] and likewise purged with dry nitrogen immediately before use.

Equilibrium and Kinetic Measurements.—Stock solutions of TCNE (0·0002—0·01M), benz[*a*]anthracene (*ca.* 0·05M), 9-bromoanthracene (*ca.* 0·1M), and 9,10-dibromoanthracene (*ca.* 0·05M) were prepared in the different solvents. Portions of these separate solutions were pipetted directly into the spectrophotometer cells. Zero time was taken as when approximately one-half of the solutions had mixed. Absorbance readings at a fixed wavelength were recorded as a function of time and extrapolated to zero time in order to evaluate the initial association constants. Rate constants were computed from the spectral data collected at various times after mixing.

RESULTS AND DISCUSSION

Initial Molecular Complex Formation.—TCNE interacts immediately with each of the donor molecules to form molecular complexes having absorption maxima in the 690—710 nm region. Intensities of these bands (at zero time) are dependent on the concentratons of both TCNE and the aromatic donor. With the lone exception of 9-bromoanthracene, none of the separate components absorb light in the same spectral region as the complex. The small absorbance of this compound was subtracted from the measured intensities to obtain the contributions due solely to the complex. Absorbance data for each of the TCNE–donor systems are consistent with a 1 : 1 interaction [equilibrium (1)].

$$\text{A(TCNE)} + \text{D(aromatic donor)} \rightleftharpoons \text{C(molecular complex)} \quad (1)$$

In carbon tetrachloride and chloroform the absorbance values at zero time (A_0) together with initial concentrations of donor $[D]_0$ and acceptor $[A]_0$ were used to calculate absorptivities (a_c) and association constants, $K_1 = [C]/([A]_0 - [C])([D]_0 - [C])$, by means of equation (2). Here, as well as throughout, square brackets without subscripts refer to equilibrium concentrations; l is

$$\frac{[A]_0[D]_0 l}{A_0([A]_0 + [D]_0 - [C])} = \frac{1}{K_1 a_c} + \frac{([A]_0 + [D]_0 - [C])}{a_c} \quad (2)$$

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[1] Part I, C. C. Thompson, *Canad. J. Chem.*, 1969, **47** 2605.

[2] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1958, **80**, 2783.

[3] L. J. Andrews and R. M. Keefer, ' Molecular Complexes in Organic Chemistry,' Holden–Day, San Francisco, 1964, pp. 148—151.

[4] P. Brown and R. C. Cookson, *Tetrahedron*, 1965, **21**, 1977.

[5] A. Wassermann, ' Diels–Alder Reactions,' Elsevier, New York, 1965, ch. 4.

[6] M. J. S. Dewar and C. C. Thompson, *Tetrahedron*, 1966, Suppl. No. 7, 97.

the path length. Full details of the solution of this equation, which is a modification of the Scott[7] form of the Benesi–Hildebrand[8] equation, have been described previously. From association constants at two temperatures ΔH° and ΔS° were computed by the usual procedure.[9] Calculated spectral and thermodynamic quantities for each system are reported in Table 1.

TABLE 1

Association constants (K), absorptivities (a_c), ΔH°, and ΔS° for TCNE–donor complexes

Donor	Solvent	K/l mol^{-1} (at 298 K)		a_c (±50) (at 298 K)	ΔH°/k J mol^{-1} (±1·0)	ΔS°/J K^{-1} mol^{-1} (±3·0)
Benz[*a*]anthracene	CCl_4	11·52 ± 0·44	(8·14 ± 0·21) [b]	1740	−18·0	−29·3
	$CHCl_3$	5·36 ± 0·10	(4·47 ± 0·47) [b]	1130	−9·6	−17·6
	C_6H_6	1·86 ± 0·15	(2·42 ± 0·08) [b]			
		10·81 ± 0·23 [a]	(9·15 ± 0·37) [a,b]	1380	−8·8	−9·2
9-Bromoanthracene	CCl_4	12·16 ± 0·11	(14·33 ± 0·66) [c]	930	−11·7	−18·8
	$CHCl_3$	4·76 ± 0·64	(5·40 ± 0·37) [c]	1010	−9·2	−18·0
	C_6H_6	0·74 ± 0·17	(0·68 ± 0·04) [c]			
		12·82 ± 0·11 [a]	(14·09 ± 0·26) [a,c]	940	−7·1	−2·9
9,10-Dibromoanthracene	CCl_4	5·72 ± 0·48	(4·56 ± 0·41) [b]	690	−11·7	−25·1
	$CHCl_3$	2·72 ± 0·23	(2·33 ± 0·13) [b]	670	−8·4	−20·1
	C_6H_6	0·51 ± 0·06	(0·59 ± 0·08) [b]			
		6·30 ± 0·40 [a]	(5·46 ± 0·25) [a,b]	690	−7·1	−8·4

[a] Association constants corrected for TCNE complexed by the solvent. [b] Temp. 313 K. [c] Temp. 288 K.

With benzene as the solvent the systems are complicated by the occurrence of competitive benzene–TCNE complexes. Corrections for this solvent complexation are essential in order to obtain a realistic association constant for a specific TCNE–donor pair. Thus, in addition to the interaction described by equation (1), we have equation (3).

$$\text{A(TCNE)} + \text{B(benzene)} \rightleftharpoons \text{E(TCNE–benzene complex)} \qquad (3)$$

Since benzene is always present in large excess, the association constant, K_2, can be written as in equation (4) which rearranges to equation (5), where $[B]_0$ is the

$$K_2 = [E]/([A]_0 - [C] - [E])[B]_0 \qquad (4)$$

$$[E] = K_2[B]_0([A]_0 - [C])/(1 + K_2[B]_0) \qquad (5)$$

concentration of benzene. The significance of TCNE–solvent complexes has been discussed by Brown and Cookson[4] in their study of solvent effects on Diels–Alder reactions. These investigators have noted that binding of TCNE by the solvent reduces the number of acceptor molecules available for complexing with an added donor as well as for subsequent formation of a Diels–Alder adduct. However, in their attempt to compensate for solvent complexation two substantial simplifications were introduced. First, in their evaluation of the amount of complexed TCNE, [E], Brown and Cookson neglected [C] in their equations corresponding to (4) and (5) above. In the case of fairly strong donors, such as anthracene and its simple derivatives, and since usually $[D]_0 \gg [A]_0$, [C] may be quite significant in comparison to $[A]_0$ and [E]. Secondly, the association constants for TCNE–solvent complexes (K_2) used by these workers were those obtained by Merrifield and Phillips[10] for dilute dichloromethane solutions. It was acknowledged that the corresponding values for an almost pure aromatic donor solution may differ substantially.

In an effort to avoid these approximations we have used a more involved procedure. The TCNE–benzene association constant, K_2, was first evaluated from the Scott equation by use of spectral data obtained in solutions containing from 55 to *ca.* 100% benzene (v/v). Dilutions [up to 45% (v/v)] were made with cyclohexane, since specific interactions with this solvent are less than those of other common organic solvents.[11] Benzene–TCNE association constants calculated in this manner are 0·97 ± 0·06, 0·77 ± 0·03, and 0·65 ± 0·03 l mol^{-1} at 288, 298, and 313 K, respectively. From these values ΔH° for the benzene–TCNE complex is −12·0 ± 0·9 kJ mol^{-1} and ΔS° is −42·3 ± 3·0 J K^{-1} mol^{-1}. The association constant determined here at 298 K is some six times larger than that (0·13 l mol^{-1}) reported in dichloromethane at 295 K.[10] Thus, in a 0·005M-TCNE solution in benzene at 298 K about 90% of the TCNE molecules are complexed with the solvent.

Next, absorbance values (A_c) were measured for benzene solutions containing TCNE plus aromatic donor at wavelengths where only the complex, C, absorbed light. With a cell path length of 0·01 m an approximate concentration of complex C was calculated from the Beer's law relation $[C] = A_c/a_c l$ by assuming initially that a_c in benzene is equal to its value in carbon tetrachloride. From equation (3) a first approximation of the concentration of complex E was calculated, and the amount of TCNE, [A]′, available for complexing with the donor, D, was computed from $[A]' = [A]_0 - [E]$. Using [A]′ in place of $[A]_0$ together with values of $[D]_0$ and A_c, the Scott equation was solved to yield new values for a_c, K_1, and [C]. With the improved values

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[7] R. L. Scott, *Rec. Trav. chim.*, 1956, **75**, 787.

[8] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

[9] G. Briegleb, 'Elektronen-Donator-Acceptor-Komplexe,' Springer–Verlag, Berlin, 1961.

[10] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

[11] C. C. Thompson and P. A. D. de Maine, *J. Phys. Chem.*, 1965, **69**, 2766.

of [C] the concentration of E was then re-evaluated and the entire process repeated until K_1 remained constant for two successive cycles. The 'corrected' association constants listed in Table 1 for benzene solutions were calculated by this procedure; the 'apparent' values were computed on the assumption that all the TCNE was available for complexing.

Table 1 shows that, in agreement with earlier work,[11] formation constants for each of the complexes decrease in going from non-polar to polar solvents. It is interesting that formation constants in carbon tetrachloride and the corrected values in benzene are nearly identical. Thus, it appears that, after allowance is made for specific complexation, benzene and carbon tetrachloride are approximately equal in their degree of solvent 'inertness'. Previously it was suggested[11] that the lower value in chloroform may be attributed to strong solvation forces in the more polar medium which impede the donor–acceptor interaction. Reference to Table 1 shows that absorptivities for the TCNE complexes of 9-bromo- and 9,10-dibromo-anthracene are virtually independent of solvent. However, absorptivities for the TCNE–benzanthracene complex decrease in the order $CCl_4 > C_6H_6 > CHCl_3$.

A significant decrease in the donor strength of anthracene is brought about by successive bromination. In carbon tetrachloride at 298 K formation constants are 12·16 and 5·72 l mol^{-1} for TCNE with 9-bromo- and 9,10-dibromo-anthracene, respectively, compared to the estimated value of 29 l mol^{-1} for TCNE–anthracene reported by Brown and Cookson.[4] Electron-withdrawing effects of the halogens are undoubtedly responsible for the observed decrease in donor activity. Deactivation of the anthracene system by increasing halogenation is reflected not only in the lower formation constants, but also in the fact that 9,10-dibromoanthracene undergoes no observable Diels–Alder reaction at temperatures between 288 and 313 K. Absorbance values for TCNE–9,10-dibromoanthracene mixtures in each of the solvents were unchanged over a period of 1 week. Preliminary studies of the TCNE–9,10-dichloroanthracene system likewise show no evidence of a Diels–Alder reaction.

The smaller enthalpies and entropies of formation in chloroform and benzene reflect the strong solvation effects and competitive complexing abilities of these solvents.

Rate Constants for the Diels–Alder Reaction.—As is well known, the overall Diels–Alder reaction involves a reversible association between the diene and dienophile to give the adduct. An example is the reaction of anthracene with TCNE. In the systems reported here a simple second-order rate law is followed until the reaction is *ca.* one-third complete. During this early phase of the reaction, before the reverse process becomes important, the classical second-order rate expression for the formation of a Diels–Alder adduct (P) from the combination of TCNE (A) and an aromatic diene (D) is given by equation (6) where $[A]_T$ and $[D]_T$ represent

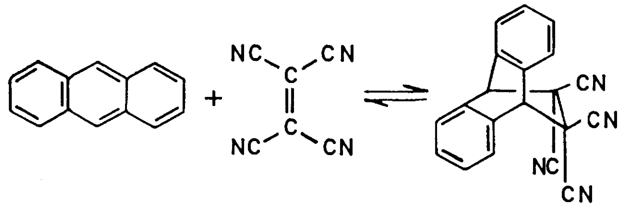
$$d[P]/dt = k[A]_T[D]_T \qquad (6)$$

the total concentrations of TCNE and diene [equations (7) and (8)]. It is important to recall that equations

$$[A]_T = [A] + [C] = ([A]_0 - [C] - [P]) + [C] \qquad (7)$$

$$[D]_T = [D] + [C] = ([D]_0 - [C] - [P]) + [C] \qquad (8)$$

(6)—(8) are independent of whether or not the initial molecular complex is a true intermediate in the mechanism leading to the final adduct.



In carbon tetrachloride and chloroform, where specific solvent–TCNE complexation is not considered, we may combine equations (2), (7), and (8) and substitute A_c/a_c for [C] so that the concentration of adduct at any time t is given by equation (9), where $\alpha = [A]_0 - A_c/a_c$ and $\beta = [D]_0 - A_c/a_c$.

$$[P] = [K_1(\alpha + \beta) \pm \{[K_1(\alpha + \beta)]^2 - 4K_1(\alpha\beta K_1 - A_c/a_c)\}^{\frac{1}{2}}]/2K_1 \qquad (9)$$

As described above, K_1 and a_c were calculated from the measured absorbance (A_c) at $t = 0$. From these values of K_1 and a_c, the known concentrations $[A]_0$ and $[D]_0$, and measured absorbances at $t > 0$ the concentration [P] was computed from equation (9). Next, $[A]_T$ and $[D]_T$ were evaluated from equations (7) and (8), and finally the standard integrated second-order rate equation (10) was solved for the total experimental rate

$$1/([A]_0 - [D]_0) \ln ([D]_0[A]_T/[A]_0[D]_T) \qquad (10)$$

constant, k. With benzene as the solvent we assume that the rate of reaction of TCNE complexed with the solvent is negligible compared with that of free TCNE. Consequently, in benzene, $[A]_0$ and $[A]_T$ were replaced by $([A]_0 - [E])$ and $([A]_T - [E])$, respectively. From rate data at two temperatures and the Arrhenius equation the procedure described by Bunnett[12] was used to calculate pre-exponential factors (A), enthalpies ($\Delta H^{\ddagger}$), and entropies ($\Delta S^{\ddagger}$) of activation. These results are given in Table 2.

Experimental rate constants for reactions of both benz[*a*]anthracene and 9-bromoanthracene vary with solvent in the order $CHCl_3 > CCl_4 > C_6H_6$. The ratios $k(CHCl_3)/k(C_6H_6)$ are *ca.* 15 in each case. Brown and Cookson[4] reported a ratio of 11 for the TCNE–anthracene system. These variations with solvent, while significant, must be considered relatively small in comparison to changes frequently observed for solvent effects on reaction rates. Correspondingly small variations with solvent have been observed for the reaction of maleic

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[12] J. F. Bunnett, in 'Technique of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 1961, vol. 8, ch. 6.

anhydride with isoprene.[13] All of these studies point toward a transition state for the Diels–Alder reaction which is only slightly more polar than the reactants.

In each of the solvents studied TCNE reacts with 9-bromoanthracene about 50 times faster than with benz[*a*]anthracene. However the 9-bromo-compound shows a three-fold decrease in reactivity compared to anthracene,[4] and the 9,10-dibromo-derivative undergoes no detectable Diels–Alder reaction in the temperature range 288—313 K. Conceivably these effects could be due to electron withdrawal, to steric hindrance by the bromine atoms, or to a combination of the two. Andrews and Keefer[14] found that 9,10-dimethylanthracene reacts more rapidly than the 9-methyl derivative and that both compounds react faster than anthracene. Since the van der Waals radii of a methyl group (2·0 Å) and a bromine atom (1·95 Å) are almost identical,[15] it appears that steric effects can be ruled out, and that deactivation of the aromatic ring systems through electron withdrawal by the halogens is the principal factor leading to the reduced rates.

TABLE 2

Second-order rate constants, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for reactions of TCNE with benz[*a*]anthracene and 9-bromoanthracene; donor concentration 0·03 mol l^{-1} except where noted

Donor	Solvent	k/l mol^{-1} s^{-1} [a] (at 298 K)		$\Delta H^{\ddagger}$/kJ mol^{-1} ($\pm$3·0)	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1} ($\pm$10)
Benz[*a*]anthracene	CCl_4	$6·3 \times 10^{-3}$	$(1·3 \times 10^{-2})$ [b]	35·1	−172
	$CHCl_3$	$3·6 \times 10^{-2}$ [d]	$(6·6 \times 10^{-2})$ [b,d]	28·9	−176
	C_6H_6	$2·4 \times 10^{-3}$	$(5·8 \times 10^{-2})$ [b]	43·2	−151
9-Bromoanthracene	CCl_4	$2·9 \times 10^{-1}$	$(2·0 \times 10^{-1})$ [c]	24·3	−176
	$CHCl_3$	1·90	(1·50) [c]	14·6	−192
	C_6H_6	$1·2 \times 10^{-1}$	$(6·8 \times 10^{-2})$ [c]	38·1	−135

[a] Rate constants are reproducible to 5% or better. [b] Temp. 313 K. [c] Temp. 288 K. [d] Donor concentration 0·05 mol l^{-1}.

These findings agree with the theoretical description of Diels–Alder reactions in terms of *para*-localization energies.[16] As predicted by this model, benz[*a*]anthracene, whose *para*-localization energy (L_p), computed by the simple HMO method, is 3·42β, should react more slowly than anthracene ($L_p = 3·31\beta$).[16] We have computed L_p values of 3·43 and 3·54β for 9-bromo- and 9,10-dibromo-anthracene respectively, using the HMO procedure with the heteroatom parameters suggested by Streitwieser.[17] Based on the reactivities reported here, the L_p value for 9-bromoanthracene should fall between those of anthracene and benz[*a*]anthracene, probably *ca.* 3·35β.

It is conceptually attractive to consider the initial complex as passing directly into the transition state and then on to the Diels–Alder adduct. But as mentioned above, and as discussed extensively by Andrews and Keefer[3] as well as others, kinetic methods alone do not enable one to distinguish between a mechanism (I) in which the complex lies on the reaction co-ordinate and a separate mechanism (II) in which complex formation is a side reaction in rapid equilibrium with free donor and acceptor. For mechanisms (I) and (II) the rate of

$$\text{(I)} \qquad A + D \underset{}{\overset{\text{fast}}{\rightleftharpoons}} C \xrightarrow{\text{slow}} P$$

$$\text{(II)} \qquad A + D \overset{\text{fast}}{\rightleftharpoons} C$$

$$A + D \xrightarrow{\text{slow}} P$$

formation of the final adduct can be written d[P]/dt = $k_{(I)}$[C] and d[P]/dt = $k_{(II)}$[A][D] respectively. Here $k_{(I)}$ is a first-order rate constant for the rate-determining conversion of C into adduct, and $k_{(II)}$ is a second-order rate constant for the combination of free A and D through a slow reaction which does not involve the complex C. If, as in the present work, $[D]_T \simeq [D]$, $k_{(I)}$ is related to the experimental rate constant by equation (11).[3] Similarly, $k_{(II)} = k_{(I)}K_1$.

$$k_{(I)} = \frac{k(1 + K_1[D_T])}{K_1} \qquad (11)$$

The total experimental rate constants for each system are found to decrease slightly with an increase in donor concentration. Such a decrease in k has been reported in other systems and attributed to changes in the ratio of free to complexed acceptor as the donor concentration is varied.[3] However in this case since the initial association constants (K_1) are known, the ratio of free to complexed TCNE is automatically taken into account in the calculation of $k_{(I)}$ and $k_{(II)}$. As the representative data in Table 3 show, $k_{(I)}$ and $k_{(II)}$ are independent of the initial donor concentration. With $k_{(I)}$ and $k_{(II)}$ known, kinetic parameters describing the two possible mechanisms can be evaluated. The results for mechanism (I) are given in Table 4, and those for mechanism (II) in Table 5.

A comparison of the rate constants from Tables 2, 4, and 5 shows that in every instance $k(CCl_4)/k(C_6H_6)$ lies between 2 and 3. Since, after correction for TCNE–benzene complexation, the TCNE–diene association constants in these two solvents are not vastly different, one must conclude that the rate-determining step in carbon tetrachloride is inherently 2—3 times faster than

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[13] M. J. S. Dewar and R. S. Pyron, *J. Amer. Chem. Soc.*, 1970, **92**, 3098.

[14] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 6284.

[15] L. Pauling, 'The Nature of the Chemical Bond,' Cornell Univ. Press, Ithaca, 1960, p. 260.

[16] R. D. Brown, *J. Chem. Soc.*, 1950, 691, 2730, 3249; 1951, 1950.

[17] A. Streitwieser, jun., 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, ch. 15.

in benzene, regardless of which of the two mechanisms is actually followed. However, since the association constants in chloroform are only *ca.* ½ the corresponding values in the other media, the absolute rate enhancement by this solvent will depend on the mechanism chosen. If mechanism (II) is correct, the rate-determining step in chloroform is about 15—20 times as fast as in benzene and 5—7 times that in carbon tetrachloride. On the other hand, if mechanism (I) is correct, the conversion of complex into adduct in chloroform is accelerated by a factor of 30—40 over that in benzene and by 10—15 compared to carbon tetrachloride.

TABLE 3

Rate constants for reaction of 9-bromoanthracene with TCNE at 288 K; experimental rate constants (k) together with corresponding values for mechanism (I) ($k_{(I)}$) and mechanism (II) ($k_{(II)}$)

Solvent	$[D]_0 \times 10^2$	k/ l mol^{-1} s^{-1}	$k_{(I)}$/s^{-1}	$k_{(II)}$/ l mol^{-1} s^{-1}
CCl_4	2·71	0·220	0·0213	0·305
	3·80	0·196	0·0212	0·304
	5·42	0·174	0·0215	0·308
	6·51	0·158	0·0213	0·305
	7·59	0·149	0·0216	0·310
$CHCl_3$	3·49	1·51	0·332	1·79
	4·66	1·40	0·325	1·76
	5·82	1·35	0·328	1·77
	6·98	1·29	0·328	1·77
	8·15	1·24	0·330	1·78

Enthalpies of activation computed from k, $k_{(I)}$, and $k_{(II)}$ all vary with solvent in the order $CHCl_3 < CCl_4 < C_6H_6$. The lower values in the more polar solvent are again suggestive of a slightly polar, and hence a more strongly solvent-stabilized, transition state. Similar results were found by Brown and Cookson [4] for the TCNE–anthracene reaction in which $\Delta H^‡$ is 17·8 and 38·5 kJ mol^{-1} in chloroform and benzene, respectively.

TABLE 4

First-order rate constants, $\Delta H^‡$, and $\Delta S^‡$ for direct conversion of molecular complex into Diels–Alder adduct [mechanism (I)]

Donor	Solvent	$k_{(I)}$/s^{-1} [a] (at 298 K)		$\Delta H_{(I)}^‡$/kJ mol^{-1} (±3·0)	$\Delta S_{(I)}^‡$/J K^{-1} mol^{-1} (±10)
Benz[*a*]anthracene	CCl_4	$7·2 \times 10^{-4}$	$(1·8 \times 10^{-3})$ [b]	45·5	−152
	$CHCl_3$	$8·8 \times 10^{-3}$	$(1·9 \times 10^{-2})$ [b]	35·9	−164
	C_6H_6	$3·0 \times 10^{-4}$	$(8·1 \times 10^{-4})$ [b]	49·0	−147
9-Bromoanthracene	CCl_4	$3·4 \times 10^{-2}$	$(2·1 \times 10^{-2})$ [c]	32·1	−163
	$CHCl_3$	$4·8 \times 10^{-1}$	$(3·3 \times 10^{-1})$ [c]	24·3	−170
	C_6H_6	$1·3 \times 10^{-2}$	$(6·9 \times 10^{-3})$ [c]	42·8	−137

[a] $k_{(I)}$ Reproducible within 5%. [b] Temp. 313 K. [c] Temp. 288 K.

TABLE 5

Second-order rate constants, $\Delta H^‡$, and $\Delta S^‡$ for reaction of free TCNE and donor [mechanism (II)]

Donor	Solvent	$k_{(II)}$/l mol^{-1} s^{-1} [a] (at 298 K)		$\Delta H_{(II)}^‡$/kJ mol^{-1} (±3·0)	$\Delta S_{(II)}^‡$/J K^{-1} mol^{-1} (±10)
Benz[*a*]anthracene	CCl_4	$8·3 \times 10^{-3}$	$(1·5 \times 10^{-2})$ [b]	28·1	−190
	$CHCl_3$	$4·7 \times 10^{-2}$	$(8·3 \times 10^{-2})$ [b]	26·9	−180
	C_6H_6	$3·2 \times 10^{-3}$	$(7·4 \times 10^{-3})$ [b]	40·9	−154
9-Bromoanthracene	CCl_4	$4·2 \times 10^{-1}$	$(3·1 \times 10^{-1})$ [c]	19·5	−187
	$CHCl_3$	2·28	(1·78) [c]	15·3	−187
	C_6H_6	$1·7 \times 10^{-1}$	$(9·7 \times 10^{-2})$ [c]	35·6	−141

[a] $k_{(II)}$ Reproducible within 5%. [b] Temp. 313 K. [c] Temp. 288 K.

As expected because of the difference in reaction rates, $\Delta H^‡$ for 9-bromoanthracene is generally of the order of 10 kJ mol^{-1} smaller than the corresponding value for benz[*a*]anthracene. In every case $\Delta H_{(I)}^‡$ is higher than the associated $\Delta H_{(II)}^‡$. This result is consistent with the fact that the initial molecular complex has a lower total enthalpy than the free donor plus acceptor. Further, since $k_{(II)} = k_{(I)}K_1$, the values computed for $\Delta H_{(I)}^‡$ and $\Delta H_{(II)}^‡$ should be related by $\Delta H_{(II)}^‡ = \Delta H^\circ + \Delta H_{(I)}^‡$. To within the limits of experimental error this relationship is realized for each of the systems studied.

The rather large negative entropies of activation are typical of Diels–Alder reactions.[4,5] Values for $\Delta S^‡$ computed for the overall reaction as well as for mechanisms (I) and (II) show only a moderate solvent dependence. Although $\Delta S^‡$ is consistently less negative in benzene compared to the other solvents, the differences are not as great as that reported for the anthracene–TCNE reaction ($\Delta S^‡$ of −125 in benzene and −205 J K^{-1} mol^{-1} in chloroform). For each of the separate mechanisms and also for the total reaction the solvent dependence of $\Delta S^‡$ is more pronounced in the case of 9-bromoanthracene than with benz[*a*]anthracene. Since the entropies of activation are negative, their variation with solvent runs counter to the observed order of the reaction rates. Thus, the lower enthalpies of activation in the more polar medium appear to be the dominant factor in accounting for the solvent dependence of these reactions.

Comparison of the entropy changes of Table 1 with those in Tables 2, 4, and 5 show that in carbon tetrachloride and chloroform $\Delta S^‡$ is 5—10 times greater than ΔS° for complex formation. In benzene the differences are even more dramatic. In fact, the values for $\Delta S_{(I)}^‡$ (Table 4) indicate directly the much greater negative entropy for the transition state relative to the initial molecular complex. It has been suggested that both the initial complex and the transition state require a similar arrangement in which the two interacting molecules are oriented in parallel planes.[14] Deuterium isotope effects on the reaction of anthracene with TCNE have been interpreted as indicating that the transition state hybridization of the 9- and 10-positions of anthracene is nearer sp^2 than sp^3.[18] Wong and Eckert [19] also conclude that electronically the transition state resembles the reactants in the Diels–Alder reaction of maleic anhydride with 1,3-butadiene. A recent perturbation treatment [20] of the anthracene–TCNE complex shows that the most stable configuration of the complex is one in which TCNE is in a plane parallel to and centred directly over the middle ring of anthracene. All of the available evidence points toward similar geometrical structures for a complex and its corresponding transition state, but with the components more tightly bound in the transition state. In the complex weak intermolecular forces will permit rotation as well as lateral motion of the donor and acceptor molecules relative to each other, whereas in the transition state such movement is severely restricted owing to incipient covalent bond formation. This restricted motion of the reactants in a cyclic, somewhat polar, transition state together with more tightly held solvent molecules will account for the large negative entropies of activation characteristic of these reactions.

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