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KINETICS AND MECHANISM OF DIELS–ALDER ADDITIONS OF TETRACYANOETHYLENE TO ANTHRACENE DERIVATIVES—I

SUBSTITUENT EFFECTS

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Abstract—The rates of addition of tetracyanoethylene to a number of 9- and 9,10-substituted anthracenes have been measured spectrophotometrically in solvent CCl_4. Substituent effects correlated well using the extended form of the Hammett equation. The importance of steric effects on the reaction was assessed by a systematic variation of the components of the data used in the above correlation.

Activation parameters ($\Delta G^{\ddagger}_{exp}$, etc.) and the corresponding overall thermodynamic parameters for adduct formation (ΔG°_{ad}, etc.) were evaluated. $\Delta G^{\ddagger}_{exp}$ was found to be linearly related to ΔG°_{ad}, the free energy of formation of the intermediate complex which confirms the role of the latter as a true reaction intermediate. From correlations between $\Delta G^{\ddagger}_{exp}$ and ΔG°_{ad}, an "early" transition state is suggested. The above thermodynamic and activation data enable detailed reaction profiles to be drawn.

The Diels–Alder reaction has achieved considerable importance in organic synthesis since its formulation by Diels and Alder in 1928.[1] Since that time there has also been considerable interest in the reaction from the standpoints of mechanism[2a–d] and theories of electrocyclic additions.[3] In this and subsequent papers[4] we report on substituent and solvent effects on the reaction of anthracene derivatives with tetracyanoethylene (ethenetetracarbonitrile, TCNE). This system was chosen because of the relative rigidity of the anthracene nucleus and the dominant addition to the central ring particularly when 9-alkyl substituents are present. Another great advantage is that the kinetic data are accurately reproducible and the reaction generally free from any complicating side reactions. TCNE was chosen as the dienophile because of its high reactivity.

RESULTS AND DISCUSSION

Most of the available evidence for the mechanism of the reaction points to a concerted process. The stereochemistry involves exclusively *cis* addition.[2b] The lack of an appreciable solvent effect also seems to preclude zwitterionic intermediates.[2c] Kinetic evidence also favours a concerted attack by the dienophile. Activation entropies are usually highly negative (between −35 and −45 cal $deg^{-1}mol^{-1}$) with correspondingly low enthalpies of activation. Inverse secondary isotope effects (k_H/k_D = 0.93 – 0.99) are low and have been taken as evidence for very small changes in hybridisation of the reaction centres in the rate determining step, arguing for a "factor" like structure for the transition state.[5,6] In spite of this evidence, the concerted nature of the reaction has recently been questioned[7] and in isolated examples radical intermediates are postulated.[8] However for the reaction between maleic anhydride and anthracene and its benzo-derivatives, a poor correlation was obtained between log(rate constant) and localisation energy for the appropriate reaction centres whereas a reasonably good linear plot was obtained using the paralocalisation energies of Brown.[9] The latter correlation is the one expected for a concerted mechanism. Recently these findings have been confirmed by Kiselev *et al.*[10]

Diels–Alder reactions are usually accompanied by the production of a transient colour which disappears as the reaction proceeds. This is attributed to the formation of a charge transfer intermediate between donor (diene) and acceptor (dienophile).

Until recently, the mechanistic importance of these intermediate complexes was not clear. The reaction may be formulated in two ways. (A = acceptor, B = donor); C_T, charge transfer complex; P, product.)

$$A + B \overset{K}{\rightleftharpoons} C_T \xrightarrow{k_1} P \qquad (1)$$

Scheme 1.

$$C_T \overset{K}{\rightleftharpoons} A + B \xrightarrow{k_2} P \qquad (2)$$

Scheme 2.

For the condition that [B] ≫ [A], it can be readily shown that for Scheme 1, the experimentally observed second order rate constant (k_{exp}) is given by

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

and for Scheme 2,

$$k_{exp} = \frac{k_2}{1 + K[B]}. \qquad (4)$$

Thus the two schemes are kinetically indistinguishable. Evidence for these formulations come from the observation that k_{exp} decreases with increasing maleic anhydride (excess) concentration for the reaction with 9,10-dimethylanthracene.[11]

Equations (3) and (4) can be rearranged into the more convenient forms (5) and (6) respectively

$$1/k_{exp} = [B]/k_1 + 1/K k_1 \qquad (5)$$

$$1/k_{exp} = K[B]/k_2 + 1/k_2 \qquad (6)$$

Table 1. Second order rate constants (k_2, $l\,mol^{-1}\,sec^{-1}$), activation parameters. ($\Delta G^{\ddagger}_{exp}$, etc. $kcal \cdot mol^{-1}$) and thermodynamic parameters for intermediate complex formation (ΔG_c°, etc. $kcal \cdot mol^{-1}$) for the Diels–Alder reaction of various anthracenes with TCNE in CCl_4

	Compound	k_2 [a]	$\Delta H^{\ddagger}_{exp}$	$-\Delta H_c^{\circ}$ [b]	$-\Delta S^{\ddagger}_{exp}$	$-\Delta S_c^{\circ}$ [b]	$\Delta G^{\ddagger}_{exp}$	$-\Delta G_c^{\circ}$ [b]
1	Anthracene	1.12	6.4 ± 0.04	3.2	36.9 ± 0.1	5.6	17.4	1.52
2	9-Methyl-	727	1.91 ± 0.11	4.3	39.0 ± 0.3	8.6	13.5	1.68
3	9-Ethyl-	318	2.29 ± 0.30	4.1	39.4 ± 0.4	8.1	14.0	1.66
4	9-Propyl-	270	2.59 ± 0.30	3.9	38.4 ± 1.0	7.5	14.1	1.65
5	9-i-Propyl-	54.7	3.50 ± 0.26	3.5	38.8 ± 0.8	6.3	15.1	1.61
6	9-t-Butyl-	89.5	3.54 ± 0.12	-	37.7 ± 0.4	-	14.8	1.62
7	9-Me_3Si-	3.73	5.11 ± 0.04	3.5	38.8 ± 0.1	6.5	16.7	1.56
8	9-Bromo-	0.218	7.78 ± 0.42	2.9	35.4 ± 1.4	4.9	18.3	1.48
9	9-Br-10-Me-	5.78	4.36 ± 0.08	2.8	40.4 ± 0.3	-	16.4	-
10	2,6-Bis(t-butyl)	14.4	5.55 ± 0.18	-	34.6 ± 0.6	-	15.9	-
11	9,10-Dimethyl-**	4×10^4	-1.48	5.6	40.5	12.7	10.6	1.80

* Calculated at 25.0°.

** From reference (12).

a Under these conditions, 9-Ph_3Si, 9-Ph_3Sn, 9,10 dibromo and 9,10 bis (Me_3Si) derivatives failed to react.

b See preceding paper.

From the slopes and intercepts of these plots k_1, k_2 and K can be evaluated though, of course, the true pathway cannot be distinguished. However, it has been recently pointed out that for the condition $K[B] \ll 1$ then, since Eqns (3) and (4) reduce to $k_{exp} = K k_1$ and $k_{exp} = k_2$ respectively, the two pathways might be distinguished from the activation energies of the reaction.[12]

For Scheme 1,

$$\Delta G^{\ddagger}_{exp} = \Delta G^{\ddagger} + \Delta G_0 \qquad (7)$$

where $\Delta G_1^{\ddagger}$ is the barrier to conversion of complex to products and ΔG_0 is the free energy of formation of the complex. Similar expressions may be written for the corresponding enthalpy and entropy terms. Thus $\Delta H^{\ddagger}_{exp}$ will be determined in part by ΔH_0.

For Scheme 2, $\Delta H^{\ddagger}_{exp}$ will be independent of ΔH_0. Thus if a sufficiently stable complex is formed such that $\Delta H_0 > \Delta H_1^{\ddagger}$ then *negative* values of $\Delta H^{\ddagger}_{exp}$ could be observed. Kiselev and Miller have found such negative values from a study of the reaction of 9,10-dimethylanthracene with TCNE in halocarbon solvents. Values of $\Delta H^{\ddagger}_{exp}$ in the range -1.6 to -3.1 kcal · mole^{-1} were found together with highly negative entropies of activation (~ -40 cal · deg^{-1} mol^{-1}). Unfortunately the data was obtained at only three different TCNE concentrations for each solvent and temperature which in our experience was not wholly satisfactory.

We report here an investigation of substituent effects at the 9 position in the reaction of a series of anthracenes with TCNE in solvent CCl_4. The rates of reaction were followed spectrophotometrically and activation energies and thermodynamic stabilities of the adducts were measured.

Table 1 lists values of the observed second order rate constants at 25°. A considerable range of reactivity is found which contrasts strongly with the limited range of values obtained for the equilibrium constants for charge transfer complex formation (see preceding paper). Alkyl substituents show a strong rate enhancement whereas electron withdrawing substituents reduce the rate appreciably, the greatest contrast being the reactivities of the 9,10-dibromo (no reaction) and 9,10-dimethyl (4×10^4 times faster than anthracene). Within the alkyl series itself there is a marked reduction in rate along the α alkylated series Me, Et, i-Pr in the Baker–Nathan sense, which suggests that hyperconjugative effects are important. However the t-Bu derivative reacts faster than isopropyl, indicating that there is a complex interaction of polar and steric effects. One reasonable hypothesis is that t-butylanthracene itself is a sterically strained molecule due to compression between the methyl groups and the peri hydrogens. Such compression would be alleviated by a change of hybridisation sp^2 to sp^3 which occurs along the reaction coordinate. It is significant in this context that UV maxima for t-butylanthracene show marked bathochromic shifts as well as lower extinction coefficients than the other alkyl derivatives (Table 2).

In some instances steric factors do appear to be important as shown by the fact that the normally electron releasing Me_3Si group shows a rate enhancement of only about three over anthracene and when two such groups occupy the 9 and 10 positions, reaction does not occur. Other bulky substituents (Ph_3Si, Ph_3Sn) also prevent reaction. The 9 methyl-, 10 bromo-derivative throws some light on the question of the existence of zwitterion intermediates. The Me and Br substituents have similar bulk (Van der Waals radius ~2.0 Å), so that a first approximation steric effects should be comparable. Clearly the +I, −I nature of the substituents would facilitate the production of a zwitterionic intermediate and the reaction should be faster than that of 9,10-dimethylanthracene. However the compound reacts slower by a factor of four powers of ten. Comparison of Me and Br substituents is complicated by the operation of direct field effects in the latter which would inhibit the approach of the TCNE which has readily polarisable π electrons. Alkyl substituents in the outer rings also facil-

Table 2. UV maxima (λ, nm) of some anthracene derivatives in CCl_4 at room temperature (log ε values in parentheses)

			‡	
Anthracene	326(3.46)	342(3.75)	358(3.90)	378(3.88)
9-Methyl-	334(3.46)	350(3.77)	368(3.98)	388(3.96)
9-Ethyl-	333(3.47)	349(3.78)	368(3.98)	388(3.97)
9-Propyl-	334(3.47)	349(3.76)	368(3.96)	388(3.94)
9-i-Propyl-	335(3.48)	350(3.77)	369(3.95)	387(3.91)
9-i-Butyl-	336(3.45)	352(3.78)	370(3.98)	385(3.95)
9-t-Butyl-	340(3.38)	358(3.68)	376(3.83)	395(3.76)
9-Me_3Si-	335(3.46)	352(3.79)	370(3.95)	389(3.91)
9-Ph_3Si-	342(3.54)	356(3.83)	374(4.01)	394(3.98)
9-Ph_3Sn-	338(3.51)	354(3.82)	371(3.99)	391(3.97)
9-Bromo-	336(3.47)	353(3.79)	372(3.96)	392(3.92)
9-Br-10-Me-	344(3.48)	362(3.83)	380(4.05)	403(4.02)
9,10-Bis-(Me_3Si)	350(3.56)	365(3.86)	384(4.07)	405(4.07)
2,6-Bis(t-butyl	-	340(3.56)	358(3.68)	377(3.58)

‡ analytical wavelength

itate reaction at the 9,10 position. 2,6-Bis-t-butylanthracene reacts about fourteen times faster than anthracene. Activation in this case is presumably by a π inductive mechanism operating along three C–C bonds.

In order to analyse the substituent effects in more detail the rate constants have been correlated using the extended form of the Hammett equation previously applied by Charton.[13]

$$Q_x = \alpha\sigma_{I,x} + \beta\sigma_{R,x} + h \quad (8)$$

where $\sigma_{I,x}$ and $\sigma_{R,x}$ represent the contribution to the overall polar effect made by inductive and resonance components and h is the constant of the correlation. The substituents are arranged in sets comprising a minimum of six members.

The combination of the sets, derived from the 9-substituted anthracenes in the main (complete) set (Set 1) and the resulting correlations are presented in Tables 2 and 3 respectively. Although Set 1 shows a correlation, it is a fairly poor one. By eliminating one value at a time, the effect on the correlation can be systematically examined until the best fit is obtained. The greatest improvement in these sets was found to be in Set 2 which excludes 9-t-butylanthracene. It should be noted that in the extended Hammett equation used for the correlation, there is no parameter to account for steric effects. The equation takes into account resonance and inductive influences produced by the substituents and any incursion of steric effects results in a poorer correlation. Thus the observed improvement on exclusion of t-butyl could reflect the steric effects discussed previously. Although exclusion of the other values changes the degree of correlation, these changes are not of any significance, except for Set 5 where the value for 9-i-propyl- is excluded which again could be due to a steric factor. Exclusion of the 9 Me_3Si group (Set 6) does not improve the correlation significantly, which suggests that the Me_3Si group has less steric hindrance than the t-Bu group which is reasonable in view of the greater Si–C bond length. The best correlation is shown in Set 7 which is obtained by exclusion of 9-t-butyl- and 9-i-propyl-anthracene. These two compounds cause improvement also by their individual elimination from the Set 1 (Sets 2 and 5). Elimination of Me_3C- and Me_3Si- (Set 9) shows no improvement over Set 2 but here there is a lower confidence level, since only six data points are included in this set. The improvement of the correlation in Set 9 is related to the exclusion of 9-t-butyl- and not 9-trimethylsilyl-. Although elimination of 9-methyl- and 9-ethyl- (Set 10) improves the correlation, it is still not comparable with the results obtained in Set 7. All this evidence indicates that, in the absence of steric effects, the extended form of Hammett equation based on electronic effects can be successfully applied to the Diels–Alder reaction of TCNE with anthracenes and this in itself strongly suggests a similar reaction pathway for all the derivatives employed. Some further inferences may be drawn from the magnitude of the β value shown in Table 4. If the transition state were close to the product, the value of the delocalised electrical effect (β) should be small since the substituent would be attached to a carbon atom with pronounced sp^3 character and interaction with the π system would be minimal. The observed β values are fairly large and $\epsilon(=\beta/\alpha)$ is greater than unity which suggests an "early" transition state. This result confirms the interpretation of isotope effects by Brown and Cookson.[6] The fact that elimination of t-Bu and i-Pr substituents markedly improves the correlation may well result from these substituents having more sp^3 character in the transition state to alleviate steric strain.

Activation parameters. The activation parameters for TCNE addition together with the thermodynamic parameters for complex formation appear in Table 1. From this data it is now possible to calculate the activation parameters for the conversion of complex into adduct using eqn (7). The results appear in Table 4 and are notable for the very small range of $\Delta S_1^{\ddagger}$ values. The principal factors therefore giving rise to the observed rate differences are thus enthalpic. The highly negative entropy values show that the initial complex is rather loosely bound which is confirmed by the observed lack of response of K_c to substituents, and the small negative values of ΔS_c°.

Another interesting feature of the results is the excellent correlation of $\Delta G_{ca,p}^{\ddagger}$ with ΔG_c° shown in Fig. 1. This provides strong support for the complex as a reaction intermediate. Furthermore plots of $\log k_{ca,p}$ vs $\bar{\nu}_{max}$ for the TCNE complexes are also linear.

Table 3. Composition of the different sets for the multiple regression analysis of data using the extended Hammett equation (+, compound included; −, compound excluded) X = 9 substituent

X	H	Me	$MeCH_2$	$Me(CH_2)_2$	Me_2CH	Me_3C	Me_3Si	Br
Set								
1	+	+	+	+	+	+	+	+
2	+	+	+	+	+	−	+	+
3	+	−	+	+	+	+	+	+
4	+	+	+	+	+	+	+	−
5	+	+	+	+	−	+	+	+
6	+	+	+	+	+	+	−	+
7	+	+	+	+	−	−	+	+
8	+	−	+	+	+	+	+	−
9	+	+	+	+	+	−	−	+
10	+	−	−	+	+	+	+	+

Table 4. Results of correlation

Set	a	β	h	R[a]	F[b]	T_α[c]	T_β[c]	n[d]	C.L.[e]	c[f]
1	- 8.74	-14.0	0.224	0.948	21.98	6.567	4.945	8	99.5	1.60
2	- 9.60	-15.7	0.182	0.973	35.92	8.424	6.533	7	99.5	1.64
3	- 8.26	-12.9	0.230	0.954	20.19	6.33	4.688	7	99.0	1.57
4	- 9.09	-14.0	0.201	0.906	9.138	1.518	4.262	7	97.5	1.54
5	- 9.06	-14.7	0.227	0.958	22.20	6.611	5.031	7	99.5	1.62
6	- 8.81	-14.4	0.165	0.943	16.25	5.669	3.177	7	99.0	1.64
7	-10.31	-17.4	0.174	0.997	275.1	23.36	18.48	6	99.9	1.68
8	- 8.37	-13.0	0.223	0.914	7.662	1.433	3.902	6	95.0	1.55
9	- 9.73	-16.6	0.075	0.972	26.02	7.167	4.293	6	99.0	1.70
10	- 7.77	-12.1	0.198	0.969	23.04	6.772	5.035	6	97.5	1.56

a: Multiple correlation coefficient; b: F-test for significance of regression;

c: T-test for significance of α and β; d: Number of points in set;

e: Confidence level (compared with the F-distribution tables, taken from reference 14);

f: Composition of electrical effect (c = β/α).

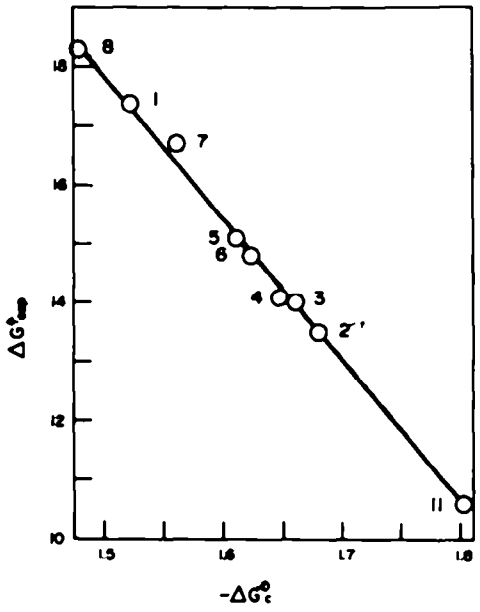

Fig. 1. Relationship between $\Delta G^{\ddagger}_{exp}$ (kcal mol^{-1}) and ΔG_c^0 (kcal mol^{-1}) the free energy of complex formation between TCNE and substituted anthracenes in CCl_4 at 25.0°. (Numbering as in Table 1.)

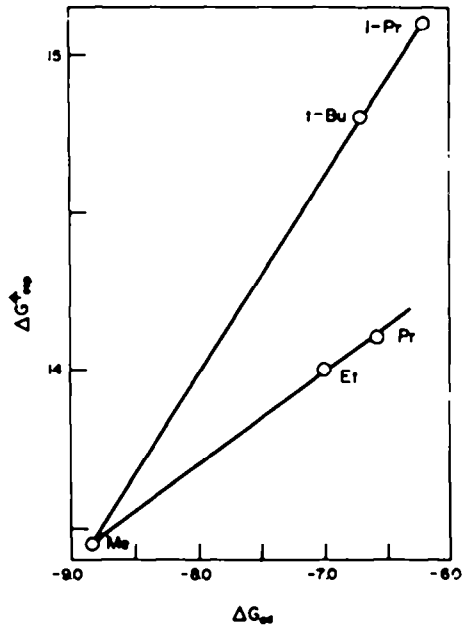

Fig. 2. Correlation between $\Delta G^{\ddagger}_{exp}$ (kcal mol^{-1}) and ΔG^0_{ad} (kcal mol^{-1}), the free energy of adduct formation between TCNE and substituted anthracenes in CCl_4 at 25.0°.

The overall thermodynamic parameters (ΔG^0_{ad}, ΔH^0_{ad} and ΔS^0_{ad}) for the reactions of the alkylanthracenes were also determined from the absorptions of fully equilibrated solutions at various temperatures. The values appear in Table 4. As expected the values of ΔS^0_{ad} are all highly negative though that of 9-methylanthracene is rather surprisingly much more positive than the other alkyl derivatives.

Values of $-\Delta G^0_{ad}$ decrease systematically along the series Me, Et, Pr, i-Pr but for t-Bu the trend is reversed. This coupled with the more positive ΔS^0_{ad} term supports the concept of a relief of peri-meso steric strain on conversion to adduct.

There is also an interesting correlation of $\Delta G^{\ddagger}_{exp}$ with ΔG^0_{ad} (Fig. 2). The Me, Et and Pr derivatives lie on a line of slope 0.29 whereas the t-Bu and i-Pr derivatives lie on a line of slope 0.63. The low slope of the correlation of the n-alkyl derivatives again suggests "early" transition states whilst those of the bulkier secondary and tertiary substituents occur somewhat "later" along the reaction coordinate. From the thermodynamic data presented here, the activation parameters for the reverse can be completed (Table 4) and quite detailed reaction profiles can be drawn.

Table 5. Thermodynamic parameters for adduct formation [ΔG°_{ad}, ΔH°_{ad} (kcal · mol^{-1}) ΔS°_{ad} (cal · deg^{-1}mol^{-1})] and calculated activation parameters for the forward (ΔG_1, etc.) and reverse (ΔG_{-1}) Diels–Alder additions of TCNE to 9-substituted anthracenes

Substituent	$-\Delta G^\circ_{ad}$	$\Delta G^\ddagger_1$	$\Delta G^\ddagger_{-1}$	$-\Delta H^\circ_{ad}$	$\Delta H^\ddagger_1$	$\Delta H^\ddagger_{-1}$	ΔS°_{ad}	$\Delta S^\ddagger_1$	$\Delta S^\ddagger_{-1}$
H	-	18.9	-	-	9.6	-	-	-31.3	-
Me	8.9	15.2	22.4	14.9	6.2	16.8	-20.2	-30.4	-18.8
Et	7.0	15.7	21.0	17.6	6.4	19.9	-35.6	-31.4	- 3.8
Pr	6.6	15.7	20.7	19.4	6.5	22.1	-43.0	-30.7	+ 4.6
i Pr	6.2	16.7	21.3	19.2	7.0	22.7	-43.6	-32.4	+ 4.8
t Bu	6.7	16.4	21.5	17.3	7.1	20.8	-35.6	-31.0	- 2.1
Me_3Si	-	18.3	-	-	8.6	-	-	-32.4	-
Br	-	19.8	-	-	10.7	-	-	-30.5	-
9,10 Me_2	-	12.4	-	-	4.1	-	-	-27.8	-

EXPERIMENTAL

Preparation and purification of materials. Spectroscopic grade CCl_4 was used throughout the investigation. The alkylanthracenes were synthesised by standard methods (see preceding paper). The preparations of the organometal (loid) derivatives will be reported elsewhere.[15] 2,6-butyl anthracene was prepared by Friedel–Crafts reaction of t-BuCl (excess) with anthracene in nitrobenzene/CS_2 mixtures.

Kinetic methods. Rates were measured spectrophotometrically using a Unicam SP 1700 UV-visible spectrophotometer equipped with a Unicam AR 25 linear recorder. A Churchill thermocirculator was used to control the temp. of the cell housing (± 0.1°). The reactions were monitored by recording the decrease in absorbance due to loss of anthracene. Analytical wavelengths varied for different anthracenes (Table 2) but were chosen as close to a maximum as possible. Traces of absorbance against time were obtained using the chart recorder. Runs were generally made under pseudo-first order conditions with [TCNE] ≥ 15[anthracene]. Under these conditions the absorbance at $t = \infty$ was almost zero. Observed pseudo-first order rate constants (k_1^{obs} sec^{-1}) were calculated from the usual relationship.

$$\ln(A_t - A_\infty) = -k_1^{obs}t + \ln(A_0 - A_\infty) \quad (9)$$

where A_0, A_t and A_∞ represent the absorption of solutions at time $t = 0$, t and ∞. k_2 values (l mole^{-1} sec^{-1}) were obtained by dividing by [TCNE]. In some cases, however, where the overall equilibrium constant for the reaction was much lower (e.g. 9-bromoanthracene), the reverse reaction was taken into account and the following modified rate equations were used.

$$-\ln(x_e - x) = \frac{k_2}{x_e}ab\,t \quad (10)$$

where x_e is the amount of adduct formed at equilibrium. Equation (10) in terms of absorbance units becomes

$$-\ln(A_t - A_\infty) = k_2 b\left(\frac{A_0}{A_0 - A_\infty}\right)\cdot t \quad (11)$$

For the alkylanthracenes, rates were often inconveniently fast under pseudo-first order conditions (particularly for 9,10-dimethylanthracene). In these cases equimolar concentrations were used and the data treated in terms of a reversible reaction,[16] yielding

$$\ln\left\{x_e\frac{(a^2 - x x_e)}{(x_e - x)a^2}\right\} = k_2\left(\frac{a^2 - x_e^2}{x_e}\right)t \quad (12)$$

which again in terms of absorbance becomes

$$\ln\frac{\frac{A_t(A_0 - A_\infty)}{A_\infty} + A_0}{(A_0/A_\infty - 1)} = k_2\left(\frac{a^2 - x_e^2}{x_e}\right)t + \ln\frac{a^2}{x_e}. \quad (13)$$

Overall equilibrium constants for adduct formation (k_{eq}) were calculated from (14)

$$k_{eq} = \frac{A_0}{aA_\infty}\left(\frac{A_0}{A_\infty} - 1\right) \quad (14)$$

from the final absorbances of runs performed at equimolar concentrations.

Values of k_1^{obs} were reproducible to within ±3% as determined by average standard deviations over several runs.

Values of the thermodynamic (ΔG°_{eq}, etc.) and activation parameters ($\Delta G^\ddagger_{obs}$, etc.) were calculated from the usual equations using a least squares computer programme.

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