Tetrahedron Vol. 37, No. 15, pp. 2657 to 2662, 1981
Printed in Great Britain.

0040-4020/81/152657-06$02.00/0
Pergamon Press Ltd.

KINETICS AND MECHANISM OF DIELS-ALDER ADDITIONS OF TETRACYANOETHYLENE TO ANTHRACENE DERIVATIVES—III

EFFECT OF SUBSTITUENTS ON RATES AND INTERMEDIATE COMPLEX FORMATION

R. M. G. Roberts* and F. Yavari
Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex CO4 3SQ, England

(*Received in the UK* 19 *January* 1980)

Abstract—In Diels-Alder additions of tetracyanoethylene to 1,2-, and 9-substituted anthracenes, formation constants (K) for the intermediate complexes have been separated from the global rate constant (k_2^{obs}). The relatively small range of values of K indicates a very small charge transfer in the complexes. The transition state for conversion of complex into adduct showed a marked degree of charge development, particularly for the 9-substituted derivatives ($\rho = -7$). Substituents in the outer rings gave good rate correlations with composite constants ($\sigma_m^+ + \sigma_p^+$) with a ρ value of -3. The substituent effects are discussed in terms of these and other parameters. Values for equilibrium constants for the overall addition (K_{eq}) are reported.

The effect of substituents on the overall rates of Diels-Alder addition of tetracyanoethylene (TCNE) to anthracene derivatives has recently received detailed attention.[1] The purpose of this paper is to extend the range of substituents to include those in the outer rings of anthracene and to attempt to separate effects on intermediate complex formation from those related to the conversion of the complex to adducts.

It has now been established from the work of Kiselev and Miller,[2] together with substantiative evidence of solvent effects obtained in these laboratories[3], that weak complexes are formed between TCNE and the anthracene derivatives and that these complexes lie on the reaction coordinate for the Diels-Alder addition process. A detailed analysis of substituent effects shows that the transition state for adduct formation is more factor-like than product-like. The kinetic scheme for the reaction may be represented by eqn (1)

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

where A, B, C and P are acceptor, donor, intermediate complex and product respectively. If conditions chosen are such that $[A] \gg [B]$, then the experimentally observed pseudo-first order rate constant (k_1^{obs}) can be written in terms of K and k_1

$$\frac{1}{k_1^{obs}} = \frac{1}{Kk_1}\frac{1}{[A]} + \frac{1}{k_1}. \qquad (2)$$

When K[A] is $\ll 1$, $k_1^{obs} = k_1K[A]$ or $k_2^{obs} = k_1K$. Thus, in principle K can be dissected from the global term, k_2^{obs} by plotting $(k_1^{obs})^{-1}$ vs $[A]^{-1}$. Such reciprocal plots are commonly used in enzymic studies but suffer from the drawback that intercepts have to be known accurately, and are very sensitive to small changes in slope. In particular if k_1 is large (as it is in some of the alkylated anthracenes), then it becomes very difficult to measure accurately the intercept in eqn (2). Such analysis therefore lends itself more to the deactivated anthracenes such as the halogens derivatives. Accordingly, the rates of reaction of a series of halogen substituted anthracenes (AnX) with TCNE were measured in dichloromethane at 25° (solvent chosen because of relatively high solubility of TCNE) employing the condition that $[TCNE] > 20[AnX]$.

One possible complicating factor is the reversible nature of Diels-Alder additions. If the value of the overall equilibrium constant, K_{eq} is greater than *ca.* 10^4 (as it is with alkylsubstituted anthracenes[1], then no correction need be made. However, for lower values of K_{eq}, the following modification has to be made[5] in calculating the true forward pseudo first order rate constant, k_1^{obs*} where b = [TCNE]

$$k^{obs*} = k^{obs}K_{eq}b(1 + K_{eq}b)^{-1}. \qquad (3)$$

A value of K_{eq} of $1 \cdot 2 \pm 0.2 \times 10^5\ l\,mol^{-1}$ has been determined for anthracene itself from spectrophotometric data of fully equilibrated reaction solutions. This value is thus high enough for the above correction to be ignored.

The values for 9-chloro and 9-bromo-anthracene are considerably lower (1990 ± 100 and $2090 \pm 50\ l\,mol^{-1}$ respectively) probably reflecting the direct field interaction of the lone pairs of electrons on the halogen substituent and the π electrons of the cyano groups.

Data obtained for anthracene itself appears in Table 1. The plot of the data according to eqn (2) shows excellent linearity (r = 0.9996). The value of K obtained was $13 \pm 3\ l\,mol^{-1}$ which is in good agreement with values obtained from previous indirect methods.[4] The method was then applied to a number of anthracene derivatives substituted in the 1, 2, and 9 positions, the results appearing in Table 2. The disadvantages inherent in using eqn (2) are apparent in the data obtained for the 9-fluoro, and 2-methyl anthracenes. The plots show reasonably good correlations (r = 0.991 and 0.999 respectively), but the standard errors involved in k_1 and K are very substantial and these values must be treated with caution. On the other hand the k_2^{obs} ($= k_1K$) values are not subject to

Table 1. Observed pseudo first-order rate constants (k_1^{obs} s^{-1}) as a function of [TCNE] for the reaction of anthracene (1.00×10^{-4}M) with TCNE in CH_2Cl_2 at 25°

10^3 [TCNE]	$10^2 k_1^{obs}$	$(k_1^{obs})^{-1}$ [a,b]	$[TCNE]^{-1}$ [a,b]
2.00	0.97	103.1	500.0
2.40	1.13	88.5	416.7
2.80	1.30	76.9	357.1
3.20	1.52	65.8	312.5
3.60	1.69	59.2	277.8
4.00	1.95	51.3	250.0
6.00	2.68	37.3	166.7
6.40	2.80	35.7	156.2
6.80	3.04	32.9	147.0
7.20	3.20	31.3	138.9
7.60	3.30	30.3	131.6
8.00	3.59	27.9	125.0

a correlation coefficient 0.9996

b plot gives k_1 = 0.369±0.070 s^{-1}, K = 13.2±2.5 ℓ mol^{-1}, and k_2^{obs} = k_1K = 4.86±0.05 ℓ mol^{-1} s^{-1}.

Table 2. Values of $k_1(s^{-1})$, K(l mol^{-1}) and k_2^{obs} (l $mol^{-1}s^{-1}$) for the reaction of TCNE with various anthracene derivatives (An–X) in CH_2Cl_2 at 25°

Substituent X	k_1	K	k_2^{obs}	r [a]	N [b]
H	0.369±0.070	13.2±2.5	4.86±0.05	0.9996	10
9-F	(0.224)[c]	(25)[c]	5.59±0.43	0.9911	5
9-Cℓ[d]	0.0193±0.0040	79±19	1.53±0.06	0.9962	6
9-Br[d]	0.0494 ± 0.002	26 ± 3	0.77 ± 0.02	0.9982	5
9-I	0.041 ± 0.004	37 ± 7	1.51 ± 0.05	0.9987	6
9-Me	122.8±34.5	25±7	3050±65	0.9993	5
1-F	0.0020±0.0002	193±24	0.383±0.017	0.9971	5
1-Cℓ	0.0042±0.0004	48±5	0.202±0.002	0.9998	5
2-F	0.026±0.006	29±7	0.751±0.013	0.9994	6
2-Cℓ	0.0068±0.0003	65±4	0.449±0.004	0.9999	5
2-Me	(2.09)[c]	(5.4)[c]	11.31±0.33	0.9987	5

a correlation coefficient

b number of data points

c value of SD on intercept exceeds that of intercept itself.

d using corrected k_1^{obs} (eq 3)

† 9-CN and 9-NO_2 reacted extremely slowly under these conditions

the same uncertainties. The ratios k_2^{obs} (Me)/k_2^{obs} (H) and k_2^{obs} (Br)/k_2^{obs}(H) for the 9 substituted derivatives (627 and 0.21 respectively) agree well with those found in a previous study in solvent CCl_4[1] (649 and 0.19 respectively).

Evidence that Diels–Alder transition states are "early" comes from widely differing mechanistic probes. Thus a study of secondary isotope effects has led to the conclusion that hybridisation of C_9 and C_{10} of anthracene is closer to sp^2 than sp^3 in the transition state leading to adduct formation with TCNE.[6] Curiously, in a similar study,[7] k_H/k_D values were found to be almost the same for the reactions of anthracene with maleic anhydride (MA, 0.95) and TCNE (0.94). TCNE is at least four orders of magnitude more reactive that MA and thus, according to the Hammond postulate, the transition state should be earlier for TCNE with a corresponding secondary isotope effect closer to unity. This result brings into question the usefulness of such measurements in delineating the finer details of mechanisms of this type. If the transition states are indeed early, then one would expect a correlation between rates and donor-acceptor properties to the two reactants,[8] whereas "late" transition states should show similarities to product structures. The former properties can be assessed from the difference ionisation potential of the donor (Ip) (itself dependent on the energy difference betweeen HOMO and LUMO levels in the donor), and the electron affinity of the acceptor (Ea).

Plots of $\log k_2^{obs}$ against (Ip–Ea) show reasonably good linearity for reactions of anthracene with both MA and TCNE.[9-11] Product-like transition states should yield correlations of log(rate constant) with the paralocalisation energies (Lp). Such correlations were observed for Diels–Alder reaction with polynuclear aromatics though the number of data points was not statistically very significant.[12] Very recent work has shown that correlations using Lp for an extended series of polycyclic aromatic hydrocarbons is not altogether satisfactory.[35] The limited data of Kiselev *et al.*[9] reveal a somewhat better correlation of $\log k_2^{obs}$ with $(\mathrm{Ip} - \mathrm{Ea})^{-1}$ ($r = 0.996$) than with Lp ($r = 0.986$). In the light of this work, we have re-examined data obtained recently in these laboratories. Table 3 shows the variation of $\Delta G\ddagger$ with Ip and Lp for a series of anthracene derivatives using TCNE as the dienophile (i.e. Ea is constant). The correlation with Ip is quite striking ($r = 0.9994$) whereas that with Lp very poor, although admittedly on a smaller sample. In addition, there is an extraordinarily good correlation with the *cis*-dienoid bond order parameter, ρ_d. This is not surprising in view of the excellent correlation between Ip and $\bar{\rho}_a$ ($r = 0.9992$ six data points from Refs. 11 and 13).

The slope of the ΔG‡/Ip correlation is very close to unity and the following relationship may be written:

$$\mathrm{Ip} = 1.01 \pm 0.02\,\Delta G\ddagger + 151.7 \pm 0.3. \qquad (4)$$

This equation should prove useful in predicting rates of reaction if values of Ip are known for a particular derivative. The above evidence strongly suggests a factor-like transition state where electron transfer is an important feature.

Effect of substituents on K

Although in some cases large uncertainties in K values are apparent, some general conclusions can be made. Firstly, substitution by halogens in various positions leads to generally enhanced K values over anthracene itself. A possible reason for this unexpected result is that some element of n-donor character occurs in the complexes. That halogens can enter into this type of bonding is illustrated by the formation of complexes, albeit ill-defined, between CCl_4 and aromatic hydrocarbons.[14] The values of K lie in a relatively limited range, suggesting that the complexes are rather weakly bonded structures. The value for the 9 methyl is surprisingly low which suggests that there is not much transfer of charge at this stage. The 1-fluoro derivative has a relatively high value. Molecular models indicate that for an assumed symmetrical attack, the cyano groups and 1-substituent approach fairly closely. Evidence from binding energies ESCA and CNDO calculations[15] shows that the cyano carbon atom has a significant positive charge which could be involved in weak electrostatic interactions with the lone pair on the halogen substituent. The K value for the 1-chloro compound is lower presumably due to the incursion of steric factors.

One interesting feature of the K determinations are the relative values of the 9-halogeno derivatives. The order suggests that the roles of the anthracene and TCNE have interchanged. A Hammett plot of $\log K^x/K_H$ vs σp shows some correlation with a ρ value of $\sim +2$. Though the errors are substantial nevertheless it appears that the electronic demand for complex formation is the reverse of that obtaining in the transition state leading from complex to products (*vide infra*).

Substituent Effects on k_1 and k_2^{obs}

The values of k_2^{obs} are generally much more reliable than those of k_1, however, it can be seen from Table 2 that both are much more sensitive to substituent effects than is K, enhanced values obtaining where electron release occurs. The effects are markedly attenuated for substituents in the outer rings. Such an effect has previously been reported for the reaction of anthracenes with MA in solvent dioxan.[16] It was noted that rates were influenced to an unexpectedly high degree by substituents in the 9– and 10– positions. This phenomenon was further examined by Stock *et al.*[17] It had already been suggested from resonance and MO

Table 3. Variation of free energy of activation, ΔG‡ (k cals mol^{-1}) with ionisation potential, I_p (k cals mol^{-1}) and paralocalisation energy Lp(β) and the mean endo-cisoid diene character order ($\bar{\rho}_d$) for the reaction of anthracene derivatives with TCNE in CCl_4

X	$\Delta G\ddagger^a$	Ip^b	Lp^c	$10^3\,\bar{\rho}_d{}^d$
H	17.4	169.0	3.31	741
9-Me	13.5	165.3	3.17	732
9-Et	14.0	165.8	-	-
9-Br	18.3	170.2	3.68	743
9,10 Me_2	10.6	162.3	3.02	726
		r=0.9994	r=0.893	r=0.9997

a Data from ref. 1

b Data from ref. 11

c,d Data from ref. 13

theory that π electron interactions between substitutents in the meso positions of anthracene should be large by comparison with the same groups in the para positions of benzene.[18] Stock studied the ^{19}F chemical shifts of a number of 10 - substituted 9-fluoroanthracenes and was able to conclude that π induction was a major factor. The substituent chemical shifts (SCS) were correlated by a four parameter equation.[5]

$$\mathrm{SCS} = \rho_I\sigma_I + \rho_R\sigma_R^\circ \qquad (5)$$

Whereas ρ_R increased only slightly along the series benzene, napthalene and anthracene (−32.1, −32.1, −36.1) very marked increases were found for ρ_I (−7.8, −12.1, −18.2) which were interpreted in terms of increased π induction in the naphthalene and anthracene series.

In the current study we have applied various forms of the Hammett equation to our data, separating the central ring substituents from those in the outer rings (Table 4). In the case of the simple Hammett plot, we have employed the usual modification for the case where substituents are directly conjugated with an electron deficient reaction centre.[19] For the 9-substituted derivatives, log k_1 correlates well with σ_p^+ values giving a ρ value of −7.5. Log k_2^{obs} correlations were similar though somewhat less precise. The 9-CN and 9-NO$_2$ reacted too slowly to measure under our conditions. This is predicted from the σ_p^+ correlation, values of k_2^{obs} of $\sim 4\times10^{-4}$ and 7×10^{-5} l mol^{-1} s^{-1} respectively being calculated leading to half lives of ~10 days and ~60 days at [TCNE] = 2×10^{-3} M. Thus it seems that the transition state has an appreciable positive charge. However, the question arises as to the relationship between ρ values obtained for polyannular systems and those of benzene. Unfortunately, very little data is available on electrophilic substitution in anthracene derivatives and even in the naphthalene series information is relatively scarce. Wells and Adcock[20] have found that application of the Hammett equation to data obtained for the alkaline hydrolysis of naphthoic esters results in precise correlations, but generating different ρ values for different substituent-reaction centre dispositions. Application of the Extended Selectivity Treatment (EST)[21] to naphthalene and benzothiophene resulted in curved plots.[22] A more recent attempt to analyse the naphthalene data resulted in the postulate of dual activation mechanisms for bicyclic aromatics employing *two* linear equations[23] in the correlation. For $0 > \rho \geqslant -4.6$, only the ring containing the reaction site was considered to be involved in the supply of electrons to satisfy the demand of the attacking electrophile and in delocalisation of positive charge in the transition state, whereas for $-4.6 > \rho$ *both* rings were involved. Also an approximately constant change in resonance energy in forming the transition state was postulated when only *one* ring is involved, whether monocyclic or the reacting ring of a polycyclic system.

In our case, substituents in the outer rings certainly have a significant effect on both k_1 and k_2^{obs}. Unlike electrophilic substituion, the Diels–Alder addition involves two reaction centres. The effect of substituents in the 1 and 2 positions on the 9 and 10 positions in anthracene approximate to those of m and p in benzene systems and hence, invoking the additivity principle:[24]

$$\log k^x/k_1 = \rho(\sigma_m^+ + \sigma_p^+). \qquad (6)$$

The k_2^{obs} data for both 1 and 2 positions correlate rather better with eqn (5) than with the individual σ^+ values. The correlation of k_1 is excellent for 2 substituents where steric factors are negligible but much less precise for the sterically sensitive 1 position. ρ values are substantially less than those obtained for 9 substituents which is further evidence of the dominance of transition

Table 4. Correlations of k_1 and k_2^{obs} with various forms of the Hammett equation (see text)

For k_1								
Substituent position		σ_m	σ_m^+	σ_p	σ_p^+ [a]	$\sigma_m+\sigma_p$	$\sigma_m^+ + \sigma_p^+$	Δ_{ij} [b]
1	r	0.973	0.971	0.613	0.005 (0.613)	0.889	0.823 (0.891)	-
	slope	-5.8	-5.5	-6.4	- (-6.4)	-3.6	-3.9 (-3.4)	-
2	r	0.978	0.977	0.961	0.814 (0.940)	1.00	0.990 (0.997)	0.992
	slope	-4.8	-4.6	-6.5	-5.1 (-4.7)/	-3.0	-2.9 (-2.5)	-2.8
9	r	-	-	0.951	0.958 (0.986)	-	-	0.878
	slope	-	-	-9.4	-7.5 (-6.6)	-	-	-4.3
For k_2^{obs} (=k_1K)								c
1	r	0.996	0.997	0.831	0.312 (0.831)	0.988	0.960 (0.989)	-
	slope	-3.6	-3.3	-5.2	- (-5.2)	-2.4	-2.7 (-2.3)	-
2	r	0.992	0.991	0.931	0.764 (0.911)	0.996	0.975 (0.990)	0.998
	slope	-2.9	-2.8	-3.8	-2.8 (-2.7)	-1.7	-1.7 (-1.5)	-1.7
9	r	-	-	0.911	0.955 (0.966)	-	-	0.871
	slope	-	-	-7.6	-7.1 (-6.1)	-	-	-4.2

a values obtained by adopting $|\sigma_p^+| = |\sigma_p|$ for electron withdrawing groups and $|\sigma_p^+| > |\sigma_p|$ for electron donating groups appear in parenthesis

b Δ_{ij} Δ5β + Δ8β see ref 25

c Δ_{ij} = Δ4α

state structures having the positive charge localised on the central ring.[17]

The compliance of the data with eqn (5) supports the postulate of a concerted attack by the incoming dienophile.

Alternative correlations have been applied to polycyclic aromatic systems. Dewar and Grisdale[25] have used the following relationship to define reaction constants:

$$\Delta_{ij} = F/_{rij} - M\pi_{ij} \qquad (6)$$

where the first term on the RHS accounts for direct electrostatic interactions and the second term form for π electronic effects, (both inductive and resonance). The term r_{ij} is the distance between the point of attachement of the substituent and the site of reaction. For the 2 substituents, the above correlation is as good as those using eqn (5) and the ρ values obtained show remarkable agreement between the two methods. However, very poor correlations resulted for 9 substituents. Thus, the rather simpler approach affords better overall correlations and confirms that the transition state is early with a pronounced development of charge and that concerted attack appears to be dominant, at least in the anthracene series.

Note on synthesis

We would like to draw attention to the ease of preparation of 1-fluoro-anthraquinones from the corresponding, more accessible, 1-chloro analogues. Replacement of chlorine by fluorine has been achieved by refluxing perbromo or perfluoro aromatic compounds with KF in sulpholane.[26] 3-Fluorophthalic anhydride was synthesised by heating the chloro-analogue with KF at 280–290° for 45 min.[27] Applying this method to the anthraquinone system, we were able to prepare 1-fluoroanthraquinone in quantitative yield. The reaction fails for 2-chloroanthraquinone presumably because of the reduced delocalisation of the negative charge in the Meisenheimer intermediate, assuming that the mechanism is nucleophilic aromatic substitution.

EXPERIMENTAL

Dichloromethane was purified by a standard method;[28] TCNE was supplied by Aldrich Chemical Co Ltd and purified by recrystallisation from benzene followed by two sublimations at 120° under 4 mm Hg. 9-Me, 9-Cl, 9-Br, 9-CN, 1-Cl and 2-Cl anthracenes were obtained from Aldrich Chemical Co. Ltd and recrystallised twice from ethanol prior to use. 9-Nitroanthracene was prepared by nitration of anthracene;[29] 2-methylanthracene was synthesised by zinc dust reduction of the corresponding anthraquinone.[30] 9-Fluoro[31] and 2-fluoroanthracene[32] were obtained by diazotisation of the corresponding aminoanthracenes and thermal decomposition of the tetrafluoroborates.

1-Fluoroanthracene

A mixture of 1-chloroanthraquinone (3g 0.0124 mole) and anhydrous KF (7.5g 0.129 mole) was heated at 300–350° on a sand bath for 1.5 hr. After cooling and adding water, the yellow product was filtered, sucked dry and recrystallised from CCl_4 to give an almost quantitiative yield of 1-fluoroanthraquinone. The product (0.3 g, 1.35 m mole) was heated at 70° for 4 hr with Zn dust (1.4 g, 0.021 g atom), $CuSO_4$ (0.01 g, 0.04 m mole) and ammonia solution (15 ml, 20%). The mixture was then filtered hot, washed with water and sucked dry. The solid was extracted with acetone (30 ml) filtered and the filtrate evaporated to give a reddish oil. This was dissolved in n-propanol (5 ml) and conc HCl added until precipitation occurred. The mixture was cooled to 0° filtered and the solid washed with methanol to give 0.15 g 1-fluoroanthracene m.p. 107–8°.

9-Iodoanthracene

Yellow mercuric oxide (43.2 g, 0.2 mol) was added to a stirred solution of trichloroacetic acid (80 g, 0.4 mol) and anthracene (35.6 g, 0.2 mol) in CCl_4 (700 ml) at room temperature. The mixture thickened appreciably, and was shaken overnight, and filtered. The yellow-green solid was washed with methanol to give 70 g (65%) 9-trichloroacetatomercurianthracene.[33] The product (40 g, 0.074 mol) was dissolved in AR acetone (400 ml) and a solution of iodine (18.8 g, 0.074 mol) in (AR acetone (200 ml) was added rapidly. The mixture was brought to reflux briefly then filtered into aqueous KI (100 g in 500 ml H_2O). The yellow precipitate was washed with aq KI and water then sucked dry to give 19.5 g (87%) crude 9-iodoanthracene[34] (m.p. 72°). Recrystallisation from methanol raised the m.p. to 77°.

Rate and equilibrium constants

The reactions were followed by monitoring the decrease in absorbance of the anthracene derivatives at the wavelengths indicated in Table 5. Absorbance measurements were made using a Unicam SP 1700 spectrophotometer equipped with a thermostatted cell compartment (25.0 ± 0.1° regulated by a Churchill thermocirculator) and a Unicam AR 25 Linear recorder. All reactions were conducted under pseudo first-order condition where $[TCNE] \geqslant 20[AnX]$. For all derivatives other than 9-Cl, 9-Br, 9-I, values of k_1 and K were obtained using eqn (2), the data

Table 5. UV data for substituted anthracenes (An X) in CH_2Cl_2 at 18°

					a			
X	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε	λ_{max}	log ε
H	325	3.48	341	3.73	359	3.83	378	3.81
9-F	330	3.34	346	3.64	365	3.79	385	3.69
9-Cl	-	-	353	3.72	370	3.94	390	3.74
9-Br	336	3.42	353	3.73	372	3.86	392	3.78
9-I	340	3.45	357	3.76	375	3.91	396	3.77
9-NO_2	-	-	348	3.45	365	3.65	383	3.56
9-Me	332	3.64	348	3.73	365	4.11	385	4.04
2-Me	325	3.68	340	3.87	355	4.00	375	3.90
1-F	327	3.65	342	3.89	358	4.04	378	3.94
2-F	327	3.71	343	3.83	359	3.88	379	3.81
1-Cl	330	3.69	345	3.95	360	4.10	380	4.26
2-Cl	328	3.48	343	3.70	361	3.79	381	3.79

a analytical wavelength used in kinetic runs

Table 6. Values of the equilibrium constant for adduct formation (K_{eq} l mol^{-1}) for 9-chloroanthracene (9-AnCl) in CH_2Cl_2 at 25°

		a		b		c
10^3[AnCl]	10^3[TCNE]	A_∞	10^4 $a-x_\infty$	x_∞	$b-x_\infty$	K_{eq}
0.55	1.00	1.979	2.24	3.26	7.74	1880
0.60	1.20	2.035	2.30	3.70	8.30	1938
0.65	1.30	2.071	2.34	4.16	8.84	2011
0.70	1.40	2.079	2.35	4.65	9.35	2116

a absorbance at 370 nm.

b x_∞ = adduct concentration.

c K_{eq} = 1990 ± 100

being analysed by an interactive data analysis programme used for simple regression analyses.

Overall equilibrium constants (Keq) for adduct formation were measured by mixing solutions of the appropriate anthracene ($\sim 2\times 10^{-2}$ M) with an equal volume of TCNE solution ($\sim 4\times 10^{-2}$ M) and allowing to come to equilibrium (30 min). The sample was diluted 20 fold and time allowed for the new equilibrium position to be established (*ca* 2hr). (This incidentially affords a method of measuring the reverse reaction rate since the position of equilibrium is dependent on the initial concentrations of diene and dienophile). Absorbance measurements were then made at the appropriate wavelength. Results for 9-chloroanthracene appear in Table 6. Values obtained were as follows: 9-Cl, 1990 ± 100; 9-Br, 2090 ± 50; 9-I, 2400 ± 100 and anthracene itself, $1.2\pm0.2\times10^5$ l mol^{-1}. All other derivatives had values $>10^4$.

REFERENCES

[1] M. Lotfi and R. M. G. Roberts, *Tetrahedron* **35** 2131 (1979) and references therein.
[2] V. D. Kiselev and J. G. Miller, *J. Am. Chem. Soc.* **97** 4036 (1975).
[3] M. Lotfi and R. M. G. Roberts, *Tetrahedron* **35** 2137 (1979).
[4] M. Lotfi and R. M. G. Roberts, *Ibid* **35** 2123 (1979).
[5] A. A. Frost and R. G. Pearson *Kinetics and Mechanism* 2nd Edn Chapt. 8. Wiley, New York (1961).
[6] P. Brown and R. C. Cookson, *Tetrahedron* **21** 1993 (1965).
[7] D. E. Van Sickle and J. O. Rodin *J. Am. Chem. Soc.* **86** 3091 (1964).
[8] K. L. Mok and M. J. Nye, *J. Chem. Soc. Perkin Trans I* 1810 (1975).
[9] V. D. Kiselev, A. I. Konovalov, E. A. Veisman and A. N. Ustygov *Zhur. Org. Khim.* **14** 134 (1978).
[10] A. I. Konovalov, *Doklady Akad Nauk SSSR* **223** 613 (1975).
[11] A. I. Konovalov and V. D. Kiselev, *Zhur. Org. Khim.* **2** 142 (1966).
[12] A. Streitwieser *Molecular Orbital Theory for Organic Chemists* Chapt. 15. Wiley, New York (1961).
[13] H. Sofer, O. E. Polansky and G. Derflinger, *Monatsch Chem.* **101** 1318 (1970).
[14] R. Foster, *Organic Charge Transfer Complexes* p. 278. Academic Press, London (1969).
[15] G. D. Stucky, D. A. Matthews, J. Hedman, M. Klasson and C. Nordling, *J. Am. Chem. Soc.* **94** 8009 (1972).
[16] J. Saver, D. Lang and A. Mielert, *Agnew. Chem. Int. Ed.* **1** 268 (1962).
[17] G. L. Anderson, R. C. Parish and L. M. Stock, *J. Am. Chem. Soc.* **93** 6984 (1971).
[18] R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.* 2221 (1961).
[19] O. Exner in *Advances in Linear Free Energy Relationships.* Editors N. B. Chapman and J. H. Shorter, Chap. 1. Plenum Press, London (1972).
[20] P. R. Wells and W. Adcock, *Aust. J. Chem.* **19** 221 (1966).
[21] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.* **1** 35 (1963).
[22] S. Clementi, P. Linda and C. D. Johnson, *J. Chem. Soc. Perkin II* 1250 (1973).
[23] A. A. Humffray and R. L. Bruce, *J. Org. Chem.* **44** 724 (1979).
[24] H. H. Jaffé, *Science* **118** 246 (1953).
[25] M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.* **74** 3539 (1962).
[26] G. Fuller, *J. Chem. Soc.* 6264 (1965).
[27] A. Heller, *J. Org. Chem.* **25** 834 (1960).
[28] A. Weissberger *Technique of Organic Chemistry*, Vol. 7. Interscience, New York (1955).
[29] C. E. Brown, C. D. Cook, C. Merritt and J. Rousseau, *Org. Synth.* Coll. Vol. 4, 711.
[30] R. Golden and L. M. Stock *J. Am. Chem. Soc.* **94** 3080 (1972).
[31] J. Rigaudy and J. Barcelo, *Compt. Rend. Acad Sc.* (*Paris*) **258** 4799 (1964).
[32] E. D. Bergmann, J. Blum, and S. Butanaro, *J. Org. Chem.* **26** 3211 (1961).
[33] K. Rasheed, *Pak. J. Sci. Ind. Res.* **10** 102 (1967).
[34] W. E. Bachmann and M. C. Kloetzel, *J. Org. Chem.* **3** 55 (1938).
[35] D. Biermann and W. Schmidt, *J. Am. Chem. Soc.* **102** 3163, 3173 (1980).