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KINETICS AND MECHANISMS OF DIELS–ALDER ADDITION OF TETRACYANOETHYLENE TO ANTHRACENE DERIVATIVES—II

SOLVENT EFFECTS

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Abstract—The effect of change of solvent on the rate of Diels–Alder addition of tetracyanoethylene (TCNE) to anthracene has been investigated using solvents CCl_4, $CHCl_3$ and CH_2Cl_2. Solvent effects were measured on the intermediate complex and on the starting materials from solubility measurements. From this, solvent effects on the transition state alone can be evaluated. These effects were remarkable similar to those measured for both the initial state and the intermediate complex suggesting an "early" transition state having a structure similar to that of the intermediate. From the correlation of $\Delta G_t^{\neq}$ (the free energy of transfer from CCl_4 to another solvent for the transition state alone) with the solubility parameter δ^2, the molar volume of the transition state can be estimated. The result again suggests that the transition state is more "factor" than product-like.

Numerous attempts have been made over the past 50 years to correlate reaction rates with certain properties of the solvents used. These attempts have met with varying degrees of success, but unfortunately no single approach seems to have universal application. Excellent reviews[1-4] have appeared recently in which the difficulties of such correlations are discussed in detail. In general, where reactions involve some degree of charge separation in the transition state, the Y,[5] Z,[6] E_T[7] and Kirkwood[8] solvent scales have been found to be apposite for rate correlations, whereas the δ (or δ^2)[9,10] scale based on the cohesive energy density of the solvent has been shown to correlate fairly well in reactions involving little change in polarity. The present paper is concerned with solvent effects on the reaction of anthracene with tetracyanoethylene (TCNE) and is an attempt to separate the solvation effects on the initial state, intermediate complex and transition state.

RESULTS AND DISCUSSION

Change of solvent in Diels–Alder reactions causes correspondingly small variations in reaction rate, a fact which has led to the conclusions that the transition state involves little charge separation and that the addition occurs by a concerted mechanism.

Thus one would anticipate good correlations between $\log k_{exp}$ (or $\Delta G^{\neq}_{exp}$) and either δ or δ^2 in accordance with regular solution theory,[9] k_{exp} and $\Delta G^{\neq}_{exp}$ being the observed second order rate constants and free energy of activation respectively. Eckert has reported such correlations in reactions of maleic anhydride with 1,3-butadiene[11] and with isoprene,[12] the dimerisation of cyclopentadiene,[13] and the addition of acrylonitrile to isoprene.[11] In each case however the correlation was only fair, with dipolar aprotic solvents such as nitromethane lying well off the lines. For example in the maleic anhydride/isoprene reaction a correlation coefficient of 0.91 is obtained for a plot of $\Delta G^{\neq}_{exp}$ against δ^2 *omitting the datum point for solvent nitromethane.* Corresponding plots using the E_T and Kirkwood Scales show almost a completely random scatter. Brown and Cookson[14] have reported activation parameters for the reaction of anthracene and TCNE in sixteen different solvents and showed that there is little if any correlation with (D − 1/2D + 1).

We have plotted their data for anthracene ($\Delta G^{\neq}_{exp}$ vs δ^2) and found that there is a reasonable correlation for aromatic solvents but considerable scatter for polar solvents. The slope of the correlation for aromatic solvents is very similar to those found for bicycloheptadiene/TCNE and 9,10 dimethylanthracene/TCNE additions.[15] However a detailed examimation of Brown and Cookson's data reveals a number of serious inconsistencies which unfortunately undermine confidence in such correlations. The data of Kiselev and Miller[15] are rather more consistent, although even here there are quite wide variations in the reported rate constants with consequent uncertainties in the values of $\Delta H^{\neq}_{exp}$ and $\Delta S^{\neq}_{exp}$, due mainly to the extremely rapid reactions involved. Plots of $\Delta G^{\neq}_{exp}$ and $\Delta H^{\neq}_{exp}$ vs δ^2 are reasonably linear provided not too great a range of solvent polarity is used (Fig. 1). The only dipolar aprotic solvent employed was acetonitrile and this falls well outside the correlation line. The corresponding plots against E_T show no apparent correlation. The data for the plots appears in Table 1. The corresponding correlation of $\log k_{exp}$ vs δ^2 is however extremely poor for the addition of fumaronitrile to dimethylanthracene.[16]

The latter data also gave a fairly poor correlation with the solvent parameter Ω devised by Berson *et al.*[17] from *endo–exo* product ratios in Diels–Alder reactions. Unfortunately solubility factors have limited this scale to the dipolar protic and aprotic solvents. In view of the above anomalies it was decided to examine in detail ground state and transition state solvent effects in a limited range of solvents of similar structure (CCl_4, $CHCl_3$, CH_2Cl_2). There is now convincing evidence that charge transfer complexes are intermediates in Diels–Alder addition reactions.[15,18] Consequently, any detailed study of solvent effects should include effects on these complexes. We have evaluated the thermodynamic

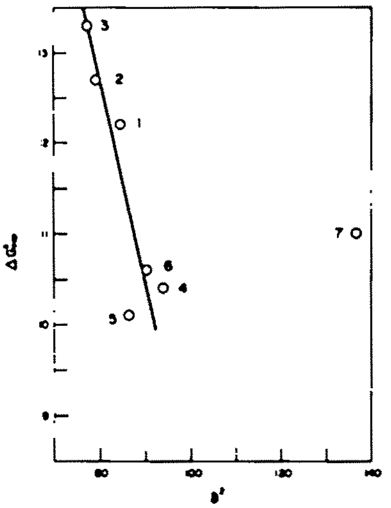

Fig. 1. Correlation of $\Delta G^{\ddagger}_{exp}$ (k. cals. mol^{-1}) with solubility parameter δ^2 (cals. ml^{-1}). Numbering as in Table 1.

Table 1. Correlations of free energy ($\Delta G^{\ddagger}_{exp}$ kcal mol^{-1})^a and enthalpy of activation ($\Delta H^{\ddagger}_{exp}$ kcal mol^{-1}) with solvent parameters δ^2 (cal ml^{-1}) and E_T (kcal mol^{-1}) for the addition of TCNE to 9,10-dimethylanthracene. (Data from Refs. 1 and 15)

	Solvent	$\Delta G^{\ddagger}_{exp}$	$\Delta H^{\ddagger}_{exp}$	δ^2	E_T
1	Benzene	12.2	1.73	84.6	34.5
2	Toluene	12.7	2.85	79.2	33.9
3	o-xylene	13.3	4.38	77.4	-
4	CH_2Cl_2	10.4	-1.79	94.0	41.1
5	$CHCl_3$^{a}	10.1	-2.74	86.5	39.1
6	$(CH_2Cl)_2$^{a}	10.4	-1.88	90.2	41.9
7	MeCN	11.0	-1.19	136.9	46.0

a - average values

parameters for complex formation by a spectroscopic method (Table 2).

Only small changes are found, the complex being somewhat less stable relative to reactants in CH_2Cl_2 than CCl_4. Interestingly, there is an excellent correlation between $\log K_c$ and δ^2 for the hydrocarbon solvents used (correlation coefficient 0.999). The corresponding activation parameters were obtained from rate measurements (Table 3). Two other substrates were examined to show the general effect of change of solvent. In all three cases the free energy term $\Delta G^{\ddagger}_{exp}$ was greater for CCl_4 than those for the other two solvents which were almost identical. The chief difference arose in each case from the enthalpy term $\Delta H^{\ddagger}_{exp}$. To complete the analysis, the solvent effects on the reactants was determined from solubility measurements (Table 4). It is immediately apparent from the data that the changes in free energy of solvation on transfer from one solvent to another are small for anthracene, and the major changes come as one might anticipate from the more polar TCNE molecule.

Solvent effects can be quantitatively separated into initial state and transition state contributions providing that the activation free energies are known with respect to a reference solvent and that the free energy of solvation is known for the reactants. The latter can be obtained by various means including solubility measurements. It is easily shown that

$$\Delta G_t^{\ddagger} = \Delta G_t^{\circ}(\text{reactants}) + \delta\Delta G^{\ddagger}_{exp} \tag{1}$$

where $\Delta G_t^{\ddagger}$ is the free energy of transfer from a reference solvent to any other for the transition state alone, ΔG_t° (reactants) a similar function for the initial state, and $\delta\Delta G^{\ddagger}_{exp}$ is the relative free energy of activation. An additional factor in the present work is the solvent effect on the intermediate complex. From Tables 2–4 it is now possible to calculate the relevant transfer free energies, enthalpies and entropies for the initial state, complex and transition state. The results appear in Table 5. The values of the solvation parameters (ΔG_t°, etc.) for anthracene in $CHCl_3$ could not be obtained (vide infra) and an average was taken of the corresponding values for CH_2Cl_2 and CCl_4. This introduces only a small uncertainty since the solvation of anthracene in these solvents is very similar and the major initial state solvent effects are associated with TCNE. Table 5 shows that the solvent effects on the initial state and complex are remarkably similar. This is in keeping with other findings that values of K_c for complex formation are not sensitive to substituent effects and that the entropies of formation are not very negative.[18] This implies that the complex is very much more "factor"-like than product-like.

The dominant changes are enthalpic rather than entropic which again indicates only small losses in vibrational freedom. The solvent effects on the transition state are more pronounced, being roughly double those on the initial state and complex and again the dominant effect is one of enthalpy. There is indeed a striking similarity between the solvent effects on the transition state and those of the complex. The results are very much in keeping with an "early" transition state which has a structure similar in character to the intermediate complex. It is, we feel, highly significant that the ΔG_t terms for complex and transition state run parallel and is further evidence for the complex being an intermediate in Diels–Alder addition.

Since the effect of solvent on the transition state has

Table 2. Equilibrium constants, K_c° (l mol^{-1}) and thermodynamic parameters (ΔG_c°, ΔH_c° kcal mol^{-1}, ΔS_c° cal deg^{-1} mol^{-1}) for complex formation between anthracene and TCNE in CCl_4, $CHCl_3$ and CH_2Cl_2

Solvent	K_c(25°)	$-\Delta G_c^{\circ}$	$-\Delta H_c^{\circ}$	$-\Delta S_c^{\circ}$
CCl_4	3.11	0.67 ± 0.05	3.20 ± 0.4	8.6 ± 1.2
$CHCl_3$	1.73	0.32 ± 0.05	2.70 ± 0.3	8.0 ± 0.8
CH_2Cl_2	1.02	0.11 ± 0.05	2.70 ± 0.3	8.7 ± 0.8

Table 3. Activation parameters* ($\Delta G^{\neq}_{exp}$, $\Delta H^{\neq}_{exp}$ kcal mol^{-1}; $\Delta S^{\neq}_{exp}$ cal deg^{-1} mol^{-1}) for TCNE addition to anthracene derivatives in CCl_4, CH_2Cl_2, $CHCl_3$

REACTION	$\Delta H^{\neq}_{exp}$	$\Delta S^{\neq}_{exp}$	$\Delta G^{\neq}_{exp}$
Anthracene (ANH)			
CCl_4	6.38 ± 0.04	-36.9 ± 0.1	17.4 ± 0.04
CH_2Cl_2	4.91 ± 0.23	-39.2 ± 0.8	16.6 ± 0.23
$CHCl_3$	4.45 ± 0.16	-40.4 ± 0.5	16.5 ± 0.16
9-Trimethylsilyl-ANH			
CCl_4	5.11 ± 0.04	-38.8 ±0.1	16.7 ± 0.04
CH_2Cl_2	3.52 ± 0.11	-41.3 ± 0.4	15.8 ± 0.11
$CHCl_3$	2.99 ± 0.02	-42.7 ± 0.08	15.7 ± 0.02
9-Bromo-ANH			
CCl_4	7.78 ± 0.42	-35.4 ± 1.4	18.3 ± 0.42
CH_2Cl_2	6.35 ± 0.12	-38.0 ± 0.4	17.7 ± 0.12
$CHCl_3$	6.23 ± 0.32	-37.8 ± 1.1	17.5 ± 0.33

* Calculated at 25.0°C

Table 4. Thermodynamic parameters (ΔG°_s, ΔH°_s kcal mol^{-1}; ΔS°_s cal deg^{-1} mol^{-1}) of solvation of anthracene and TCNE in solvents CCl_4, $CHCl_3$ and CH_2Cl_2

THERMODYNAMIC PARAMETER	ANTHRACENE			TCNE		
	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$
$\Delta H^{\circ *}_s$	6.47 ± 0.26	6.52 ± 0.34	-	12.0 ± 0.5	8.20 ± 0.49	9.53 ± 0.30
ΔS°_s	16.2 ± 0.8	18.4 ± 1.1	-	28.4 ± 1.6	23.2 ± 1.5	24.2 ± 1.0
ΔG°_s *	1.64 ± 0.26	1.03 ± 0.34	-	3.54 ± 0.5*	1.28 ± 0.49	2.31 ± 0.30

* calculated at 25°C

Table 5. Free energy (ΔG_t kcal mol^{-1}), enthalpy (ΔH_t kcal mol^{-1}) and enthropy contributions ($-T\Delta S_t$ kcal mol^{-1}) for transfer from solvent CCl_4 to $CHCl_3$ and CH_2Cl_2

Parameter [b]	∑ reactants [a]		complex		transition state	
	$CHCl_3$	CH_2Cl_2	$CHCl_3$	CH_2Cl_2	$CHCl_3$	CH_2Cl_2
ΔH_t	-2.5	-3.8	-2.0	-3.3	-4.4	-5.3
$-T\Delta S_t$	+1.0	+0.9	+0.8	+0.9	+2.0	+1.6
ΔG_t	-1.6	-2.9	-1.2	-2.4	-2.3	-3.7

a - values of ΔG°_s (anthracene) etc. for $CHCl_3$ were taken as the average of those values for CH_2Cl_2 and $CHCl_3$.

b - negative sign implies greater stability with respect to CCl_4.

been elucidated, it should be possible to correlate the $\Delta G_t^{\neq}$ with the solvent parameter δ and hence a value for the molar volume of the transition state (V_{tr}) can be estimated.

From regular solution theory

$$RT \ln k/k_0 = V_A(\delta_A - \delta)^2 + V_B(\delta_B - \delta)^2 - V_{Tr}(\delta_{Tr} - \delta)^2 \quad (2)$$

where V_A and V_B are the molar volumes of reactants A and B and δ_A, δ_B, δ_{Tr} are the relevant solubility parameters. δ is the solubility parameter of the solvent.

Since the initial state solvent effects have been separated out we can write

$$\Delta G_t^{\neq} = V_{Tr}(\delta_{Tr} - \delta_s)^2 - V_{Tr}(\delta_{Tr} - \delta_R)^2 \quad (3)$$

for solvents R (=reference) and S, $\Delta G_t^{\neq}$ being the free energy of transfer from solvent R to solvent S.

Equation (3) can be rearranged to

$$\Delta G_t^{\neq}/\delta_s - \delta_R = V_{Tr}\delta_s + V_{Tr}\delta_R - 2V_r\delta_{Tr} \qquad (4)$$

and hence a plot of the LHS of (4) vs δ_s gives slope V_{Tr} and intercept $V_{Tr}(\delta_R - 2\delta_{Tr})$. Unfortunately in this work only three solvents were used. If CCl_4 is taken as the reference then the slope of the above plot gives a value of V_{Tr} of ca 800 ml. From the intercept, δ_{Tr} is calculated 10.9. Both these values are quite reasonable.

The molar volume of anthracene (V_{AnH}) is 160.2 ml.[19] The molar volume of TCNE has not been measured, but adopting a similar procedure to that used to determine V_{Tr}, values of 220 ml and 13.1 are obtained for V_{TCNE} and δ_{TCNE} respectively. Again the values are reasonable (V_{TCNE} is somewhat high) and confirm the general validity of the approach, though of course more data in other solvents is needed for accurate analysis. The δ value for TCNE compares with 11.7 for acetonitrile and 13.0 for DMSO which seems about right. V_{Tr} thus appears to be considerably larger than $V_{AnH} + V_{TCNE}$ and is consistent with an "early" transition state where the reactants are still some distance apart.

EXPERIMENTAL

Solvents CCl_4, $CHCl_3$ and CH_2Cl_2 were purified by standard procedures. TCNE was sublimed twice before use and blue fluorescent anthracene was chromatographed on alumina.

Determination of solubilities

(a) *Anthracene.* An excess of finely powdered anthracene was added to 5 ml of the appropriate solvent and shaken in a thermostatted water bath for a minimum of 12 hr. The contents of the flask were allowed to settle for 1 hr before sampling. Aliquots were withdrawn and the absorbance measured at 358 nm after appropriate dilution. The concentration of anthracene was calculated from a calibration line obtained using the data in Table 6. The solubilities of anthracene at various temps in CCl_4 and CH_2Cl_2 appear in Table 7. Results in $CHCl_3$ were rather erratic. Radical species are known to form in this solvent, particularly at elevated temps. One of the products of decomposition of $CHCl_3$ is dichlorocarbene which is known to undergo facile addition to anthracene, thus considerably altering the solubility.

(b) *Tetracyanoethylene.* The same general procedure was adopted. Aliquots were removed and added to a 0.5 M soln of mesitylene in CH_2Cl_2. TCNE forms a stable coloured CT complex with mesitylene (λ_{max} 460 nm). The absorbance was measured at this wavelength and the (TCNE) determined from the calibration graph (Table 6). The solubilities appear in Table 7.

Table 6. Absorbances of anthracene solutions in CCl_4 (λ = 358 nm) and of TCNE/mesitylene solutions in CH_2Cl_2 (λ = 460 nm)

10^5[AnH](M)	1	3	7	10	12		
A_{358}	0.083	0.280	0.689	0.860	0.1040		
10^5[TCNE](M)	1	2	3	4	5	6	7
A_{460}	0.095	0.136	0.164	0.282	0.287	0.346	0.402

Table 7. Solubilities, C (mol l^{-1}) of anthracene and TCNE in solvents CCl_4, $CHCl_3$ and CH_2Cl_2 at various temperatures

Anthracene

CCl_4	T	27.0	32.6	34.8	38.4	41.2	45.1	52.8	56.9	62.4
	10 C	0.71	0.81	0.88	0.93	1.05	1.23	1.53	1.75	2.22
CH_2Cl_2	T	26.5	27.7	29.8	30.6	32.9	34.0	35.7	37.1	
	10 C	1.86	1.95	2.05	2.09	2.25	2.40	2.60	2.69	

TCNE

CCl_4	T	34.8	38.2	41.1	44.4	45.3	50.6	51.0	
	10^2C	0.43	0.44	0.90	0.97	0.89	1.25	1.22	
$CHCl_3$	T	29.8	30.6	34.1	34.8	38.8	45.3	50.4	50.9
	10^2C	2.6	2.8	3.3	3.4	4.4	5.5	7.1	7.6
CH_2Cl_2	T	26.5	27.7	29.8	30.6	32.9	34.0	35.7	
	C	0.120	0.133	0.138	0.145	0.154	0.171	0.188	

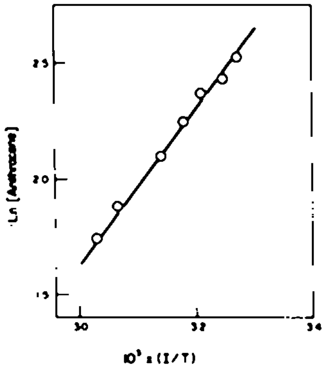

Fig. 2. Plot of ln (anthracene solubility) vs T^{-1} (°K^{-1}).

Thermodynamic constants of solvation

The free energy of solvation is defined by

$$\Delta G^\circ_s = -RT \ln C \qquad (5)$$

where C is the concentration of dissolved solute for a saturated solution. Separating ΔG°_s into its component parameters ΔH°_s, ΔS°_s yields

$$\ln C = -\frac{\Delta H^\circ_s}{RT} + \frac{\Delta S^\circ_s}{R} \qquad (6)$$

from which these parameters can be evaluated from data at various temperatures. Figure 2 shows a typical plot for anthracene.

Rate constants and complex formation constants

These were determined spectrophotometrically in the manner described in the preceding paper.[18]

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