The Effect of Dichloromethane on the Molecular Complexes of Tetracyanoethylene

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Abstract: In order to determine the true equilibrium constants for molecular complexes of tetracyanoethylene in dichloromethane solution, the complexation of tetracyanoethylene by dichloromethane must be considered. The equilibrium constant for the tetracyanoethylene–dichloromethane complex determined in the present study by competitive complexation experiments on four tetracyanoethylene–methylated benzene complexes in dichloromethane–carbon tetrachloride solutions is 0.29 M^{-1} at 25°. This value is much larger than previously estimated by other workers.

Most of the equilibrium constants reported for the molecular complexes of tetracyanoethylene (TCNE) were determined in the solvents chloroform or dichloromethane.[2-6] However, Merrifield and Phillips[2a] have indicated that TCNE forms a complex with dichloromethane (DCM). The equilibrium constant for this complex was estimated by these workers by a comparison of the effect of the solvents diethyl ether and DCM on the equilibrium constants of several other TCNE complexes. The equilibrium constant for the TCNE–ether complex in chloroform was determined directly, under the assumption that there was no interaction between TCNE and chloroform. A value of 0.21 was obtained for the equilibrium constant in mole fraction units for the TCNE–DCM complex. In view of the indirect method used to determine this equilibrium constant, and the similarity between chloroform and the complexing solvent DCM, it was of interest to study the TCNE–DCM complex directly in the commonly accepted noninteracting solvent, carbon tetrachloride. The equilibrium constant for the TCNE–DCM complex would be of obvious importance for the determination of the true equilibrium constants for donor–TCNE complexes obtained when DCM is the solvent.

In order to obtain a direct comparison with the results of Merrifield and Phillips, four of the methylated benzene derivatives used by these workers were employed in the present study. The main advantage of this system is that the visible absorption bands of the TCNE–methylated benzene complexes are well removed from the absorption bands of the uncomplexed components, affording a facile, interference-free method for the determination of the corresponding equilibrium constants.

The effect of DCM on a typical donor–TCNE complex is shown in Figure 1. The method of Benesi and Hildebrand (BH)[7] is applied to the benzene–TCNE complex in four DCM–CCl_4 mixtures. As shown in Figure 1, the slope of the line is linearly dependent on the DCM concentration, while the intercept is essentially unchanged. Since, in the BH method, the intercept is inversely proportional to the molar absorptivity of the complex, and the slope is inversely proportional to the product of the molar absorptivity and the equilibrium constant of the complex, then from Figure 1, the equilibrium constant of the complex is inversely proportional to the DCM concentration, and the molar absorptivity of the complex is independent of the DCM concentration. These changes are too large to be due to a nonspecific solvent effect; therefore, the competitive formation of a TCNE–DCM complex is assumed.

Mathematical Equations

The equilibrium constants for the systems studied were obtained by the general equations and scheme developed by Tamres.[8] Two competitive equilibria are considered

$$\mathrm{T} + \mathrm{B} \rightleftharpoons \mathrm{TB} \tag{1}$$

$$\mathrm{T} + \mathrm{S} \rightleftharpoons \mathrm{TS} \tag{2}$$

where T, B, S, TB, and TS are TCNE, methylated benzene, DCM, TCNE-methylated benzene complex, and TCNE–DCM complex, respectively. The equilibrium constant for the first equilibrium will be called K_{CT}, and the constant for the second equilibrium will be called K_{S}. The appropriate mass action expressions are

$$K_{\mathrm{CT}} = \frac{[\mathrm{TB}]}{[\mathrm{T}][\mathrm{B}]} = \frac{[\mathrm{TB}]}{([\mathrm{T}_0] - [\mathrm{TB}] - [\mathrm{TS}])([\mathrm{B}_0] - [\mathrm{TB}])} \tag{3}$$

$$K_{\mathrm{S}} = \frac{[\mathrm{TS}]}{[\mathrm{T}][\mathrm{S}]} = \frac{[\mathrm{TS}]}{([\mathrm{T}_0] - [\mathrm{TB}] - [\mathrm{TS}])([\mathrm{S}_0] - [\mathrm{TS}])} \tag{4}$$

where all concentrations are in molarity, and the zero subscript indicates initial concentration. Since $[\mathrm{S}_0]$ was made very much larger than $[\mathrm{T}_0]$ in this work, $([\mathrm{S}_0] - [\mathrm{TS}]) \cong [\mathrm{S}_0]$. Using this approximation, eq 3 and 4 can be solved simultaneously, by eliminating [TS], to give eq 5. Since there are no overlapping absorption bands at the maxima of the molecular complex bands under investigation, the substitution, $[\mathrm{TB}] = A/\epsilon b$, can be made for the concentration of the TCNE–

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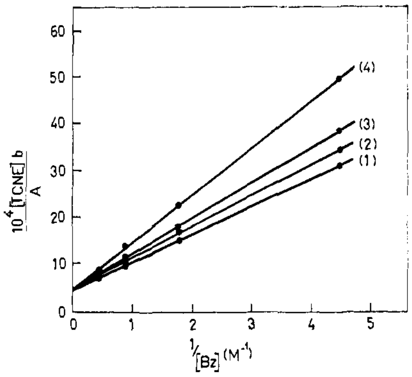

Figure 1. Benesi–Hildebrand plot for the TCNE–benzene complex in DCM–CCl_4 solutions; (1) 0.157 *M* DCM; (2) 0.943 *M* DCM; (3) 1.73 *M* DCM; (4) 3.30 *M* DCM.

methylated benzene complex, where A is the absorbance at the maximum of the molecular complex band, b is the path length of the absorption cells, and ϵ is the

$$\frac{1}{K_{CT}} = \frac{1}{1+[S_0]K_S} \times \left[\frac{[T_0][B_0]}{[TB]} - [B_0] - [T_0] + [TB]\right] \tag{5}$$

molar absorptivity of the TCNE–methylated benzene complex. With this substitution, eq 5 becomes

$$\frac{1}{K_{CT}} = \frac{1}{1+[S_0]K_S} \times \left[\frac{[T_0][B_0]\epsilon b}{A} - [B_0] - [T_0] + \frac{A}{\epsilon b}\right] \tag{6}$$

Equation 6 is essentially the Rose–Drago equation,[9] but includes the solvent complexation term, $1/(1 + [S_0]K_S)$. Under the condition that [TB] is small, as is the case with weak complexes, and, when there is a large excess of $[B_0]$ over $[T_0]$, eq 6 can be reduced to the competitive complexation form of the familiar Benesi–Hildebrand equation

$$\frac{[T_0]b}{A} = \frac{1+[S_0]K_S}{\epsilon K_{CT}[B_0]} + \frac{1}{\epsilon} \tag{7}$$

The use of eq 6 or 7 depends on the experimental conditions and approximations involved. However, both equations permit one to obtain an apparent equilibrium constant for the TCNE–methylated benzene complex

$$K_{app} = K_{CT}/(1 + [S_0]K_S)$$

or, upon rearranging

$$K_{CT} = K_{app}(1 + [S_0]K_S) \tag{8}$$

Equation 8 is essentially the same as that derived by Drago, *et al.*[10]

Table I. Data for TCNE-Methylated Benzene Complexes[a]

Donor	10^2 [donor], M	A	10^4-[TCNE], M	K_{APP}, M^{-1}	ϵ, M^{-1} cm^{-1}
Bz	22.00	0.218	6.630	0.740	2,350
	55.00	0.452			
	110.0	0.694			
	219.9	0.968			
Tol	9.330	0.190	7.010	1.76	1,910
	28.00	0.436			
	46.60	0.600			
	93.30	0.867			
Mes[b]	2.238	0.180	3.773	7.89	3,168
	3.730	0.270			
	7.460	0.440			
	22.38	0.777			
HMB	0.4975	0.225[c]	0.6012	111	5,100
	0.9950	0.323			
	1.990	0.415			
	5.970	0.547			
	9.950	0.600			

[a] Solvent, CCl_4; b = 1 cm; temperature, 25°; DCM = 0.157 *M*. [b] Mes data are for 0.0760 *M* DCM. [c] The path length for the HMB series was 2.0 cm.

The two unknowns in eq 8, K_{CT} and K_S, were evaluated by the following method. Three trial values of K_S were inserted into eq 8, and, for a particular value of K_{app} determined at a known $[S_0]$, K_{CT} was calculated for each trial. The calculated values of K_{CT} were then plotted against the trial values of K_S, and a straight line was drawn through the points. This procedure was repeated for each of the K_{app} and $[S_0]$ pairs determined experimentally. The coordinates of each of the points of intersection of these lines are possible values for the two equilibrium constants sought. Theoretically, all the lines should intersect at one point; however, experimental uncertainties necessitate the averaging of the clustered intersections. The deviations of all points differed from the respective averages by less than two standard deviations, so all intersections were retained. The resulting averages of the coordinates of the intersections represent the best values for the equilibrium constants sought. The graphical method, which allows for visual detection of any bias of the intersections, showed only random experimental scatter. All systems were solved analytically also, and the results agreed well within experimental error with the graphical results.

Experimental Section

The electronic spectra were obtained on a Beckman Model DK-2 spectrophotometer equipped with a thermostated temperature cell set at 25°. The accuracy of temperature control was ±0.2°. The TCNE obtained from Aldrich Chemical Co. was three times sublimed under vacuum (mp 198–199°). The hexamethylbenzene (HMB) obtained from Aldrich Chemical Co. was sublimed twice under vacuum (mp 164–165°). Spectroquality DCM was shaken with NaOH and $CaCl_2$, distilled, and stored in the dark in a ground-glass stoppered bottle. A 0.05 *M* stock solution of TCNE in DCM remained colorless for 2 months if the DCM was treated in this manner. Benzene (Bz), toluene (Tol), mesitylene (Mes), and carbon tetrachloride were Matheson Coleman and Bell spectroquality materials, and were used without further purification.

The concentration of the TCNE–DCM stock solution increased with time, due to the high volatility of DCM. Therefore, three stock solutions were prepared, four aliquots of each solution rapidly diluted in CCl_4, and the ultraviolet spectra obtained immediately thereafter. The average value of the molar absorptivity of the TCNE absorption band at 276 mμ was 1.50×10^4 M^{-1} cm^{-1}. The three values agreed to within 2%. The stock solution was then stored in a septum-capped vial, and aliquots for the sample solution were delivered with a noncorrosive, gas-tight syringe. A TCNE blank was prepared after each series of solutions, the spectrum obtained, and the TCNE concentration calculated from the known molar absorptivity at 276 mμ.

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Table II. Molecular Complexes for TCNE and Several Methylated Benzenes in DCM-CCl_4 Solution at 25°

Donor	λ, mμ	K_{CT}, M^{-1}	ε, M^{-1} cm^{-1}	K_S, M^{-1}
Bz	385	0.850 ± 0.040	2,400 ± 23	0.31 ± 0.050
Tol	411	1.72 ± 0.070	2,050 ± 46	0.29 ± 0.050
Mes	464	8.10 ± 0.10	3,245 ± 63	0.28 ± 0.050
HMB	535	120.0 ± 7.6	5,022 ± 60	0.28 ± 0.020

In accordance with the suggestion of Kuntz, Gasparro, Johnston, and Taylor,[11] all equilibrium constants were calculated in terms of molarity units.

Results and Discussion

Typical data for the complexes of the four methylated benzenes with TCNE in DCM-CCl_4 are presented in Table I. The TCNE complexes with benzene and toluene were analyzed by the modified Benesi-Hildebrand equation (7) and the TCNE complexes with mesitylene and hexamethylbenzene were analyzed by the modified Rose-Drago equation (6). The system was also investigated at 0.943, 1.73, and 3.30 M DCM. The results from the four concentrations of DCM are summarized in Table II.

The four mean values of K_S reported above were analyzed for significant differences by means of a t test with a null hypothesis.[12] The null hypothesis could not be rejected at the 90% confidence limit; therefore the data were pooled. The average value determined for the equilibrium constant of the TCNE-DCM complex at 25° in CCl_4 is 0.29 ± 0.020 M^{-1}.

In agreement with the findings of Merrifield and Phillips, there is a large solvent effect on the equilibrium constants calculated for molecular complex systems in which TCNE is the acceptor. As shown here, this effect is due to the competitive formation of a complex between the solvent DCM and the strong acceptor, TCNE. However, these workers reported a value of 0.21 for the equilibrium constant in mole fraction units for the TCNE-DCM complex at 22° which does not agree with the results of the present study. The value of this constant reported here is 0.29 M^{-1}, which is equivalent to 2.64 in mole fraction units. In view of the direct method of analysis used in this study, the value obtained here is considered more reliable.

The K_{CT} reported in Table II are the equilibrium constants in molarity units for the TCNE-methylated benzene complexes in pure CCl_4, as determined in DCM-CCl_4 mixtures. In order to corroborate these results, the same complexes were investigated in pure CCl_4. The results of this study, presented in Table III, are in complete agreement with the results from the mixed solvent study.

Table III. Molecular Complexes for TCNE and the Methylated Benzenes in CCl_4 at 25°

Donor	λ, mμ	K_{CT}, M^{-1}	ε, M^{-1} cm^{-1}
Bz	385	0.887 ± 0.030	2,240 ± 52
Tol	411	1.76 ± 0.061	2,230 ± 63
Mes	464	8.54 ± 0.340	3,057 ± 93
HMB	535	123 ± 8.8	5,140 ± 140

The values obtained here for K_{CT} for the TCNE-methylated benzene complexes in CCl_4 are further corroborated by the results of Briegleb, *et al.*[13] These workers reported equilibrium constants in mole fraction units in CCl_4 solution at 20°, 10.7 for the TCNE-benzene complex, and 1530 for the TCNE-HMB complex. The enthalpy of formation was reported as −3.34 kcal/mol for the TCNE-benzene complex, and −7.75 kcal/mol for the TCNE-HMB complex. The reported equilibrium constants were evaluated at 25° by means of the reported enthalpies, and the resultant constants were expressed in terms of molarity by means of eq 9, given by Andrews and Keefer[14]

$$K_C = K_N\bar{v}_S + (\bar{v}_S - \bar{v}_D) \qquad (9)$$

where K_C is the equilibrium constant in units of molarity, K_N the constant in terms of mole fraction units, $\bar{v}_S$ the molar volume of the solvent, and $\bar{v}_D$ the molar volume of the donor. The results of these calculations are 0.955 for the equilibrium constant of the TCNE-benzene complex and 119 for the equilibrium constant of the TCNE-HMB complex. In view of the complexity of the six component systems investigated here, the agreement is quite good. The TCNE-methylated benzene complexes were also investigated in pure DCM at 25°, and these results are presented in Table IV. For the sake of comparison, the values of K_{CT} from Table II, extrapolated to pure DCM by means of eq 8, are also included.

Table IV. Molecular Complexes for TCNE and the Methylated Benzenes in DCM at 25°

Donor	K_{CT}(extrap), M^{-1}	K_{APP}(det), M^{-1}
Bz	0.153	0.174
Tol	0.310	0.336
Mes	1.46	1.61
HMB	21.6	22.9

In order to compare the results of the present study with those of Merrifield and Phillips, the K_{CT} obtained here expressed in units of molarity in CCl_4 were changed to K_{CT} expressed in mole fraction units in DCM, $K_{N,DCM}$, by means of eq 8 and 9. The results of these calculations are shown in Table V, together with the results of Merrifield and Phillips and the experimental values determined here.

When the limits of uncertainty of the values obtained here, and the slight difference in temperature are taken into account, the agreement is rather good. It is felt that the agreement here serves to validate the interpretation of competitive complexation of TCNE by

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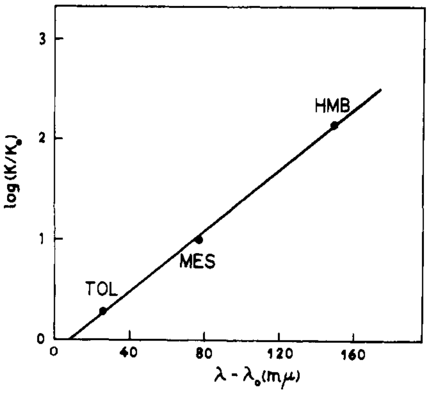

Figure 2. Charge-transfer plot for the TCNE–methylated benzene complexes.

DCM when DCM is the solvent in these complex systems.

Following the suggestion of Dewar and Thompson,[6] any reference to the complexes investigated herein as "charge-transfer" complexes has been avoided. These workers suggested, instead, that these species be called molecular complexes, or π-molecular complexes, until such time that the interaction between the donor and acceptor has been demonstrated to be charge transfer in nature. Further, it was suggested that a linear plot of log K/K_0 *vs.* $\lambda - \lambda_0$ would demonstrate this charge-transfer nature, where K is the equilibrium constant of the substituted base compound, K_0 the constant for the unsubstituted base compound, λ the wavelength of maximum absorbance for the complex of TCNE with the substituted compound, and λ_0 the wavelength of maximum absorbance for the complex of TCNE with the unsubstituted compound. The plot for the complexes investigated here is shown in Figure 2. The excellent linearity of this plot suggests that the complexes formed between TCNE and the methylated benzene derivatives are indeed charge-transfer complexes.

Table V. Comparison of K_N for TCNE–Methylated Benzene Complexes in DCM

Donor	$K_N{}^a$	$K_{N,DCM}{}^b$ (extrap)	$K_{N,DCM}{}^b$ (exptl)
Bz	2.00	1.56	1.71
Tol	3.70	3.20	3.56
Mes	17.3	15.1	16.6
HMB	263	222	235

[a] Reference 1, temperature 22°. [b] This work, temperature 25°.

Summary

By a competitive complexation technique, the equilibrium constants for the complexes of TCNE with four methylated benzenes in the relatively inert solvent, CCl_4, were evaluated, and simultaneously, the equilibrium constant for the TCNE–DCM complex was determined to be $0.29 \pm 0.020\ M^{-1}$ at 25°. The technique employed is generally useful in the study of molecular complexes in solution in that weak solvent complexes with the donor or acceptor can be studied quantitatively, while simultaneously determining the donor–acceptor complex parameters in an inert solvent. In this way, the method could be used to extend the determination of complexing parameters in inert solvents for those complexes which are insoluble in these solvents, since a more polar solvent could be added to increase the solubility of the complex and the effect of the added solvent on the complex equilibrium could be accounted for. The species active in the competitive complex formation can be determined by a preliminary investigation of the donor and acceptor separately in the mixed solvents, and the appropriate equilibrium expressions can then be applied to obtain equilibrium constants for the donor–acceptor complex and the solvent complex, in the inert solvent.