PRESSURE EFFECT ON THE EDA-COMPLEXES FORMED BETWEEN BENZENE, TOLUENE AND TETRACYANOETHYLENE IN CARBON TETRACHLORIDE

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The intermolecular charge transfer spectra of tetracyanoethylene with benzene and toluene in carbon tetrachloride have been studied as a function of pressure up to 1500 kg/cm² at 25°C.

The equilibrium constants and molar extinction coefficients at high pressure were determined from Scott's equation, and these values were increased with increasing pressure. The volume changes ΔV for the formation of the complexes from their components were $-3.4\,cm^3$/mole for benzene-TCNE complex, and $-4.9\,cm^3$/mole for toluene-TCNE complex. The absorption maxima shifted to longer wavelength with increasing pressure. The causes of the small spectral shift were considered from the viewpoint of charge transfer interaction in solution.

Introduction

Since Mulliken[1] presented the well known theory of the charge transfer interaction between e-lectron donor and acceptor, it has been widely applied to many interesting research subjects[2,3,4]. According to this theory, both the ground and excited states are sensitive to the extent of the overlap between the π orbital of donor molecule and that of acceptor molecule, and this should cause the change in equilibrium constants K. the excitation energy $h\nu_{ct}$ and the transition moment. The electron-donor-acceptor-complexes (EDA-complexes) should be thus affected by the pressure and solvent.

Drickamer and co-workers[5,6] have investigated the pressure effects on crystalline EDA-complexes. Offen[7] has observed the absorption spectra of solid anthracene–1,3,5–trinitrobezene complex to shift to longer wavelength and its optical density to increase with increasing pressure in agreement with other measurements. Offen and Kadhim[8] have studied the absorption spectra of many aromatic hy-drocarbon-TCNE complexes in polymer matrices and concluded that the increase in optical density could be related to electronic transition strengths without correction for complexation equilibria. On the other hand, the increase in optical density in solutions is due to two distinct pressure effects: one

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3) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, London (1969)
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is the effect on K, and the other on the molar extinction coefficient ε. Ham[9] has investigated the absorption of aromatic hydrocarbon-iodine complexes in n-heptane at 2000 atm, but his results were only qualitative. Ewald[10] has evaluated the values of K, ε, f, and $h\nu_{ct}$ of π-π complexes in solutions and found the volume change $\varDelta V$ of the formation of the EDA-complexes from their components. The trends in K for benzene-TCNE complex in methylene chloride, however, differed from those obtained by Gott and Maisch[11] for the same solution.

Methylene chloride is not necessarily a good solvent for the EDA-complexes containing TCNE, as Ewall and Sonnessa[12] reported that it acted as a weaker donor to TCNE.

In the present work we have studied the π-π complexes formed between benzene, toluene as donor and TCNE as acceptor in carbon tetrachloride. The reason why we made choice of carbon tetrachloride as the solvent was as follows: it was commonly accepted as the noninteracting solvent, and so it did not set up a competitive equilibrium with TCNE, thus not affecting the equilibribrium constant measurements for the EDA-complexes.

Experimentals

Materials

TCNE was purified twice by recrystallizations from chlorobenzene and then by sublimation at 100°C under reduced pressure (m.p. 198–200°C). Benzene, toluene and carbon tetrachloride were spectrograde reagents and were used without further purification.
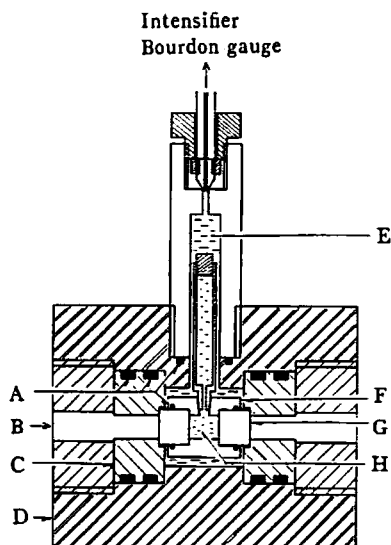

Fig. 1 High pressure vessel for spectral measurement
A: "O"-ring,   B: Light path,
C: Window plug.   D: Cylinder,
E: Silicone oil,   F: Sample cell,
G: Quartz window,   H: Sample solution

 9) J. Ham, *J. Amer. Chem. Soc.*, **76**, 3881 (1954)
10) A.H. Ewald, *Trans. Faraday Soc.*, **64**, 733 (1968)
11) J.R. Gott and A.J. Maisch, *J. Chem. Phys.*, **39**, 2229 (1963)
12) R.X. Ewall and A.J. Sonnessa, *J. Amer. Chem. Soc.*, **92**, 2845 (1970)

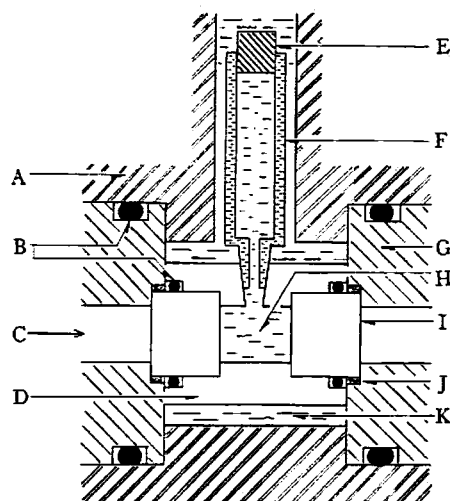Pressure Effect on the EDA-Complexes Formed Between Benzene, Toluene and Tetracyanoethylene   81

Fig. 2   Sample cell

A: Cylinder,	B: "O"-ring,
C: Light path,	D: Teflon,
E: Glass piston,	F: Syringe,
G: Window plug,	H: Sample solution,
I: Quartz window,	J: Araldite,
K: Silicone oil	

Apparatus and procedure

The design of the high pressure vessel for spectral measurement is shown in Fig. 1. The high pressure vessel which was made of stainless steel could be used up to 3000 kg/cm². Pressure was applied through a piston cylinder type intensifier using silicone oil as a pressure transmitting medium. The high pressure vessel had two 1-cm-thick quartz windows which were attached to the window plugs by Araldite. As shown in Fig. 2, the sample cell which was made of cylindrical teflon and glass inlet was set up so that both ends of the cylindrical teflon cell could be closed by two quartz windows. The pressure in the vessel is transmitted to the solution by the glass piston of the syringe. As the distance between the window plugs can be kept constant (26.0 mm), the light path length is always invariant (ca. 10 mm) throughout repeated measurements. Strictly speaking, the path length varies with pressure due to the expansion of the vessel, however, no correction was made in this experiment, because such correction was within the experimental error under the pressure range of the present study. The pressure was measured with a Bourdon gauge which was calibrated against a Heise Bourdon gauge corrected with the free piston gauge in Kobe Steel Ltd. Thermostated water was circulated around the high pressure vessel and the temperature was regulated within ±0.05°C.

All the equilibrium measurements were performed with the donor in large excess over the acceptor. The concentration of TCNE was ca. 10^{-4} mole/l, and that of the donor was between 10^{-2} and 10^{-1} mole/l and was varied at least five fold for any one system. Both concentrations were adjusted so as to keep the optical density within measurable range. The concentrations of the solutions at high pressure were corrected with the density calculated by using the Tait equation[13] for the pure solvent.

The spectra were measured on a single beam spectrophotometer (Hitachi EPU-2) adapted to the high pressure vessel. On the measurement of spectrum at high pressure by the single beam spectrophotometer, it is usual to measure the transmittances of the sample solution and solvent seperately

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13) R.E. Gibson and O.H. Loeffler, *J. Amer. Chem. Soc.*, **63**, 898 (1941)

and then to calculate the optical density in reference to solvent. However, since the positioning of high pressure vessel and/or the stability of spectrophotometer often cause considerable error in re- producibility, the transmittance of the sample solution at high pressure was first measured in referece to air (I). The transmittance of solvent in reference to air (I') was measured by a seperate run and the optical density of solution was calculated by -log (I/I'). The path length of the sample cell was determined by comparing the optical density with that in the quartz cell with the path length of 1 cm at atmospheric pressure. All measurements were carried out only to 1500 kg/cm² at 25°C, because the solution froze at higher pressure.

Results

Spectra

The typical absorption spectra of benzene-TCNE and toluene-TCNE systems in carbon tetra- chloride at various pressures are shown in Figs. 3 and 4, respectively. TCNE, benzene and toluene have no absorption in the visible region. Therefore, the absorption bands can be attributed to the EDA-complexes. As seen in both figures, the large increase in the optical density and the slight shift of the absorption maxima to longer wavelength are observed with increasing pressure, but these band shapes do not change. The maximum absorptions at 1 atm and 1500 kg/cm² are, respectively, observed at 385 and 389 nm for benzene-TCNE, and 411 and 415 nm for toluene-TCNE. Such red shift of the band maximum with increasing pressure is usually observed for neutral-neutral EDA-complexes in solution[9,10,11] and also in solid,[5,7,8] except for hexamethylbenzene-TCNE complex[8,10,11].

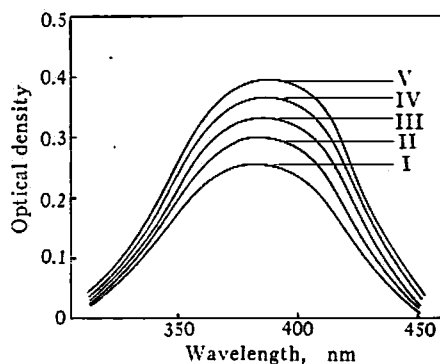Fig. 5 shows the increase in the optical density at the maximum absorption as a function of pres-

Fig. 3   Absorption spectra of benzene-TCNE complex in carbon tetrachloride at var- ious pressures at 25°C (initial conc., benzene: 0.3859 mole/l, TCNE: 4.664× 10⁻⁴ mole/l)
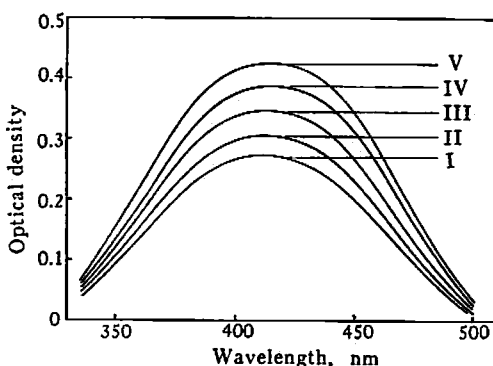I : 1 atm, II : 400 kg/cm², III : 800 kg/ cm², IV: 1200 kg/cm², V : 1500 kg/ cm²

Fig. 4   Absorption spectra of toluene-TCNE com- plex in carbon tetrachloride at various pres- sures at 25°C (initial conc., toluene: 0.1895 mole/l, TCNE: 4.704 × 10⁻⁴ mole/l)
I : 1 atm, II: 400 kg/cm², III: 800 kg/cm², IV: 1200 kg/cm², V : 1500 kg/cm²
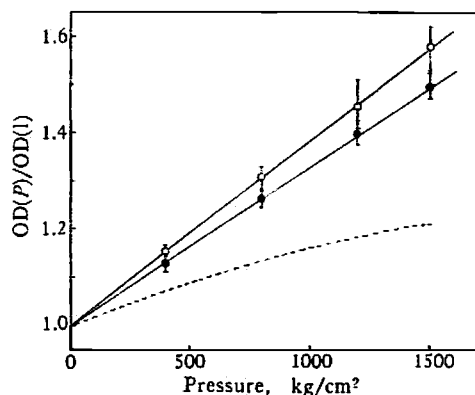
Fig. 5   Increase in the optical density at maximum absorption as a function of pressure. The dotted line is the square of the relative density of solvent.
●: benzene-TCNE,
○: toluene-TCNE

sure, OD(P)/OD(1) representing the ratio of the optical density of a given solution at the pressure $P \text{kg/cm}^2$ to that at 1 atm. And the dotted line is the square of the relative density of solvent calculated using the Tait equation.

Equilibrium measurement

The formation of EDA-complexes is reversible.

$$D + A \rightleftharpoons Complex. \tag{1}$$

The visible absorption bands of these complexes were distinguished from those of parent components, and it is known that only 1 : 1 complexes are formed in solutions[12, 14]. Accordingly, Scott's equation[15] of the modified Benesi-Hildebrand relation[16] can be applied to a series of solutions in which one of the components (the donor in this case) is in large excess,

$$\frac{[A]_o[D]_o d}{OD} = \frac{1}{\varepsilon}[D]_o + \frac{1}{K\varepsilon}, \tag{2}$$

wherere $[A]_o$ and $[D]_o$ are, respectively, the initial concentrations (mole/l) of the donor and acceptor. OD is the optical density in solution with the light path length of d cm, ε is the molar extinction coefficient of the EDA-complex, and K is the equilibrium constant for the complex formation. Scott's plots for the benzene-and toluene-TCNE complexes at various pressures are shown in Figs. 6 and 7, respectively, where OD is measured at maximum absorption and the concentrations are corrected for compression at high pressure. The linearity of Scott's plot is quite satisfactory; hence the values of K and ε_{max} at various pressures can be calculated from the slopes and intercepts. Oscillator strength f were also calculated from the relation,

$$f = 4.319 \times 10^{-9} \times \Delta\nu_{\frac{1}{2}} \times \varepsilon_{max}, \tag{3}$$

where $\Delta\nu_{\frac{1}{2}}$ is the band half-width. Since the change of $\Delta\nu_{\frac{1}{2}}$ with increasing pressure is small, the change of f may be mainly due to the change of ε_{max}. The values of K and ε_{max} at 1 atm are in satisfactory agreement with those obtained by Ewall and Sonnessa[12]. The volume change ΔV associated

14) R.E. Merrifield and W.D. Phillips, *J. Amer. Chem. Soc.* **80**, 2778 (1958)

15) R.L. Scott, *Rec. Trav. Chim.*, **75**, 787 (1956)

16) H.A. Benesi and J.H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949)
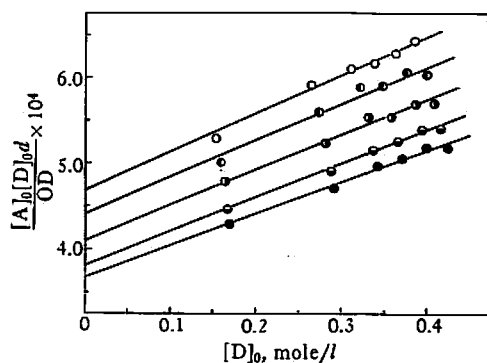
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Fig. 6   Scott plots for benzene-TCNE complex in carbon tetrachloride at various pressures at 25°C
○: 1atm, ◐: 400 kg/cm², ◑: 800 kg/cm², ◓: 1200 kg/cm², ●: 1500 kg/cm²

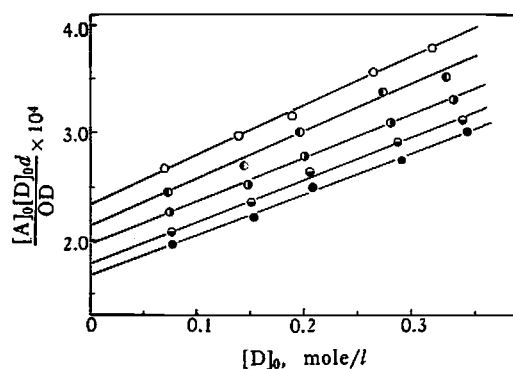
Fig. 7   Scott plots for toluene-TCNE complex in carbon tetrachloride at various pressures at 25°C
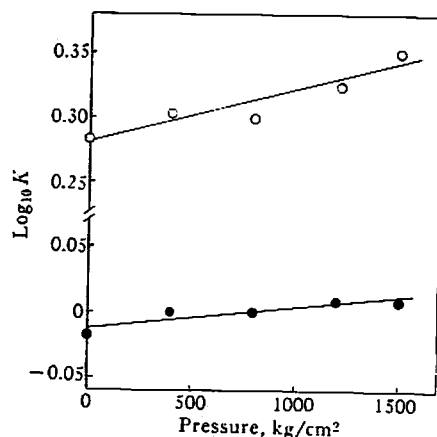○: 1atm, ◐: 400 kg/cm², ◑: 800 kg/cm², ◓: 1200 kg/cm², ●: 1500 kg/cm²

Fig. 8   Pressure effect on the equilibrium constants
●: benzene-TCNE   ○: toluene-TCNE

with the formation of the EDA-complex from its components can be calculated from the equilibrium constant by the following equation,

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} + \Delta a \cdot \beta, \tag{4}$$

where Δa is the change of the number of molecules on both sides of the equilibrium and β is the compressibility of the solution. (In this study, β of the solvent was used.) The ΔV's were calculated from the slopes of the curves which were approximately regarded as straight lines (Fig. 8). The numerical

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values are listed together in Table 1.

Consideration

Assuming the K and ε remained unchanged at high pressure, the relative increase in optical density would be about the square of the relative density of solvent since the EDA-complex depends only upon the concentrations of two components. As shown in Fig. 5, the increase in the optical density with pressure at the absorption maximum is partly due to the increase of concentrations caused by compression. Correcting the contraction of solvent at high pressure, the enhancements of the absorption can be ascribed to the increase in K and ε as seen in Table 1. The changes in K and f with pressure are in accord with the original prediction of Mulliken[1] concerning the sensitivity of the EDA-complex to pressure. Ham[9] concluded that the observed changes in intensity with pressure could be interpeted mainly in terms of the increase in K, assuming the ε of complex remained constant. His assumption, however, seems to be unreasonable according to the present results and the others[10,11]. Gott and Maisch[11] observed the small decrease in K and the increase in f with pressure for benzene-TCNE complex in methylene chloride. The trend in K was not theoretically interpreted. However, they explained that if the competitive solvent-TCNE complex formation became more effective at high pressure, the observed values of K would be decreased with increasing pressure. On the other hand, Ewald[10] obtained the opposite trend in K with that found by Gott and Maisch for the same system. Furthermore, he reported the increases in both K and f with pressure for a number of π-π complexes in solution. Apparently, these tendencies are similar to our present results.

From the X-ray diffraction studies of Wallwork[17], the structures of some complexes are known in the solid state. In the chloranil-hexamethylbenzene complex, for example, the molecular planes are parallel and distance between them is 3.51 Å. Actually, the distance between them is smaller than

Table 1 Equilibrium constants and spectroscopic parameters for the EDA-complexes of
Benzene- and Toluene-TCNE in carbon tetrachloride at 25°C

Press.	Benzene-TCNE				Toluene-TCNE			
kg/cm²	K l.mole⁻¹	ε_{max} cm⁻¹l.mol⁻¹	f	λ_{max} nm	K l.mole⁻¹	ε_{max} cm⁻¹l.mole⁻¹	f	λ_{max} nm
1	0.964	2.21	0.052	385	1.92	2.22	0.060	411
	0.887±0.030[a]	2.24±0.052[a]			1.76±0.061[a]	2.23±0.063[a]		
400	1.00	2.29	0.052		2.01	2.34	0.063	
800	1.00	2.44	0.057		1.99	2.55	0.068	
1200	1.02	2.57	0.062		2.11	2.62	0.070	
1500	1.02	2.70	0.066	389	2.24	2.67	0.072	415
ΔV cm³/mole	−3.4				−4.9			

a : ref. 12

17) S.C. Wallwork, *J. Chem. Soc.*, 494 (1961)

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the sum of the van der Walls radii[18] of the components in the solid state. Also in solution, the volume of the complex is probably smaller than the sum of the molecular volume of the components, and so, the volume change accompanying the formation of the EDA-complex will be negative, which results in the increase of K with pressure.

The observed values of ΔV are -3.4 and -4.9 cm^3/mole for benzene- and toluene-TCNE, respectively, and the former one is in good agreement with that reported by Ewald for benzene-TCNE in methylene chloride (-3 cm^3/mole).

Shuler[19] has predicted a red shift due to a decrease in the intermolecular distance at high pressure, using a free electron model to describe an EDA-complex. The change in intermolecular distance at high pressure seems to be small: Drickamer[20] has estimated that pressures up to 50000 atm are required to bring about a significant compression of ordinary chemical bonds. Therefore, it may be concluded that the spectral shift is mainly due to the solvent effect in the present condition (up to 1500 kg/cm^2), rather than the shortening of the intermolecular distance of an EDA-complex. The effect of the solvent upon the electronic transition is complicated and has not been satisfactorily treated theoretically. Bayliss[21] has attempted to explain the influence of non-polar solvent on the electronic transitions. Using the model of an oscillating point dipole at the center of a spherical cavity in an infinite dielectric, he derived an expression for frequency shift from the vapor phase to the solution in terms of the refractive index of the solvent,

$$\Delta\nu \propto \frac{n^2-1}{2n^2+1}. \tag{5}$$

This formula suggests that the pressure should induce the red shift because the density is related with the refractive index. Bayliss's treatment is originally applied only to the absorption of a system in which no interaction between no-bond and dative structure exists. However, Ham[9] has applied this theory with partial success to his pressure studies of the EDA-complexes. The hexamethylbenzene-TCNE complex, however, shows first a small shift to longer wavelength and then a larger shift to shorter wavelength with increasing pressure in both solution[10, 11] and solid state.[8] Offen and Abidi[22] studied that the spectral shift in the absorption spectra of the EDA-complexes in several solvents. They showed that the polar solvents often caused a blue shift relative to non-polar solvents and that this effect could not be described by the classical solvation theory. They discussed the blue shift in terms of the solvation of two valence bond structures describing both the ground and excited states. A typical energy diagram is pictured in Fig. 9. The energy of dative structure is reduced in a polar solvent and so the enhanced mixing of states results in larger splittings of the ground and excited state (β_1^2/Δ and $-\beta_1^2/\Delta$). Accordingly, they concluded that a blue shift occurred when the additional splitting due to the enhanced perturbation was larger than the reduced energy of dative structure in a polar medium. Apparently, the observed shift is a balance between the red shift due to the decrease

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20) H. Fishman and H.G. Drickamer, J. Chem. Phys., 24, 548 (1956)
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in $\varDelta$ and the blue shift due to additional splitting $(\beta_0{}^2/\varDelta + \beta_1{}^2/\varDelta)$. Similarly, the spectral shift at high pressure could be interpreted from the similar point of view.
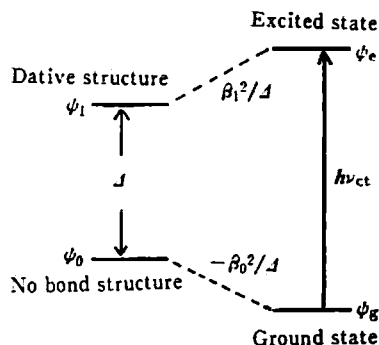
Fig. 9 Charge-transfer interaction diagram

$$h\nu_{ct} = \varDelta + \frac{\beta_0{}^2 + \beta_1{}^2}{\varDelta} + \cdots$$

$\beta_0 = W_{01} - W_0 S_{01}$
$\beta_1 = W_{01} - W_1 S_{01}$
$\varDelta = W_1 - W_0$
$W_{01} = \int \psi_0 H \psi_1 d\tau$
$S_{01} = \int \psi_0 \psi_1 d\tau$

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