툴루엔과 요오드 사이의 전하이동착물에 대한 압력의 영향(Ⅰ)

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The Effect of Pressures on the Formation of Charge Transfer Complexes of Toluene with Iodine(I)

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요 약. 툴루엔과 요오드 사이의 전하이동착물의 안정도에 미치는 압력과 온도의 영향을 n-헥산 용액에서 자외선 분광광도법으로 연구하였다. 압력은 1에서 1,200 bar, 온도는 25 °C에서 60 °C 사이에서 측정하였다. 착물의 평형상수는 압력 및 온도의 증가와 더불어 증가 및 감소하고 흡수계는 대체로 증가함을 알았다. 이들 각 평형정수로 부터 착물 형성에 따른 부피, 엔탈피, 자유에너지 및 엔트로피 변화 양을 구하였다. 또한 압력의 증가에 의한 red-shift, 온도의 증가에 의한 blue-shift 현상 및 압력 변화에 의한 진동자 세기와의 관계를 열역학적 함수와 관계지워 설명하였다.

Abstract. The effect of pressures and temperatures on the stabilities of the toluene-iodine charge transfer complex have been investigated through ultraviolet spectrophotometric measurements in n-hexane. The stabilities of complexes were measured at 25~60 °C under 1~1,200 bars.

The equilibrium constant of the complex was increased with pressure and decreased with temperature raising. The absorpiton coefficient was increased with both pressure and temperature. Changes of volume, enthalpy, free energy and entropy for the formation of complexes were obtanied from the equilibrium constants. The red-shift observed a higher pressure, the blue-shift at a higher temperature and the relation between pressure and oscillator strength were discussed by means of thermodynamic functions.

Introduction

After Bensei and Hildebrand[1] first demonstrated the formation of one to one molecular cmoplex between benzene and iodine in carbon tetrachloride solution, studies were extended to other systems by a number of workers[2~4]. Among the various experimental techniques used[5], spectrophotomertic measurement was one of the most common methods. Utilizing spectrophotometric data, the

equili brium constants for the formation of molecular complexes were calculated by the method proposed by Benesi and Hildebrand[1] or the methods modified by other investigators[6].

The basic theory of electron donor acceptor complexes has changed little since Mulliken's theory[7]. According to this theory the stability of complexes and the energy of charge transfer absorption are sensitive to changes in the overlap of molecular orbitals of donor and acceptor molecules. A small change in the separation of the two components should cause large changes in the formation constant K and the charge-transfer(CT) energy. The complexes should thus be sensitive to hydrostatic pressure. Ham[8] for iodine-benzene system found general agreement with this prediction, but analysis of his results was difficult because of overlap between CT band and iodine absorption band. Gott and Maisch[9], however, for the TCNE-beneze system obtained results contrary to Mulliken's prediction.

The effect of pressure on solid CT complexes has been investigated by Drickamer and co-workers[10,11]. Offen[12] found CT absorption of TNB-ANT complexes moving to lower energies with pressure increase.

Ewald[13,14] measured the effect of increased hydrostatic pressure on the formation constant K and the CT-absorption energy of EDCA in solution and came to the conclusion that large part of the effect could be explained by changes in the solvation of donors, acceptors and EDAC.

Pressure and temperature increase can affect the solution spectrum of a given CT-complex by changing the CT energy, the oscillator strength of the CT transition and the equilibrium constant of complex formation, the last two being observed as an increase in absorbancy. As a rule, increased pressure causes a red-shift of the absorption in solution as for solid complexes[10~12]. Exceptional blue-shifts have been observed for the same com-

plexes in liquid and in solid solution[9,16].

The most marked change with pressure in CT-absorption spectra in solution is the increase in absorbancy. To ascribe all of this to an increase in the transition moment as predicted by Mulliken would, however, negelect the effect of pressure on the association equilibrium between complex and its component molecules. Only a complete analysis of absorbancy over a range of donor and acceptor concentrations will allow one to evaluate the two distinct pressure effects on K and absorption coefficient ε in liquid solutions. The effect on K can be due to the volume of the complex being smaller than that of the components. Offen and Kadhim[16], using a solid polymer as solvent for the complexes, consider that all the increase in absorbancy is due to increase in oscillator strength under these conditions.

In the present work we have examined the effect of pressure and temperature on the formation of one to one CT-complexes with iodine of toluene in n-hexane. We measured the absorbancy of their liquid solutions over a range of concentrations, pressures and temperatures and were able to evaluate K, ε and ΔG, ΔH, ΔS, Δv and f. From the change of K with pressure we have found the volume change ΔV which accompanies the formation of 1 mole of complex from its components.

Experimental Section

Materials. Samples of Merck Co. iodine (superpure grade), toluene(uvasol grade) and n-hexane(uvasol grade) were used without purification.

Preparation of Stock Solutions. The solution of iodine in n-hexane was prepared by weighing an appropriate quantity of iodine into a volumetric flask, and a adding n-hexane solvent to make up to volume. The solution thus prepared was diluted further to suitable

concentrations. The solutions of toluene in n-hexane was prepared by weighing an appropriate quantity of toluene into a volumetric flask and adding n-hexane to make up to volume. Each solution was freshly prepared at room temperature before making absorption spectrum measurements and wrapped with black paper to prevent any photochemical reaction in solution. The concentration of iodine was ca. 10^{-4} mole· 1^{-1} and that of toluene was 10^{-1} lmole· l^{-1} These were varied at least three fold for any one system. Both concentrations were adjusted so as to keep the absorbancy within suitable limits.

Apparatus. The spectra were measured on a Cary models 17 H spectrophotometer modified to accommodate a high pressure cell. The apparatus has already been described in detail[17]. A high pressure optical cell has been used with a spectrophotometer and with equipment to generate and to measure elevated pressure. *Fig.* 1 shows the high pressure cell. It has two windows of synthetic colourless sapphire with a thin walled teflon cylinder between them which contains the solution. Using this arrangement the solution samples are in contact with sapphire and teflon only and thus a highly corrosive solution can be investigated. Spectra of toluen-iodine complex could be observed at high pressure without corrosion by iodine complex. The cell was kept at constant temperature

Fig. 1. High pressure optical cell; S_1, S_2 sapphire windows; N_1, N_2 stainless steel tightening screwed covers; T teflon cylinder; O teflon O-rings; K teflon capillary.

by circulating water through it supplied by a thermostat. The external part of the cell was made of brass. The test solution was injected, using glass syring, through a capillary into the high pressure cell which then connected to a high pressure apparatus.

The Spectrophotometric Measurements. The absorbancies of stock solutions of iodine and toluene in n-hexane were measured over the region of wave lengths from 270 to 700 mμ, using the pure solvent, n-hexane, as the blank. Then, the stock solution of toluene was mixed at various ratios with the solution of the iodine*. The absorbancies of the resulting solution were immediately measured. The prolonged keeping of the mixture solutions was avoided as otherwise slow chemical changes might have occured. The blank in this case was the n-hexane solution of toluene with the same concentration as those of solutions containing iodine. High pressure optical cell was maintained at the desired temperatures 25, 40 and 60 °C, by a thermostat within ±0.1 °C. The absorbancies of solution at the complex absorption maximum were usually determined in the neighborhood of 300mμ.

Results and Discussion

A set of spectra of toluene-iodine CT-complexes in n-hexane at various pressures in shown in *Fig.* 2. The broad absorption bands are typical of EDAC in solution and one reason why quantitative determination of the absorption maximum is often difficult. When comparing spectra at different pressures and temperatures, it is necessary to allow for change in density of solution.

In the prerent work, the various parameters are discussed individually.

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* The total volume after mixing was assumed to be the sum of the two solutions for calculation of concentrations of the resulting solutions.
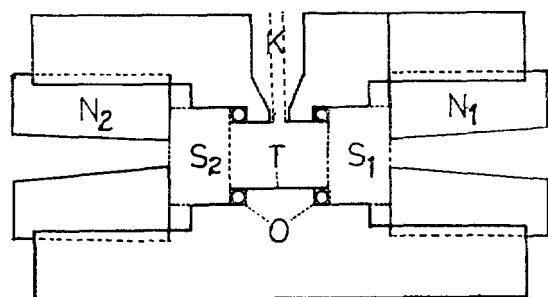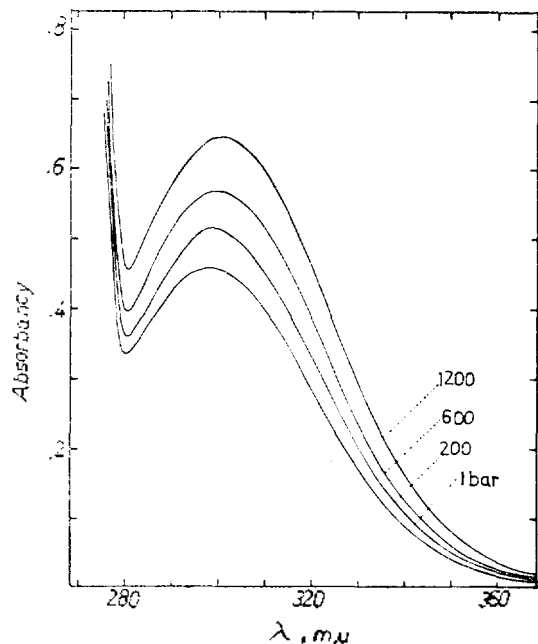
Fig. 2. Absorption spectrum for the system of toluene(0. 336M) with iodine(4. 45×10^{-4}M) complex in n-hexane at various pressures (25°C).

Calculation of Equilibrium Constant for the CT-Complex Formation.

The absorption spectra of the individual stock solution of iodine, or toluene in n-hexane did not indicate the presence of maximum absorption peaks in the vicinity of 300 mμ. On the other hand, the absorption spectra of the solution of a mixture of toluene with iodine did indicate the presence of absorption maxima in the region of wave lengths near 300 mμ. The maximum absorption observed is attributed to the formation of complexes of toluene with iodine in solution.

These complexes are assumed to be one to one molecular complexes of which was first proposed by Benesi and Hildebrand for the system of benzene-iodine in carbon tetrachloride[1].

$$A+D \rightleftharpoons C \qquad (1)$$

Where D denotes the donator molecules, A acceptor molecules and C the one to one molecular

complex $D \cdot A$. The equation of Benesi and Hildebrand has been modified for high pressures in order to calculate the equilibrium constant K and the absorption coefficient ε, i. e.

$$\frac{[A]_0 \cdot d \cdot (\rho/\rho_0)}{\log(I_0/I)} = \frac{1}{K \cdot \varepsilon} \cdot \frac{1}{[D]_0} + \frac{1}{\varepsilon} \qquad (2)$$

which is now in the from, $y=mx+b$. Where $[A]_0$ and $[D]_0$ are the initial molar concentration of acceptor and donor respectively, $\log(I_0/I)$ is absorbancy(A) at λ_{max}, d is the internal distance between the sapphire windows. It was always 1.06 cm. ρ_0 and ρ are densities of solution at 25°C and 1 bar and at the temperature and pressure of experiment respectively. The values of the rations ρ/ρ_0 for the solutions were derived from results of Kuss and Taslimi[18]. The values of the equilibrium constant K and absorption coefficient ε were found from equation(2). After the values of A were determined experimentally, the quantities of y term were plotted against x term. The plots indicated good linearity between the two quantities in all the system examined. Hence, the values of m and b term were calculated from the slopes and the intercept of the straight lines. The least square method was utilized to determine slopes and intercepts. Knowing the values of $1/(K \cdot \varepsilon)$ and $1/\varepsilon$, the value of K and ε were calculated. Since linearities were observed between y and x experimentally, it can be concluded that the assumption of the formation of one to one complexes should be correct.

The Toluene-iodine CT-complexes Formation.

Data obtained at temperature 25, 40, 60 °C and pressure 1, 200, 600, 1200 bar on the system of toluene with iodine in n-hexane are summarised in Tables 1 to 3. The data show a straight line relationship between y and x (see Fig. 3 to 5).

These linearities indicate that the assumption of the formation of one to one molecular complex toluene-iodine is being correct as it was discussed

Table 1. Formation of $C_6H_5CH_3 \cdot I_2$ in *n*-hexane at various pressures(25 °C).

$C_6H_5CH_3$, mole·l^{-1} $[D]_0$	I_2, 10^4 mole·l^{-1} $[A]_0$	Pressure(bar)							
		1		200		600		1200	
		A	$y \times 10^4$	A	$y \times 10^4$	A	$y \times 10^4$	A	$y \times 10^4$
0.111	4.45	0.138	25.7	0.204	23.8	0.229	22.0	0.268	19.7
	5.00	0.210	25.3	0.231	23.6	0.266	21.3	0.305	19.4
	6.00	0.245	26.0	0.265	24.3	0.297	22.9	0.346	20.6
		Av 25.6		Av 23.9		Av 22.1		Av 19.9	
0.224	4.45	0.342	13.8	0.377	12.9	0.422	12.0	0.472	11.2
	5.00	0.385	13.8	0.422	12.9	0.480	11.8	0.542	10.9
	6.00	0.462	13.8	0.508	12.9	0.572	11.9	0.647	11.0
		Av 13.8		Av 12.9		Av 11.9		Av 11.0	
0.336	4.45	0.457	10.3	0.514	9.46	0.568	8.89	0.645	8.16
	5.00	0.526	10.1	0.583	9.37	0.648	8.76	0.723	8.20
	6.00	0.630	10.1	0.700	9.36	0.786	8.78	0.864	8.27
		Av 10.2		Av 9.39		Av 8.81		Av 8.21	
0.443	4.45	0.602	7.84	0.663	7.33	0.706	7.15	0.797	6.62
	5.00	0.685	7.74	0.755	7.23	0.829	6.90	0.885	6.69
	6.00	0.816	7.80	0.901	7.27	0.965	7.06	1.076	6.61
		Av 7.79		Av 7.28		Av 7.04		Av 6.64	

Table 2. Formation of $C_6H_5CH_3 \cdot I_2$ in *n*-hexane at various pressures(40 °C).

$C_6H_5CH_3$, mole·l^{-1} $[D]_0$	I_2, 10^4 mole·l^{-1} $[A]_0$	Pressure(bar)							
		1		200		600		1200	
		A	$y \times 10^4$	A	$y \times 10^4$	A	$y \times 10^4$	A	$y \times 10^4$
0.111	4.45	0.147	30.9	0.169	28.3	0.185	26.9	0.211	24.8
	5.00	0.170	30.6	0.187	28.7	0.208	26.9	0.238	24.6
	6.00	0.201	31.0	0.228	28.3	0.250	26.9	0.283	24.9
		Av 30.8		Av 28.4		Av 26.9		Av 24.7	
0.224	4.45	0.282	16.4	0.313	15.3	0.353	14.1	0.400	13.0
	5.00	0.318	16.3	0.350	15.3	0.401	14.0	0.446	13.1
	6.00	0.380	16.4	0.423	15.2	0.475	14.1	0.542	13.0
		Av 16.4		Av 15.3		Av 14.1		Av 13.0	
0.336	4.45	0.411	11.2	0.454	10.5	0.491	10.1	0.576	9.05
	5.00	0.455	11.4	0.494	10.9	0.552	10.4	0.631	9.29
	6.00	0.563	11.1	0.620	10.4	0.679	9.89	0.764	9.21
		Av 11.2		Av 10.6		Av 10.1		Av 9.18	
0.443	4.45	0.555	8.32	0 596	8.02	0.662	7.52	0.743	7.02
	5.00	0.627	8.28	0.680	7.90	0.760	7.36	0.857	6.94
	6.00	0.740	8.43	0.793	8.12	0.895	7.50	0.976	7.21
		Av 8.35		Av 8.01		Av 7.46		Av 7.05	

Table 3. Formation of $C_6H_5CH_3 \cdot I_2$ in n-hexane at various pressures(60°C).

$C_6H_5CH_3$, mole·l^{-1} [D]$_0$	I_2, 10^4 mole·l^{-1} [A]$_0$	Pressure(bar)							
		1		200		600		1200	
		A	$y \times 10^4$	A	$y \times 10^4$	A	$y \times 10^4$	A	$y \times 10^4$
0.111	4.45	0.130	34.8	0.147	31.7	0.163	29.9	0.177	29.0
	5.00	0.148	34.1	0.161	32.5	0.177	31.1	0.204	28.4
	6.00	0.173	35.0	0.196	32.1	0.210	31.3	0.238	29.1
		Av 34.6		Av 32.1		Av 30.8		Av 28.9	
0.224	4.45	0.236	19.0	0.254	18.4	0.298	16.4	0.331	15.8
	5.00	0.265	19.1	0.280	18.7	0.344	16.0	0.371	15.6
	6.00	0.312	19.4	0.332	19.0	0.385	17.1	0.448	15.5
		Av 19.2		Av 18.7		Av 16.5		Av 15.6	
0.336	4.45	0.380	12.5	0.402	11.6	0.420	11.0	0.495	10.4
	5.00	0.408	12.4	0.453	11.6	0.502	10.9	0.570	10.1
	6.00	0.480	12.6	0.532	11.8	0.596	11.0	0.675	10.3
		Av 12.5		Av 11.7		Av 11.0		Av 10.3	
0.443	4.45	0.452	9.93	0.504	9.25	0.567	8.60	0.633	8.10
	5.00	0.512	9.86	0.567	9.25	0.640	8.57	0.720	8.01
	6.00	0.610	9.93	0.681	9.24	0.764	8.62	0.864	8.18
		Av 9.91		Av 9.25		Av 8.60		Av 8.10	
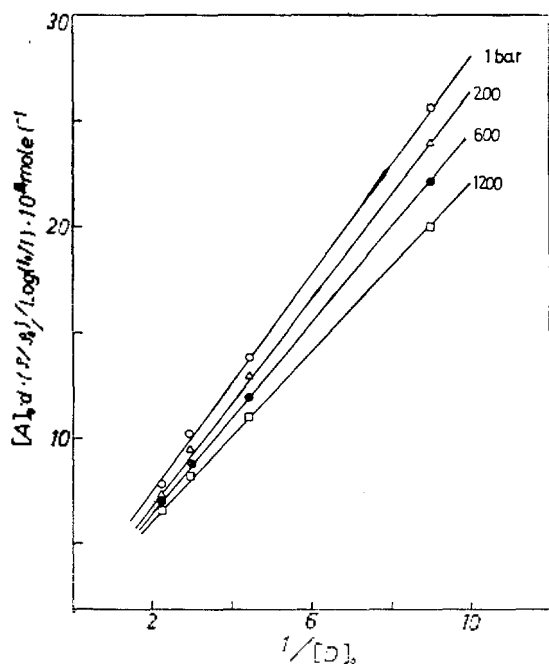
Fig. 3. Plot of $[A]_0 \cdot d \cdot (\rho/\rho_0)/\mathrm{Log}(I_0/I)$ versus $1/[D]_0$ of the toluene-iodine system at various pressures(25 °C).
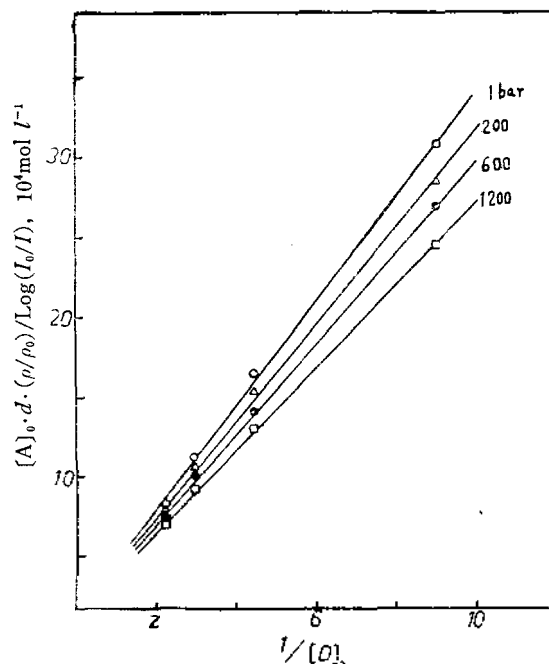
Fig. 4. Plot of $[A]_0 \cdot d \cdot (\rho/\rho_0)/\mathrm{Log}(I_0/I)$ versus $1/[D]_0$ of the toluene-iodine system at various pressures(40 °C).

previously[1].

The results of the present study at 25 °C and 1 atm are now compared with those reported in the literature. Keefer and Andrews[2] reported an equilibrium constant value of 0.16 for the complex, toluene-iodine in carbon tetrachloride. And Ketelaar[19] reported a value of 2.24(as K_x) for complexes in n-hexane. The results of this study are similar to those of previous studies.

Fquilibrium Constants, Absorption Coefficients and Volume Changes. The value of K and ε can be calculated directly only if they are obtained by fitting a linear equation(2). The equilibrium constants in molar concentration units and absorption coefficients are summarizes in *Table 4* where the results are presented showing the influence of temperature and pressure on K and ε. It can be seen that both K and ε increase with the pressure at the constant temperature. Furthermore, under the constant pressure, K decreases with temperature. On the other hand, ε increases with temperature.

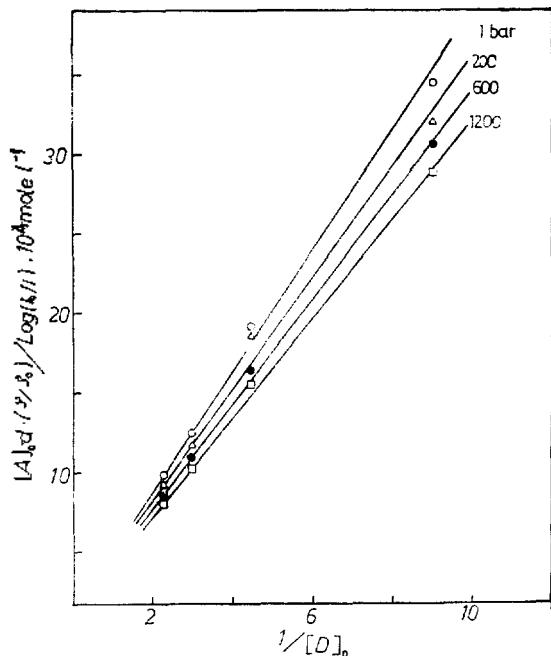We have found an increase in K and ε for the toluene-iodine complex at high pressure. These

Fig. 5. Plot of $[A]_0 \cdot d \cdot (\rho/\rho_0)/\text{Log}(I_0/I)$ versus $1/[D]_0$ of the toluene-iodine system at various pressures(60 °C).
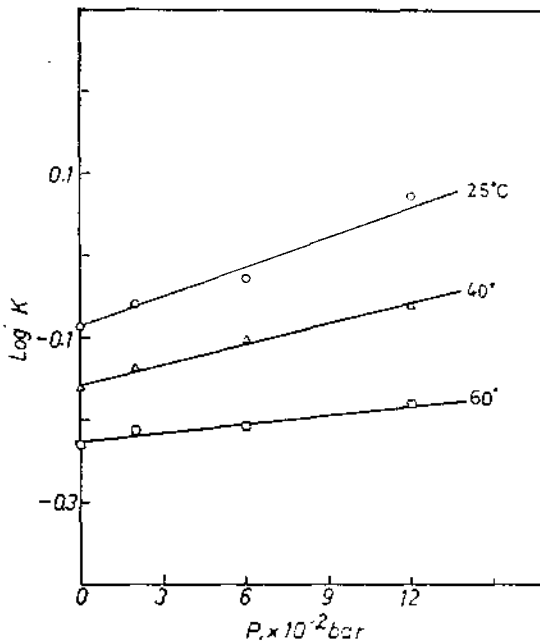
Fig. 6. Pressure dependence of log K for the toluene-iodine system at several temperatures.

Table 4. Equilibrium constants and absorption conefficients of $C_6H_5CH_3 \cdot I_2$ complexes.

Temperature (°C)	Pressure (bar)							
	1		200		600		1200	
	K	ε	K	ε	K	ε	K	ε
25	0.820	4426	0.873	4443	0.937	4501	1.19	4410
40	0.689	4444	0.758	4412	0.789	4457	0.865	4446
60	0.591	4626	0.614	4819	0.619	4930	0.660	4992

Table 5. Absorption maxima and volume change of $C_6H_5CH_3 \cdot I_2$ formation.

Temperature (°C)	λ_{max} (mμ)				ΔV (cm^3 mole^{-1})
	Pressure (bar)				
	1	200	600	1200	
25	298. 0	299. 4	300. 3	302. 0	3. 2
40	297. 4	298. 6	299. 4	300. 6	2. 0
60	295. 1	295. 8	296. 6	298. 0	1. 0

Table 6. Thermodynamic functions[a] of $C_6H_5CH_2 \cdot I_2$ in n-hexane at various pressures.

Temperature (°C)	Pressure (bar)											
	1			200			600			1200		
	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$
25		118	6. 6		81	7. 0		39	8. 0		-99	10. 7
40	1860	232	6. 7	2000	172	6. 9	2350	148	8. 0	3290	90	10. 8
60		348	6. 6		323	7. 0		318	8. 0		275	10. 7

[a] ΔG, ΔH in cal·mole^{-1}, ΔS in cal·mole^{-1}·deg^{-1}.

is a smaller increase in oscillator strength and thus indicating that the bandwidth decreases at high pressure. The quantitative results differ from those of Gott and Maisch[9].

The volume changes ΔV associated with the formation of CT-complexes from their components can be calculated from the equilibrium constants by the following equation

$$\frac{d \ln K}{dP} = -\frac{\Delta V}{RT} \qquad (4)$$

and are given by the slopes of lines as shown in *Fig.* 6.

The volume changes associated with the formation of the CT-complexes, and their absorption maxima are given in *Table* 5.

In studying the influence of pressure and temperature on λ_{max}, it was found that a red–shift or a blue–shift takes place depending on whether the pressure or temperature increase. Such behaviour was also reported by Ewald[13,14]. Also the volume change ΔV was found to decrease with increasing temperature. The decrease in component
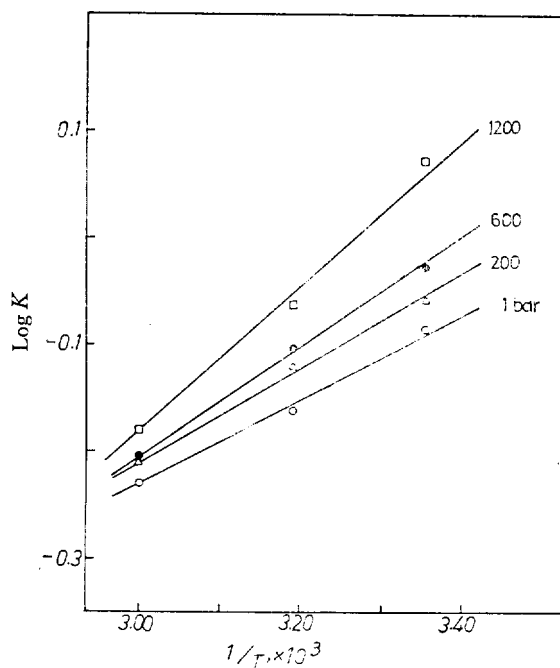
Fig. 7. Temperature dependence of log K for the toluene–iodine system at various pressures.

separation caused by compression will be small compared with the difference between the sum of the van der Waals radii and the CT band length

and will not be reflected in the observed ΔV. The measured values of ΔV represent the change in volume when the complex is formed from its components.

The structures of some complexes are known in the solid state from the X-ray diffraction work of Wallwork[20]. One can calculate the volume change associated with the formation of the complexes from their components by using Wallwork's distances and van der Waals radii[21] to calculate the van der Waals volumes of both the separate components and the complexes. The generel agreement of ΔV calculated from the structure of the solid complex and the measurements in solution is consistent with the assumption that similar complexes are formed in the two cases. The magnitude of ΔV is connected with the magnitude of K, but exceptionally large values of ΔV can occur where steric effects prevent the formation of a complex.

Thermodynamic Functions. The value of free energy, enthalpy and entropy of complex formation was calculated from the equilibrium constant. The value of free energy was derived from the equation:

$$\Delta G^{\circ} = -RT \ln K.$$

Good linearity was obtained from the plots of the log K vs. 100/T (*Fig.* 7). From the slope the enthalpy of the complex formation ΔH was calculated. Then for each temperature the free energy of the complex formation ΔG and entropy of that ΔS was calculated. The results obtained are summerized in *Table* 6.

The values of ΔH and ΔS have been calculated from experimental results at 1 bar and found similar to the values reported by Ketelaar[19]. Although the accuracy of the data is not great they show a definite increase of ΔH and ΔS with pressure. There is an increase in oscillator strength at high pressure which is pararelled by the in-

creases in ε_{max}. And hence there is no increase in bandwidths.

Pressure-, Temperature Shift and Oscillator Strength. The CT-bands are charakteristically broad and thus the ν_{max} were estimated by taking the mean of the maxima of all the measurement on a particular system. The accuracy is usually greater at higher pressure and low temperatures due to the greater intensity of the band (see *Fig.* 2).

The oscillator strength f of the CT-absorption could be evaluated directly by graphical method on a wave number scale. Its value was estimated from $\varepsilon_{max} \Delta \bar{\nu}_{1/2}$, using the equation[13,22]

$$f = 4.319 \times 10^{-9} \varepsilon_{max} \Delta \bar{\nu}_{1/2}$$
$$= 10.36 \times 10^{-9} \varepsilon_{max} (\nu_{max} - \nu_{1/2L}) \tag{5}$$

Where $\Delta \nu_{\frac{1}{2}}$ is the band width at $\varepsilon = \varepsilon_{max}/2$ and $\nu_{1/2L}$ is the half-hight frequency at the red side of the maximum of the CT-band. The shifts of absorption maxima observed at various pressure are shown in *Table* 7, *Fig.* 8 and 9 while some value of oscillator strength are shown as a function of pressure in *Fig.* 10.

The dependence of oscillator strength on pressure for various temperatures is generally not significant, although it increases slightly with temperature. Further, it was found that its dependence on temperature is rather significant for a given pressure. These results are presented in *Table* 7 and *Fig.* 10.

In *Fig.* 8 the pressure shift of CT-absorption maxima are presented. It can be seen that the red-shift increases with pressure but not significantly with temperature. The dependence of red shift on pressure for a given temperature would indicated a low energy for complex formation(see *Table* 6). Further results are shown in *Fig.* 9 where it can be seen that the blue shift is increasing with the temperature under a given pressure. Also, the shif tincreses with pressure at

Table 7. Pressure and temperature shift[a] of $C_6H_5CH_3 \cdot I_2$ CT–absorption maxima and oscillator strength of $C_6H_5CH_3 \cdot I_2$ CT–bands.

Temperature (°C)	Pressure(bar)											
	1			200			600			1200		
	$\Delta\nu$	$\Delta\nu'$	$f\times10^2$	$\Delta\nu$	$\Delta\nu'$	$f\times10^2$	$\Delta\nu$	$\Delta\nu'$	$f\times10^3$	$\Delta\nu$	$\Delta\nu'$	$f\times10^2$
25	0	0	12.8	157	0	12.9	257	0	12.9	420	0	12.8
40	0	68	13.6	135	90	13.7	225	100	13.7	358	130	13.9
60	0	330	15.1	80	407	15.4	171	415	15.9	330	425	15.9

[a] $\Delta\nu$, $\Delta\nu'$ in cm^{-1}.
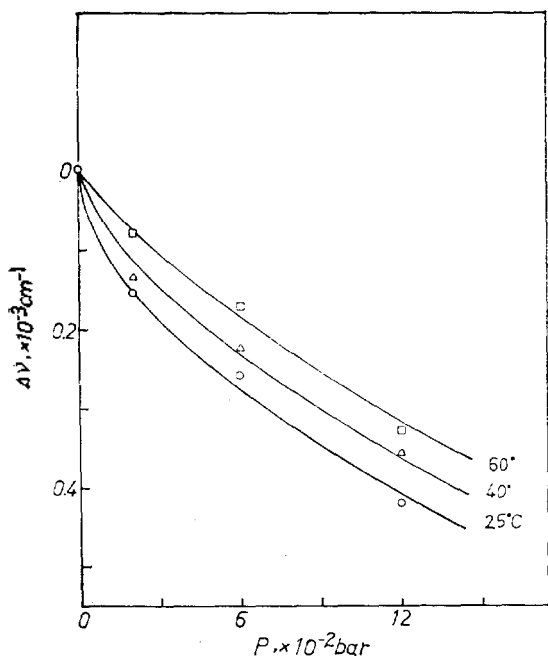
Fig. 8. Pressure shift of toluene–iodine CT–complex absorption maxima at several temperatures.
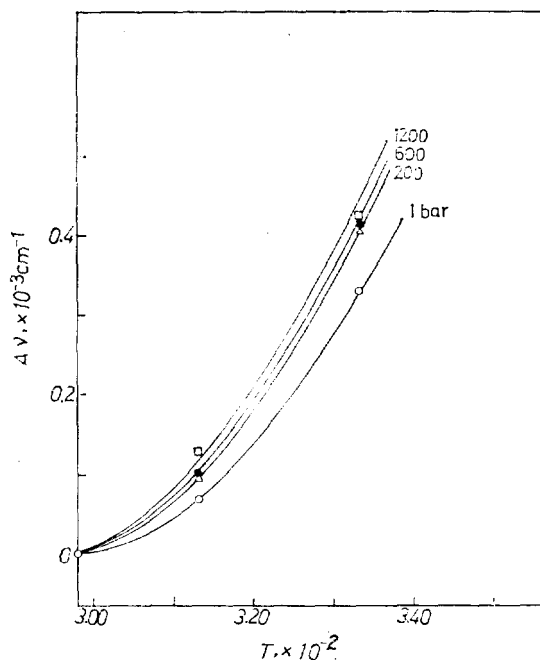

Fig. 9. Temperature shift of toluene–iodine CT–complex absorption maxima at various pressures.

a given temperature.

Briegleb[4] has shown that in the TCNE+PYR complex the absorption intensity shift is in favour of the low energy band on cooling to −180 °C. Similar intensity shifts with change of pressure were also found by Offen and Kadhim[16]. Offen and Eliason[23] have also shown that PYR alone shown an abnormally large pressure-induced red-shift coupled with an increase in the oscillator strength at its lowest band. Hence the large in-

crease in the oscillator strength found for CA+PYR is probably due to a similar shift in the relative intensity of the two CT-bands, since the oscillator strength was estimated from $\Delta\nu_{1/2L}$ of the low energy band.

The effects of pressure and temperature are clearly shown by the results. The red-shift of the CT-band due to increased interaction with the solvent occurs for every complex. In every case, $\Delta\nu$ is nearly a linear function of the density
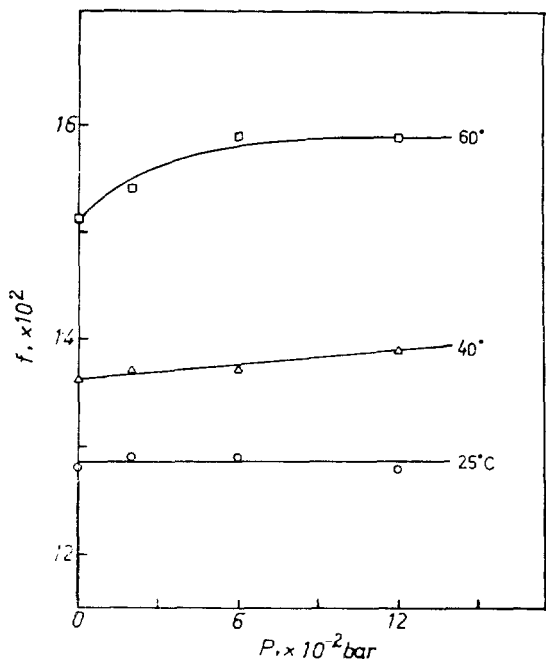
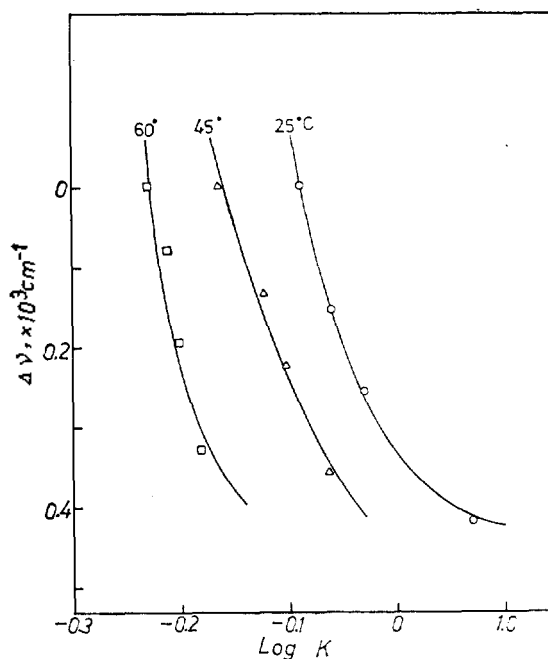Fig. 10. Pressure dependence of oscillator strength for the toluene-iodine system at several temperatures.

Fig. 11. Relation between $\Delta\nu$ and log K at several temperatures.

of the solvent. The oscillator strength increases with pressrue and temperature in all cases.

These pressure effects can be understood in terms of the model suggested by Prochorow and Tramer[24] to explain the vapour-phase →solution shift of the CT-band of CO(CN)$_2$ complexes. The characteristic broadness of the CT-bands and the small energy of formation of the complexes suggest that their ground state has a shallow and broad potential energy curve. Their excited state, with its strong component of Coulombic interaction, should have a much deeper potential energy curve and a smaller equilibrium separation. This model can account for the sensitivity of the CT-band maximum to pressure changes and for the absence of broadening. The greater the value of K, the deeper should be the potential energy minimum of the ground state and the less the red-shift for a given pressure. This is in agreement with the observed results.

In Fig. 11, the relation between K and $\Delta\nu$ is shown. Here, it is seen that the curve have similar patterns and as the temperature is increased, K becomes smaller for a given shift phenomena. The results also indicate that the rate fo red-shift with log K, for any temperature, decreases as K increases.

Apparently, the observed shift is a balance between the red-shift due to decreased separation in the ground state, and a blue-shift due to the lowering of the ground state energy by increased resonance between the no-bond and the dative-bond structure, as suggested by Offen and Abidi[25]. The exceptional blue-shift observed for complexes with large K at high pressure could also indicate that the difference between the equilibrium separation of the ground and excited state is so small that under compression, excitation raises the complex to the repulsive part of the excited state energy curve.

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