

벤젠과 요오드 사이의 전하이동착물에 대한 압력과 온도의 영향

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The Effect of Pressure and Temperature on the Benzene-Iodine Charge Transfer Complex in *n*-Hexane

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요약. 벤젠과 요오드 사이의 전하이동착물의 안정도에 미치는 압력과 온도의 영향을 *n*-헥산 용매 내에서 자외선 분광 광도법으로 연구하였다. 압력은 1에서 1600 bar, 온도는 25, 40, 60°C에서 측정하였다. 착물 형성에 대한 평형상수는 압력이 증가함에 따라 증가하고, 온도가 상승함에 따라 감소하였으며 착물의 흡수계수는 압력 및 온도와 함께 같이 증가함을 알았다. 이들 각 평형상수로 부터 착물 형성에 따른 부피, 엔탈피, 자유에너지 및 엔트로피 변화량을 구하였다. 또한 압력의 증가에 의한 red-shift, 온도의 상승에 의한 blue-shift 현상 및 압력 변화에 의한 진동자 세기의 관계를 열역학 함수와 관계지워 설명하였다.

ABSTRACT. The effect of pressure and temperature on the stabilities of the benzene-iodine charge transfer complex have been investigated through ultraviolet spectrophotometric measurements in *n*-hexane. The stabilities of the complexes were measured at temperatures of 25, 40 and 60°C up to 1600 bars. The equilibrium constant of the complex formation was increased with pressure and decreased with temperature raising. The absorption coefficient was increased with both pressure and temperature. Changes of volume, enthalpy, free energy and entropy for the formation of complexes were obtained from the equilibrium constants. The red-shift at 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

The basic theory of electron donor-acceptor complexes has changed little since Mulliken's theory¹. According to this theory a small change in the separation of the two constituents in the complex should give rise to large changes in the formation constant K and the electron transfer energy $h\nu^2$. Thus a remarkable influence of hydrostatic pressure on the com-

plexes might be expected.

Experimental works on the influence of pressure on the charge transfer complexes have been reported by Ham³, Gott and Maisch⁴. Torihash *et al.*⁵ have investigated the influence of pressure on the light absorption and fluorescence of *s*-tetracyanobenzene complexes. Also Ewald^{6,7} has measured the effect of hydrostatic pressure on the formation constant K_x and the charge transfer absorption energy of electron

donor-acceptor complexes in solution, and concluded that a large part of the effect of pressure could be explained by changes in the solvation of donors, acceptors and the complexes. Recently Kwun *et al.*⁸⁻¹⁰ and Scholz¹¹ have investigated the charge transfer complexes under the condition of several temperatures and pressures and have discussed among others the problems of contact charge transfer complexes. According to that result the elevated pressure causes an increase of the charge transfer absorption, and, as a rule, gives rise to a red shift of the absorption maxima whereas blue shifts have been reported in the exceptional cases for liquid solutions and for solids.^{4,12} A temperature increase causes a blue shift of the absorption band.

In the present study we have examined the effect of pressure and temperature on the formation of the *one to one* charge transfer complex of benzene with iodine in *n*-hexane. We measured the absorbancy of its liquid solution over a range of several concentrations, pressures and temperatures, and were able to evaluate the equilibrium constant K_c , the extinction coefficient

ϵ and the thermodynamic quantities ΔV , ΔH , ΔG and ΔS . The red-shift observed at 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, and the correlation between the differences of the electron transfer energies $h\nu$ and the difference of free energies ΔG of the complex formation for the pressure variation is considered.

EXPERIMENTAL

Materials. Samples of Merck Co. iodine (superpure grade), benzene (uvasol grade) and *n*-hexane (uvasol grade) as the solvent were used without further more purification.

Preparation of Stock Solution. The solutions of iodine and benzene in *n*-hexane were prepared by the general procedures. Each solution was freshly prepared at room temperature before measuring the absorption spectrum and wrapped with the black paper to prevent any photochemical reaction in solution. The concentration of benzene was 2.50, 3.60, 4.50, 5.63

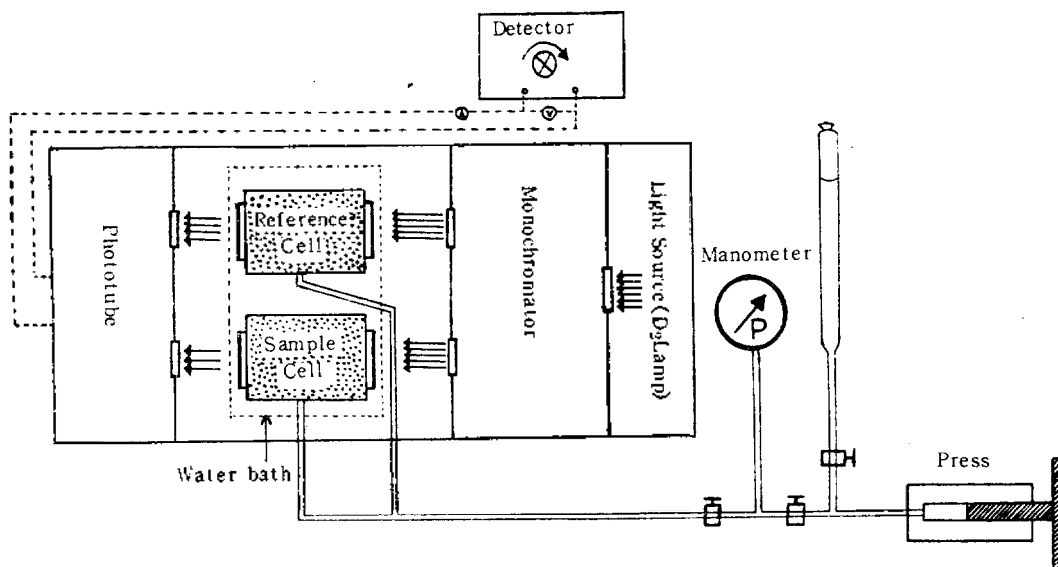


Fig. 1. Scheme of the apparatus for the experiment

$\times 10^{-1} \text{ mol. l}^{-1}$ and that of iodine was 3.50, 5.01, $6.44 \times 10^{-4} \text{ mol. l}^{-1}$. 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 Bausch & Lomb spectronic 505 spectrophotometer modified to accommodate a high pressure cell. The scheme of the apparatus used in experiment is shown in Fig. 1. A pair of high pressure optical cells have been used together with the equipment to generate and to measure elevated pressures. It has two windows of synthetic colourless sapphire with a thin walled teflon cylinder between them which contains the solution. Each sapphire window is sealed by an O-ring which is protected by an U shape teflon ring. Using this arrangement the solution samples are in contact with sapphire and teflon only and thus highly corrosive solutions can be investigated. The external part of the cell was made of brass and was kept at constant temperature by circulating water through it supplied by a thermostat. The test solution was injected, using teflon syringe, through a capillary into the high pressure cell which then connected to a high pressure apparatus.

Spectrophotometric Measurement. The absorbancies of the stock solutions of iodine and benzene in *n*-hexane were measured over the wave lengths from 270 to 570 nm, using the pure solvent, *n*-hexane, as the blank. Then, the solution of benzene was mixed at appropriate ratio with the solution of iodine. The absorbancies of the resulting solutions were immediately measured. The prolonged keeping of the mixture solutions was avoided as otherwise slow chemical changes might have occurred. The blank in this case was the *n*-hexane solution of benzene with the same concentrations

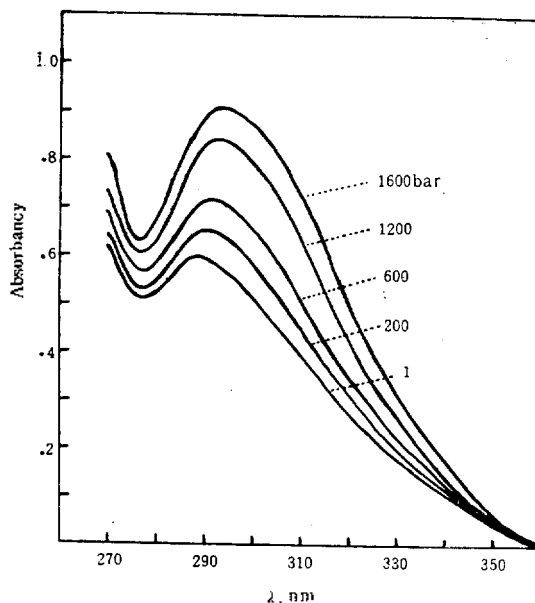


Fig. 2. Absorption spectrum for the charge transfer complex of benzene (0.360 M) with iodine ($6.44 \times 10^{-4} \text{ M}$) in *n*-hexane at various pressures (25°C).

as those of the solutions containing iodine. The high pressure optical cell was maintained at the desired temperatures 25, 40 and 60°C, by a thermostat within $\pm 0.1^\circ \text{C}$. The absorbancies of the solutions at the complex absorption maxima were usually determined in the neighborhood of 290 nm.

RESULTS AND DISCUSSION.

A set of spectra of benzene-iodine CT-complexes in *n*-hexane at various pressures is shown in Fig. 2. The broad absorption bands are typical of electron donor-acceptor complexes in solution and one reason why quantitative determination of the absorption maximum is often difficult. Thus, it is necessary to allow for change in concentration of the solution when the absorption spectra are compared at the different pressures and temperatures. In the present study, the various parameters are discussed individually.

Calculation of Equilibrium Constant for the CT-Complex Formation. The absorption spectra of the individual stock solutions of iodine or benzene in *n*-hexane did not indicate the presence of maximum absorption peaks in the vicinity of 290 nm. On the other hand, the absorption spectra of the mixture solution of benzene with iodine indicated the presence of absorption maxima in the region of wave lengths near 290 nm. The maximum absorption observed is attributed to the formation of complexes of benzene with iodine in solution. These complexes are assumed to be *one to one* molecular complexes of which was proposed by Benesi and Hildebrand for the benzene-iodine system in carbon tetrachloride¹³.



Where D denotes the donator molecule, A acceptor molecule, and C the *one to one* molecular complex D-A. In the case studied in this paper, the stock solution of iodine in *n*-hexane did not show any absorption in the vicinity of 290 nm, though it was reported to be absorption by iodine solution in carbon tetrachloride¹⁴ in the same range. We assumed that the observed absorbancies at the absorption maxima are due to only the complexes. Thus, equilibrium constant of equation (1) in *n*-hexane is much larger than that in carbon tetrachloride (see Table 6. of reference 14 and Table 1). In order to obtain the formation constant *K* and the absorption coefficient ϵ , the equation of Benesi and Hildebrand has been used together with an additional factor to allow for the change of density due to the pressure and temperature variations, *i. e.*

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

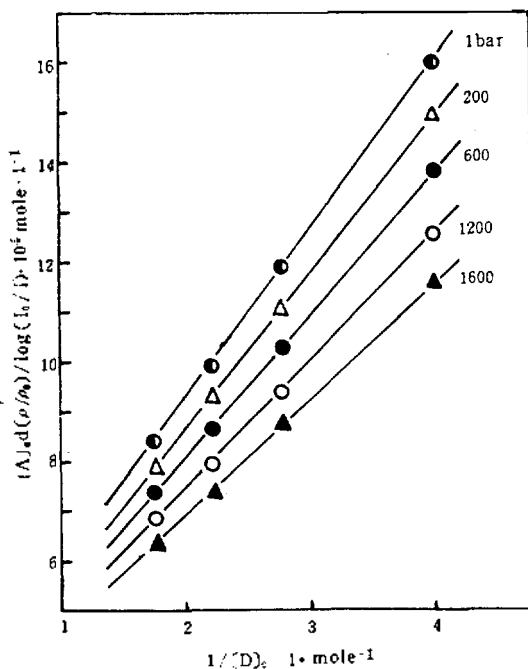


Fig. 3. Plot of $[A]_0 d (\rho/\rho_0) / \log(I_0/I)$ versus $1/[D]_0$ of the benzene-iodine system in *n*-hexane at 25°C and at various pressures.

Where $[A]_0$ and $[D]_0$ are the initial molar concentration of acceptor and donor respectively, $\log(I_0/I)$ is absorbancy (*A*) at the absorption maxima λ_{\max} , *d* is the internal distance between the sapphire windows. It was always 1.10 cm. ρ_0 and ρ are densities of solution at 25°C and 1 bar and at the experimental temperature and pressure respectively.

The values of the ratios ρ/ρ_0 for the solutions were derived from the results of Kuss and Taslimi.¹⁵ After the values of absorbancies were determined experimentally, the quantities of $[A]_0 \cdot d \cdot (\rho/\rho_0) / \log(I_0/I)$ were plotted against $1/[D]_0$. The plots indicated good linearities between the two quantities in all the system examined. Hence, the values of K_c and ϵ were calculated from the slopes and the intercepts of the straight lines. The least square method was utilized to determine the slopes and inter-

Table 1. Absorption maxima, equilibrium constants, absorption coefficients and volume change of $C_6H_6 \cdot I_2$ CT-complexes.

Temp. ($^{\circ}C$)	Pressure (bar)	λ_{max} (nm)	K_c ($l \cdot mole^{-1}$)	ϵ ($l \cdot mole^{-1} \cdot cm^{-1}$)	$-\Delta V$ ($cm^3 \cdot mole^{-1}$)
25	1	288.4	0.689	4255	5.89
	200	289.8	0.722	4367	
	600	290.6	0.755	4505	
	1200	292.1	0.856	4545	
	1600	293.3	0.903	4608	
40	1	287.9	0.570	4405	5.26
	200	289.2	0.612	4484	
	600	289.9	0.632	4587	
	1200	291.2	0.706	4630	
	1600	292.3	0.729	4695	
60	1	286.0	0.449	4587	4.04
	200	286.8	0.464	4739	
	600	287.5	0.498	4785	
	1200	288.9	0.546	4926	
	1600	290.0	0.554	5102	

cepts.

The Benzene-Iodine CT-Complexes Formation.

The data obtained at temperature, 25, 40, and $60^{\circ}C$ and under pressure, 1, 200, 600, 1200, and 1600 bar on the system of benzene with iodine in *n*-hexane show a straight line relationship between the left hand side of equation (2) and $(D)_0^{-1}$ in each respectively, of which one of example at $25^{\circ}C$ is presented in Fig. 3. These linearities indicate that the assumption of the formation of *one-to-one* molecular complex between benzene and iodine is being correct as it was discussed previously.¹³ The results of the present study at $25^{\circ}C$ and 1 atm are now compared with those reported in the literature. Benesi and Hildebrand¹³ reported an equilibrium constant value of 1.73 (as K_2) for this complex in carbon tetrachloride, Andrews and Keefer¹⁶ reported a value of 0.15 for the complex in the same solvent, and Scholz¹¹ reported a value of 0.276 for the complex in *n*-heptane. The results of this study are not similar to those

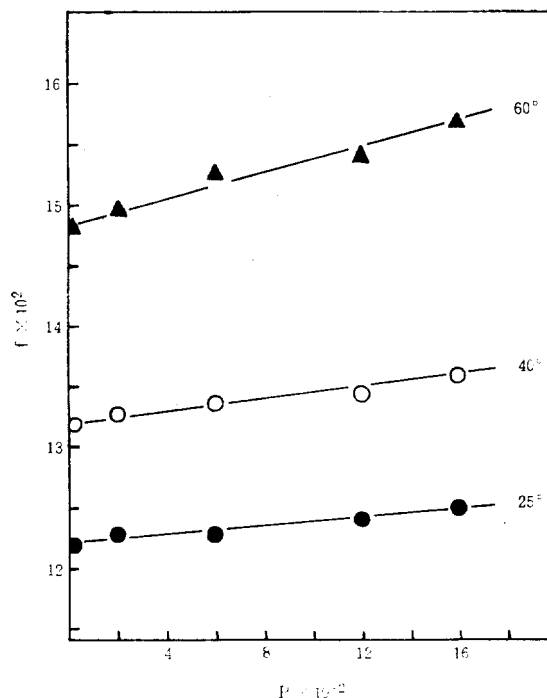


Fig. 4. Pressure dependence of $\log K_c$ for the benzene-iodine charge transfer complex in *n*-hexane at several temperatures.

of previous studies because they differ from sol-

Table. 2 Thermodynamic functions of $C_6H_6 \cdot I_2$ CT-complex at various pressures.

Temp. (°C)	Pressure (bar)														
	1			200			600			1200			1600		
	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$	$-\Delta H$	ΔG	$-\Delta S$
25		121	6.22		43.7	6.54		22.4	6.79		12.1	6.87		6.42	7.01
40		1732	212		1904	134		2001	121		2034	107		2083	102
60		336	6.21		267	6.52		257	6.78		247	6.85		241	6.98
		a. v. 6.21			a. v. 6.52			a. v. 6.78			a. v. 6.85			a. v. 6.99	

ΔH , ΔG in cal·mole⁻¹, ΔS in cal·mole⁻¹·deg⁻¹

vent used to solvent.

Equilibrium Constants, Absorption Coefficients and Volume Change. The equilibrium constants in molar concentration units and absorption coefficients are summarized in Table 1 where the results are presented showing the influence of temperature and pressure on K_c and ϵ . It can be seen that both K_c and ϵ increases with the pressure at the constant temperature. On the other hand, K_c decreases with temperature raising at constant pressure, but ϵ increases with temperature. We have found an increase in K_c and ϵ for the complex of benzene with iodine at a higher pressure. There is a smaller increase in oscillator strength and thus some indication that the band width decreases at a higher pressure. The quantitative results differ from those of Gott and Maisch⁴. The volume changes, ΔV associated with the formation of the CT-complexes from their components can be calculated from the equilibrium constants by the following equation.

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = -\frac{\Delta V}{RT} \quad (3)$$

They are given by the slopes of lines such as shown in Fig. 4. The volume changes associated with the formation of the CT-complex and their absorption maxima are given in Table 1. In studying the influences of pressure and temperature on the formation of CT-complex, the decrease in the component separation caused by compr-

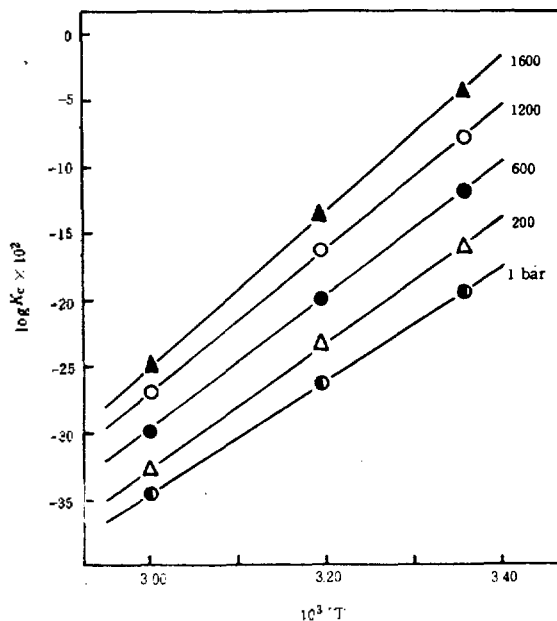


Fig. 5. Temperature dependence of $\log K_c$ for the benzene-iodine charge transfer complex in *n*-hexane at various pressures.

ession will be small compared with the difference between sum of the van der Waals radii and the charge transfer bond length and thus it 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. Therefore, the negative sign of ΔV indicate that molar volume of the complex is smaller than sum of the molar volumes of its components. Thus, the complexes are looser at a higher temperature since the volume change, ΔV is found to decrease with temper-

Table 3. Thermodynamic properties for the $C_6H_6 \cdot I_2$ CT-complex formation at 25°C and various pressures.

1. P(bar)	1	500	1000	1500
2. ΔV (cm ³ ·mole ⁻¹)	-5.89	-5.22	-4.54	-3.87
3. $\partial \Delta V / \partial T$ (cm ³ ·mole ⁻¹ ·deg ⁻¹)	5.35×10^{-2}	4.60×10^{-2}	3.81×10^{-2}	3.07×10^{-2}
4. ΔH (kJ·mole ⁻¹)	-7.25	-8.23	-8.48	-8.70
5. $\partial \Delta H / \partial P$ (10 ⁻¹ J·mole ⁻¹ ·bar ⁻¹)	-20.7	-18.1	-15.4	-12.7
6. $\Delta V - T(\partial \Delta V / \partial T)$ (cm ³ ·mole ⁻¹)	-21.8	-18.9	-15.9	-13.0
7. $\Delta U = \Delta H - P\Delta V$ (kJ·mole ⁻¹)	-7.25	-7.97	-8.02	-8.11
8. $\partial \Delta U / \partial P$ (10 ⁻¹ J·mole ⁻¹ ·bar ⁻¹)	-15.2	-12.5	-9.82	-7.13
9. $-T(\partial \Delta V / \partial T) - P(\partial \Delta V / \partial P)$ (cm ³ ·mole ⁻¹)	-15.9	-13.0	-10.0	-7.12
10. ΔG (kJ·mole ⁻¹)	0.50	0.13	0.06	0.03
11. ΔS (J·mole ⁻¹ ·deg ⁻¹)	-26.2	-27.9	-28.9	-29.1
12. $-\partial \Delta G / \partial T$ (J·mole ⁻¹ ·deg ⁻¹)	-24.7	-26.3	-28.8	-29.5
13. $\partial \Delta S / \partial P$ (J·mole ⁻¹ ·deg ⁻¹ ·bar ⁻¹)	-4.29×10^{-3}	-2.73×10^{-3}	-1.17×10^{-3}	-0.39×10^{-3}

ature raising in Table 1.

Thermodynamic Functions. The value of free energy, enthalpy and entropy change due to the complex formation was calculated from the equilibrium constants. Since good linearity was obtained from the plots of $\log K_c$ versus $1/T$ such as Fig. 5, enthalpy of the complex formation ΔH was calculated from the slope. Then free energy of the complex formation ΔG and entropy of that ΔS were calculated. The results obtained are summarized in Table 2.

ΔH and ΔS do not vary with temperature, accordingly ΔG is a linear function of temperature in the range considered. If Fig. 4 is the curves with very small curvature at constant temperature, it is sufficient to write

$$\ln K_c = a + bP + cP^2 \quad (4)$$

Consequently $\partial \ln K_c / \partial P = b + 2cP$ and $\partial^2 \ln K_c / \partial P^2 = 2c$, which means that ΔG and its derivatives ΔH and ΔS are assumed to be quadratic functions of pressure. The pressure derivatives of ΔH , ΔG and ΔS have been obtained by the least square method. Table 3 shows smoothed values of thermodynamic properties at 1, 500, 1000, and 1500 bar derived from Table 2. The data of Table 3 permit a check of internal

Table 4. Pressure and temperature shift of $C_6H_6 \cdot I_2$ CT-absorption maxima and oscillator strength of $C_6H_6 \cdot I_2$ CT-bands at various temperature.

Temp. (°C)	Pressure (bar)	$(\nu_1 - \nu_p)_{\max}$ (cm ⁻¹)	$(\nu_1 - \nu_{25})_{\max}$ (cm ⁻¹)	$f \times 10^2$
25	1	0		12.2
	200	168		12.3
	600	263		12.3
	1200	439		12.4
	1600	579		12.5
40	1	0	60.2	13.2
	200	156	71.5	13.3
	600	240	83.1	13.4
	1200	394	106	13.4
	1600	523	117	13.6
60	1	0	291	14.8
	200	97.5	361	15.0
	600	182	371	15.3
	1200	351	380	15.4
	1600	482	388	15.7

consistency. For example $\partial \Delta H / \partial P$ (line 5 in Table 3) has to be equal to $\Delta V - T(\partial \Delta V / \partial T)$. Other relations hold for the pressure derivatives of ΔU as indicated in Table 3, hence line 8 has to be equal to line 9, line 11 equals line 12. Even a further differentiation with respect to P of line 3, 5, 6, 8, 9, and 13 gives constant values independent of pressure. Alth-

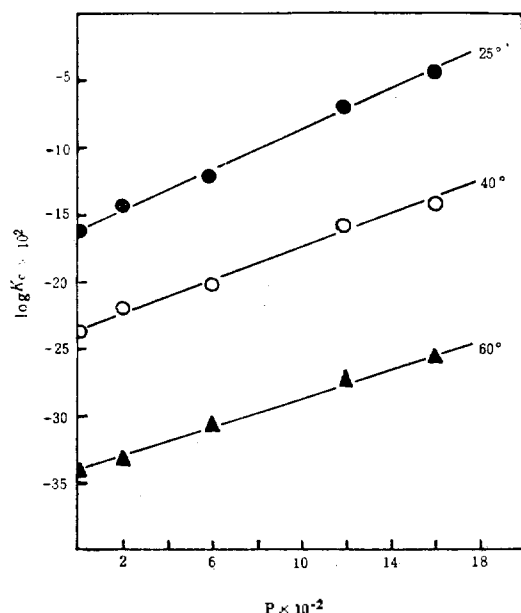


Fig. 6. Pressure dependence of oscillator strength for the benzene-iodine system in *n*-hexane at several temperatures.

ough the accuracy of the data in Table 3 is not great, they show a definite decrease of ΔH , ΔG and ΔS with pressure. And hence there is an increase in the stability of complex at a higher pressure which is paralleled by the increase in the physical restraints imposed upon the complex components.

Pressure, Temperature Shift and Oscillator Strength. The shifts of absorption maxima and the values of oscillator strength observed at various pressures and temperatures are shown in Table 4. 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. The CT-bands are characteristically broad and thus the ν_{\max} were estimated by taking the mean of the maxima of all the measurements on a particular

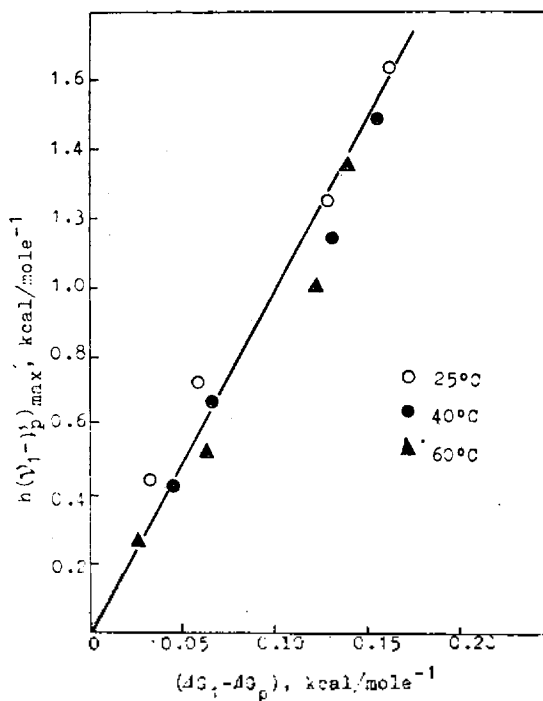


Fig. 7. Correlation between the difference of electron transfer energies $h\nu_{\max}$ and the difference of free energies ΔG of the complex formation for pressure variation in the benzene-iodine system.

system. 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 $\epsilon_{\max} \cdot \Delta\nu_{1/2}$ using the equation.¹⁷

$$f = 4.319 \times 10^{-9} \epsilon_{\max} \cdot \Delta\nu_{1/2} \\ = 1.036 \times 10^{-8} \epsilon_{\max} (\nu_{\max} - \nu_{1/2L}). \quad (5)$$

Where $\Delta\nu_{1/2}$ is the bandwidth at $\epsilon = \epsilon_{\max}/2$ and $\nu_{1/2L}$ is the half-height frequency at the red side of the maximum of the CT-band. The oscillator strength shows a linear increase with pressure up to 1600 bars in Fig. 6. $\partial f / \partial p$ is 1.22 , 2.24 , $4.46 \times 10^{-6} \text{ bar}^{-1}$ at 25 , 40 and 60°C respectively. It can be seen that the shift increases with pressure but not significantly with temperature. The dependence of red shift on pressure for a given temperature would

indicate a low energy for complex formation (see Table 1). Further results are shown that the blue shift is increasing with temperature under a given pressure. Also, the red shift increase with pressure at a given temperature. The correlation between $h\nu_{\max}$ and ΔG for the benzene-iodine system is shown in Fig. 7. The red shift of the band maximum at different pressures are plotted as a function of the respective change of ΔG (Table 2). For the pressure variation the result indicates a reasonable linearity of which the slope is 8.6 (precise to ± 0.3) for each temperature. Thus, for the benzene-iodine system the following relationship holds

$$\partial(h\nu_{\max})/\partial P = 8.6 \partial(\Delta G)/\partial P \quad (6)$$

On the other hand, for the temperature variation a linear relationship for $(\nu_t - \nu_{25})_{\max}$ as a function of $\Delta G_t - \Delta G_{25}$ is less obvious. An interpretation of the expression depends on the model used for the charge transfer complexes. For instance, if one supposes that the variation at the depth of potential in the ground state is described by ΔG , then the numerical factor in the equation should give an information about the shift or a deformation of the potential of the excited state. Apparently, the observed shift is a balance between the red shift due to decreased separation in the ground state and the 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 Abidi¹⁸.

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