

듀렌과 요오드 사이의 전하이동착물에 대한 압력과 온도의 영향

權五千[†] · 金正林

한양대학교 이과대학 화학과

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

Oh Cheun Kwun and Jeong Rim Kim

Department of Chemistry, Hanyang University, Seoul 133, Korea

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요 약. 듀렌과 요오드 사이의 전하이동착물의 안정도에 미치는 압력과 온도의 영향을 *n*-헥산 용액에서 자외선 분광 광도법으로 연구하였다. 압력은 1에서 1600 bar, 온도는 25, 40, 60°C 사이에서 측정하였다. 착물의 평형상수는 압력 및 온도의 증가와 더불어 증가 및 감소하고 흡수계수는 대체로 증가함을 알았다. 이들 각 평형상수로부터 착물형성에 따른 부피, 엔탈피, 자유에너지 및 엔트로피 변화량을 구하였다. 또한 압력의 증가에 의한 red-shift, 온도의 증가에 의한 blue-shift 현상 및 압력변화에 의한 진동자 세기의 관계를 열역학적 함수와 관계지워 설명하였다.

ABSTRACT. The effect of pressures and temperatures on the stabilities of the durene-iodine charge transfer complex have been investigated through ultraviolet spectrophotometric measurements in *n*-hexane. The stabilities of complexes were measured at 25, 40 and 60°C under 1~1600 bars. The equilibrium constant of the complex 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 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.

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 separating distance 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 complexes might be expected.

Experimental work on the influence of pressure on charge transfer complexes has been reported by Ham³, Gott and Maisch⁴ and for solid complexes by Drickamer *et al.*^{5,6} and Offen *et al.*^{7,8}. Mataga *et al.*⁹ have investigated the influence of pressure on the light absorption and fluorescence of *s*-tetracyanobenzene comple-

xes. Recently Ewald^{10,11} has measured the effect of hydrostatic pressure on the formation constant K and the charge transfer absorption energy of electron donor-acceptor complexes in solution, and concluded that a large part of the effect could be explained by changes in the solvation of donors, acceptors and the complexes. Kwun^{12,13} and Scholz¹⁴ have investigated charge transfer complexes in a wide temperature and density range and have discussed among others the problem of contact charge transfer complexes. Elevated Pressure causes an increase of the charge transfer absorption, and, as a rule, gives rise to a red shift of the absorption as for solid complexes⁵⁻⁷. Blue shifts have been reported in exceptional cases for liquid solutions and for solids^{4,15}. A temperature increase causes a blue shift of the absorption band.

In the present work we have examined the effect of pressure and temperature on the formation of one to one charge transfer complexes with iodine of durene in *n*-hexane as one of the series of polymethylbenzene-iodine CT-complexes.

We measured the absorbancy of their liquid solutions over a range of concentrations, pressures and temperatures and were able to evaluate the equilibrium constant K , the absorption coefficient ϵ and the thermodynamic quantities ΔG , ΔV , ΔH , 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.

EXPERIMENTAL

Materials. Samples of *n*-hexane (uvasol grade, Merck, Germany), iodine (superpure grade, Merck, Germany) and durene (ultrapure grade, Tokyo Kasei, Japan) were used without purification.

Preparation of Stock Solution. The solutions of iodine and durene in *n*-hexane were prepared by the procedures described previously¹³.

Each solution was freshly prepared at room temperature before measuring the absorption spectrum and wrapped with black paper to prevent any photochemical reaction in solution. The concentration of durene was 1.15, 2.32, 3.58, $4.63 \times 10^{-1} \text{ mole} \cdot \text{l}^{-1}$ and that of iodine was 2.32, 3.09, $4.02 \times 10^{-4} \text{ mole} \cdot \text{l}^{-1}$. 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 apparatus has already been described in detail¹².

A pair of high pressure optical cells have been used together with 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 glass syringe, through a capillary into the high pressure cell which then connected to a high pressure apparatus.

Spectrophotometric Measurements. The absorbancies of the stock solutions of iodine and durene in *n*-hexane were measured over

the wave lengths ranging from 280 to 580 nm using the pure solvent, *n*-hexane, as the blank. Then, the solution of durene 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 durene with the same concentrations 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 solution at the complex absorption maximum were usually determined in the neighborhood of 300 nm.

RESULTS AND DISCUSSION

A set of spectra of durene-iodine CT-complexes in *n*-hexane at various pressures is shown in Fig. 1. The broad absorption bands are typical of electron donor-acceptor complexes in

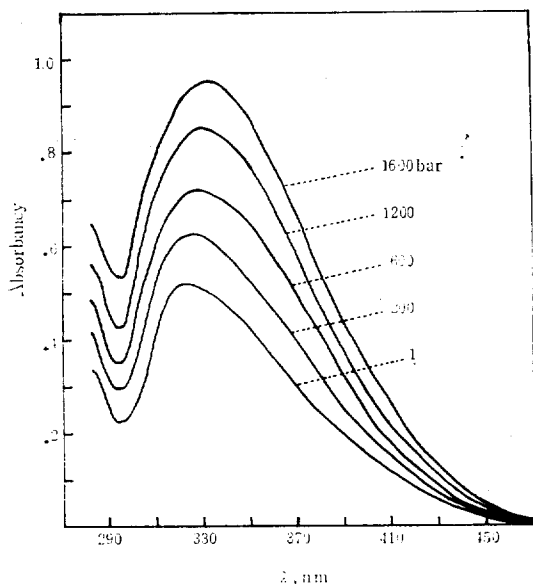
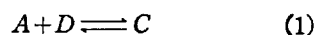


Fig. 1 Absorption spectrum for the charge transfer complex of durene (0.358 M) with iodine (2.32×10^{-4} M) in *n*-hexane at various pressures (25°C)

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 present work, 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 durene in *n*-hexane did not indicate the presence of maximum absorption peaks in the vicinity of 300 nm. On the other hand the absorption spectra of the solution of a mixture of durene with iodine indicated the presence of absorption maxima in the region of wave lengths near 300 nm. The maximum absorption observed is attributed to the formation of complexes of durene 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 tetrachloride¹⁶.



Where *D* denotes the donator molecules, *A* acceptor molecules and *C* the one to one molecular complex *D*·*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.*

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

Which is now in the form, $y = mx + b$. Where $[A]_0$ and $[D]_0$ are the initial molar concentration of acceptor and donor respectively, $\log(I_0/I)$ is absorbancy (*A*) at 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 Taslimi¹⁷. The values of the equilibrium constant K and absorption coefficient ϵ were found from equation (2). After the values of absorbancies (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 K 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 intercepts. 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 Durene-Iodine CT-Complexes Formation. The data obtained at temperature 25, 40, 60°C and pressure 1, 200, 600, 1200, 1600 bar on the system of durene with iodine in *n*-hexane show a straight line relationship between y and x in each respectively, of which one of example at 25°C is presented in Fig. 2.

These linearities indicate that the assumption of the formation of one to one molecular complex between durene and iodine is being correct as it was discussed previously¹⁶.

The results of the present study at 25°C and 1 atm are now compared with those reported in the literature. Keefer and Andrews¹⁸ reported an equilibrium constant value of 0.63 for the complex, durene iodine in carbon tetrachloride. And Ketelaar¹⁹ reported a value of 5.05 (as K_x) for the complex in *n*-hexane. The results of this study are similar to those of previous studies.

Equilibrium 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 summarized in Table 1 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 increases with the pressure at the constant temperature. On the other hand, K decreases with temperature at constant pressure, but ϵ increases with temperature. We have found an increase in K and ϵ for the durene-iodine complex at higher pressure.

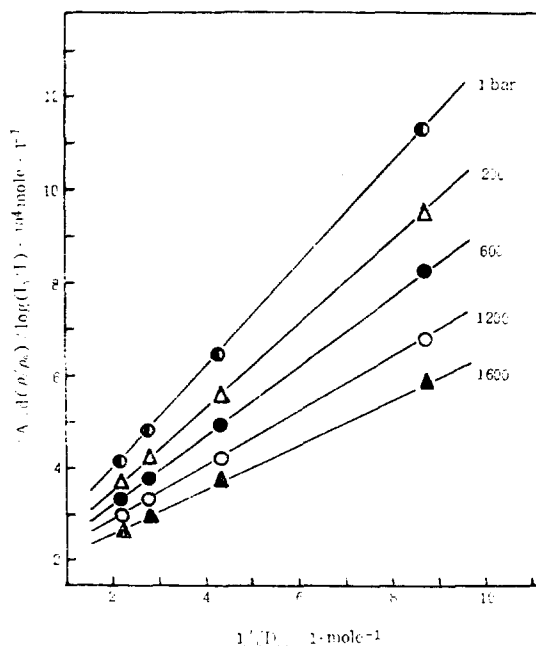


Fig. 2 Plot of $[A]_0 d(\rho/\rho_0)/\log(I_0/I)$ versus $1/[D]_0$ of the durene-iodine system in *n*-hexane at 25°C and at various pressures

There is a smaller increase in oscillator strength and thus some indication that the bandwidth decreases at higher pressure. The quantitative results differ from those of Gott and Maisch⁴. The volume changes ΔV assoc-

iated with the formation of the CT-complexes from their components can be calculated from the equilibrium constants by the following equation. They are given by the slopes of lines such as shown in Fig. 3.

$$\frac{d \ln K}{dP} = -\frac{\Delta V}{RT} \quad (3)$$

The volume changes associated with formation of the CT-complex and their absorption maxima are given in Table 1. In studying the influences 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^{10,11}. Also the volume change ΔV was found to decrease with increasing temperature. The decrease in component separation caused by compression will be small compared with the difference between the sum of the van der Waals radii and the charge

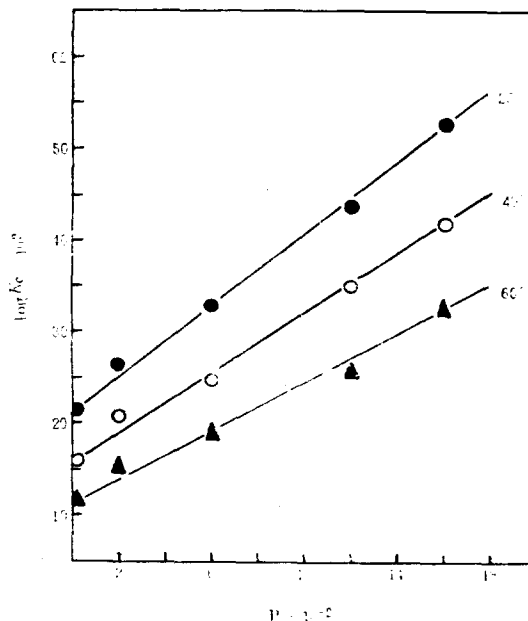


Fig. 3 Pressure dependence of $\log K_c$ for the durene-iodine charge transfer complex in *n*-hexane at several temperatures

Table 1. Absorption maxima, equilibrium constants, absorption coefficients and volume change of $C_6H_2(C_6H_5)_4 \cdot I_2$ CT-complexes

Temp. (°C)	Pressure (bar)	λ_{\max} (nm)	K_c (l·mole ⁻¹)	ϵ (l·mole ⁻¹ ·cm ⁻¹)	$-\Delta V$ (cm ³ ·mole ⁻¹)
25	1	326.0	1.63	5602	10.5
	200	327.2	1.90	5903	
	600	328.5	2.11	6116	
	1200	329.6	2.75	6242	
	1600	330.7	3.35	6460	
40	1	325.0	1.45	5917	8.92
	200	326.1	1.68	6211	
	600	327.3	1.78	6369	
	1200	328.3	2.22	6410	
	1600	329.5	2.61	6623	
60	1	324.2	1.31	6135	6.83
	200	325.2	1.45	6452	
	600	326.3	1.54	6667	
	1200	327.2	1.77	6803	
	1600	328.3	2.01	6944	

transfer bond 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 Wallwork²⁰. 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 to calculate the van der Waals volumes of both the separate components and the complexes. The general 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 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. In the studies of the series, the equilibrium constant of the

complex formation between durene and iodine is smaller than that between mesitylene²¹ and iodine but the change in volume is the reverse. Thus it is found that the steric hindrance effects occur more strongly in the case of durene.

Thermodynamic Functions. The value of free energy, enthalpy and entropy of complex formation was calculated from the equilibrium constant. Since good linearity was obtained from the plots of $\log K$ versus T^{-1} such as Fig. 4, 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 for each temperature. The results obtained are summarized in Table 2.

The values of ΔH and ΔS calculated from experimental results at 1 bar found similar to the values reported by Ketelaar¹⁹.

If Fig. 3 is the curves with very small curva-

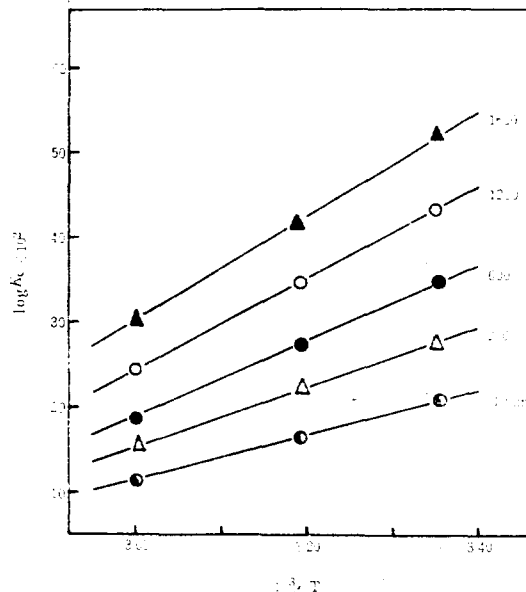


Fig. 4 Temperature dependence of $\log K_c$ for the durene-iodine charge transfer complex in *n*-hexane at various pressures

Table 2. Thermodynamic functions of $C_6H_2(CH_3)_4 \cdot I_2$ CT-complex at various pressures

Temp. (°C)	Pressure (bar)														
	1			200			600			1200			1600		
	$-\Delta H$	$-\Delta G$	$-\Delta S$	$-\Delta H$	$-\Delta G$	$-\Delta S$	$-\Delta H$	$-\Delta G$	$-\Delta S$	$-\Delta H$	$-\Delta G$	$-\Delta S$	$-\Delta H$	$-\Delta G$	$-\Delta S$
25		290	3.16		380	3.84		442	4.48		599	7.33		716	7.60
40	1233	231	3.20	1526	323	3.84	1788	359	4.53	2784	496	7.31	2980	597	7.61
60		179	3.16		246	3.84		286	4.48		378	7.23		462	7.56
		AV. 3.17			AV. 3.84			AV. 4.50			AV. 7.29			AV. 7.59	

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

ture at given temperature, it is acceptable to write

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

Where a , b and c are constants.

Consequently this equation means that ΔG , ΔH and ΔS are assumed to be quadratic functions of pressure. The pressure derivatives of ΔG , ΔH and ΔS have been obtained by the least square method. Table 3 shows the 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 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.

The data in Table 3 show a definite decrease

Table 3. Thermodynamic properties for the $C_6H_2(CH_3)_4 \cdot I_2$ CT-complex formation at 25°C under various pressures

1. P (bar)	1	500	1000	1500
2. ΔV ($cm^3 \cdot mole^{-1}$)	-10.5	-9.72	-8.92	-8.12
3. $\partial \Delta V / \partial T$ ($cm^3 \cdot mole^{-1} \cdot deg^{-1}$)	10.5×10^{-2}	9.85×10^{-2}	9.19×10^{-2}	8.51×10^{-2}
4. ΔH ($kJ \cdot mole^{-1}$)	-5.16	-7.44	-10.0	-12.3
5. $\partial \Delta H / \partial P$ ($J \cdot mole^{-1} \cdot bar^{-1}$)	-4.14	-3.90	-3.67	-3.43
6. $\Delta V - T(\partial \Delta V / \partial T)$ ($10cm^3 \cdot mole^{-1}$)	-4.18	-3.91	-3.63	-3.35
7. $\Delta U = \Delta H - P\Delta V$ ($kJ \cdot mole^{-1}$)	-5.16	-6.95	-9.14	-11.1
8. $\partial \Delta U / \partial P$ ($J \cdot mole^{-1} \cdot bar^{-1}$)	-3.21	-3.06	-2.88	-2.69
9. $-T(\partial \Delta V / \partial T) - P(\partial \Delta V / \partial P)$ ($10cm^3 \cdot mole^{-1}$)	-3.13	-3.02	-2.90	-2.78
10. ΔG ($kJ \cdot mole^{-1}$)	-1.24	-1.74	-2.27	-2.83
11. ΔS ($J \cdot mole^{-1} \cdot deg^{-1}$)	-13.3	-19.6	-25.8	-31.7
12. $-\partial \Delta G / \partial T$ ($J \cdot mole^{-1} \cdot deg^{-1}$)	-13.2	-18.5	-23.8	-29.5
13. $\partial \Delta S / \partial P$ ($J \cdot mole^{-1} \cdot deg^{-1} \cdot bar^{-1}$)	-13.8×10^{-3}	-12.9×10^{-3}	-12.1×10^{-3}	-11.2×10^{-3}

of ΔG , ΔH and ΔS with pressure elevation. And hence there is an increase in the stability of complex at higher pressure which is paralleled by the increase in the physical restraints imposed upon the complex components.

Pressure, Temperature Shift and Oscillator Strength. The CT-bands are characteristically broad and thus the ν_{max} were estimated by taking the mean of the maxima of all the measurement on a particular 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 $\epsilon_{max} \Delta \nu_{1/2}$, using the equation²²

$$f = 4.319 \times 10^{-9} \epsilon_{max} \Delta \nu_{1/2} \\ = 10.36 \times 10^{-9} \epsilon_{max} (\nu_{max} - \nu_{1/2L}) \quad (5)$$

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 shift of absorption maxima and the values of oscillator strength observed at various pressures and temperatures are shown in Table 4. Ewald^{10,11}, Kwun^{12,13} and Scholz¹⁴ have reported similar shifts.

The dependence of oscillator strength on pressure for various temperatures is generally

 Table 4. Pressure and temperature shift of $C_6H_2(CH_3)_4 \cdot I_2$ CT-absorption maxima and oscillator strength of $C_6H_2(CH_3)_4 \cdot I_2$ at various pressures and temperatures

Temp. (°C)	Pressure (bar)	$(\nu_1 - \nu_p)_{max}$ (cm^{-1})	$(\nu_r - \nu_{25})_{max}$ (cm^{-1})	$f \times 10^2$
25	1	0		21.1
	200	113		21.4
	600	233		21.6
	1200	335		21.6
	1600	433		21.8
40	1	0	74.4	23.0
	200	104	103	23.4
	600	186	112	23.6
	1200	277	120	23.6
	1600	320	138	23.8
60	1	0	170	25.2
	200	68.6	188	25.8
	600	123	206	26.2
	1200	218	222	26.2
	1600	294	249	26.7

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 oscillator strength shows a linear increase with pressure up to 1600 bars in Fig. 5. $\partial f / \partial P$ is 3.96, 5.47, 8.35 $\times 10^{-6} bar^{-1}$ at 25, 40 and 60°C respectively.

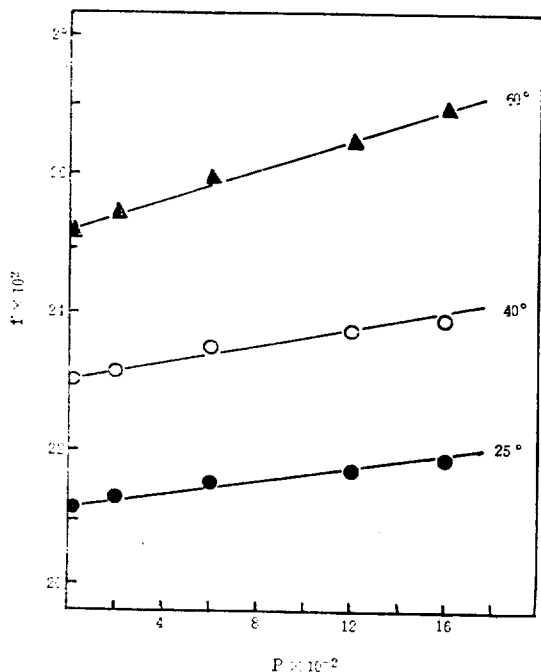


Fig. 5 Pressure dependence of oscillator strength for the durene-iodine system in *n*-hexane at several temperatures

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 4). Further results are shown that the blue shift is increasing with the temperature under a given pressure. Also, the red shift increases with pressure at a given temperature.

The durene-iodine system in *n*-hexane solution can be compared with the toluene-iodine, the xylene-iodine and the mesitylene-iodine system in the previous studies^{12,13,21}, at temperatures of 25, 40 and 60°C under pressures of 1, 200, 600, 1200 and 1600 bars. The main properties are similar in all systems observed. The formation constant of CT-complex is increasing, however, in the order, toluene < xylene < durene < mesitylene. This can be explained to be caused that the electron density

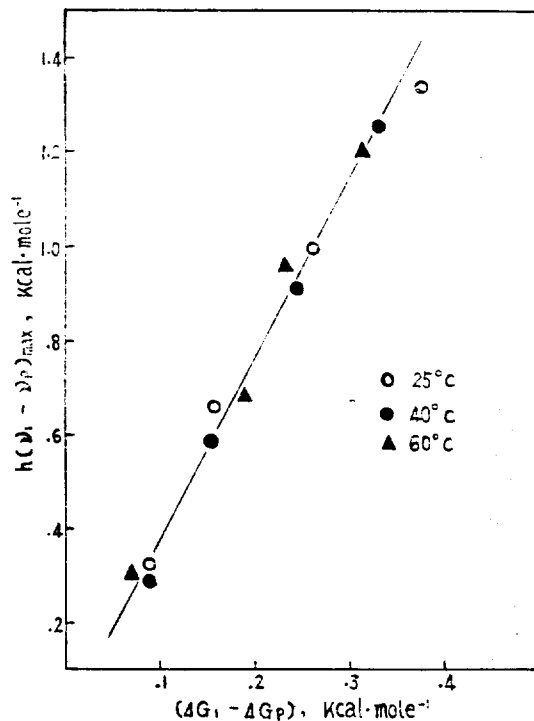


Fig. 6. Correlation between the difference of electron transfer energies $h\nu_{\max}$ and the difference of free energies ΔG of the complex formation for pressure variation in the durene-iodine system

increase with the number of methyl radicals around the benzene ring, as suggested by Andrews and Keefer¹⁸ for the aromatic compounds, but steric hindrance effect in the case of durene is larger than that of mesitylene. A similarity exists in the temperature dependence of the volume change and in the pressure dependence of the oscillator strength.

For the toluene-iodine, the xylene-iodine and the mesitylene-iodine system, $\partial\Delta V/\partial T$ and $\partial f/\partial P$ are both positive, also it is positive for the durene-iodine system. Attempts are described in the literature for correlating the electron transfer energy $h\nu_{\max}$ to ΔG values of complex formation. Briegleb²³ reported an almost linear relationship between the quantities for the series of successively methylated benzene molecules.

The correlation between $h\nu_{\max}$ and ΔG for the

durene-iodine system is shown in Fig. 6. The red shift of the band maxima at different pressures (Table 4) are plotted as a function of the respective change of ΔG (Table 2). For the pressure variation a straight line results. The slope of this line is 3.3 (precise to ± 0.5) for each temperature. Thus for durene-iodine the following relationship holds

$$\partial(h\nu_{\max})/\partial P = 3.3 \partial\Delta G/\partial P \quad (6)$$

For the temperature variation a linear relationship for $\nu_i - \nu_{25}$ as a function of $\Delta G_i - \Delta G_{25}$ is less obvious.

An interpretation of the expressions depends on the model used for the charge transfer complexes. If one supposes as in reference¹¹ that the variation at the depth of potential in the ground state is described by ΔG , then the numerical factors in the equation should give information about the shift or 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 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 Abidi²⁴. 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 state 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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