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고압, 고온 유체의 물성연구. 메시틸렌과 요오드 사이의 전하이동착물에 대한 압력과 온도의 영향

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

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요 약. 메시틸렌과 요오드 사이의 전하이동착물의 안정도에 미치는 압력과 온도의 영향을 *n*-헥산용액에서 자외선 분광광도법으로 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 변화양을 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 mesitylene-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 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 theory[1]. Accordng 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 constank 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 Ham[3], Gott and Maisch[4] and for solid complex 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 complexes. 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 Scholz[14] has investigated charge transfer complexes in a wide temperature and density range and has 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 complexes[5~7]. 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 mesitylene 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 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 Merck Co. iodine (superpure grade) and *n*-hexane (uvasol grade) were used without purification.

Mesitylene(reagent grade, Kanto, Japan) was distilled through a 100 cm column packed with glass helices. The boiling point observed was 164.7 °C and the index of refraction $n_D^{20}=1.4994$.

Preparation of Stock Solution. The solutions of iodine and mesitylene in *n*-hexane were prepared by the procedures described previously[13].

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 mesitylene was 1.44, 2.30, 3.45, 4.61×10^{-1}mole·l^{-1} and that of iodine was 1.52, 2.32, 3.19×10^{-4}mole·l^{-1}. These were varied at least three fold for any one system. Both concentrations were adjusted so as to keep the abosorbancy within suitable limits.

Apparatus. The spectra were measred on a Bausch & Lomb spectronic 505 spectrophotometer modified to accommodate a high pressure cell. The apparatus has already been described in detail[12].

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 mesitylene 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 mesitylene 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 occured. The blank in this case was the *n*-hexane solution of mesitylene 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 ±1°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 mesitylene-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 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 mesitylene 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 mesitylene 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 mesitylene 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[16].

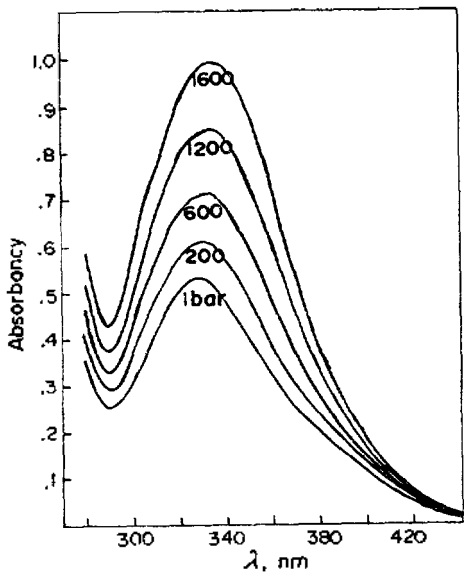

Fig. 1. Absorption spectrum for the system of mesitylene (0.345 *M*) with iodine (2.32×10^{-4} *M*) complex in *n*-hexane at various pressures (25°C).

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

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 to the equilibrium constant K and the absorption coefficient ε, *i.e.*

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

Which is now in the form, $y=mx+b$. Where $[A]_0$ and $[D]_0$ are the initial molar concentration of accoptor 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 1.10cm. 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 rations ρ/ρ_0 for the solutions were derived from the results of Kuss and Taslimi[17]. 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.

The Mesitylene-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 mesitylene 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 mesitylene and iodine is being correct as it was discussed previously[16].

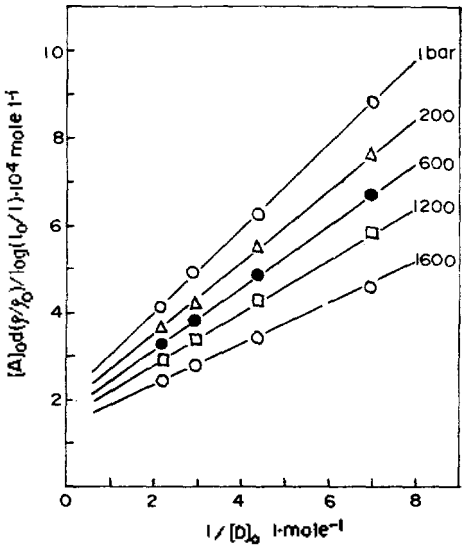

Fig. 2. Plot of $[A]_0 \cdot d \cdot (\rho/\rho_0)/\log(I_0/I))$ versus $1/[D]_0$ of the mesitylene-iodine system at various pressures (25 °C).

The results of the present study at 25 °C and 1 atm are now compared with those reported in the literture. Keefer and Andrews[18] reported an epuilibrium constant value of 0.82 for the complex, mesitylene-iodine in carbon tetrachloride. And Ketelaar[19] reported a value of 5.37 (as K_x) for complexes in *n*-hexane The results of this study are similar to those of previous studies.

Equilibrium Constants, Absorption Coefficients and Volume Changes. 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 mesitylene-iodine complex at higher pressure.

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 Maisch[4]. 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. They are given by the slopes of lines such

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

as shown in *Fig.* 3. The volume changes associated with formation of the CT-complex and their absorption maxima are given in *Table* 1. In studing the influence of pressure and temperature on λ_{max}, it was found that a red-shift or a blue-shift takes place depending

Table 1. Absorption maxima, equilibrium constants, absorption coefficients and volume change of $C_6H_3(CH_3)_3 \cdot I_2$ CT-complexes.

Temperature (°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	328.4	1.93	5183	8.48
	200	330.0	2.17	5501	
	600	331.2	2.34	5765	
	1200	332.4	2.87	5987	
	1600	333.4	3.47	6228	
40	1	327.5	1.68	5651	6.94
	200	328.8	1.89	5964	
	600	329.7	1.92	6135	
	1200	330.8	2.28	6257	
	1600	331.7	2.69	6433	
60	1	326.0	1.49	5945	6.15
	200	327.2	1.59	6160	
	600	328.2	1.64	6457	
	1200	329.0	1.77	6682	
	1600	329.7	2.07	6855	

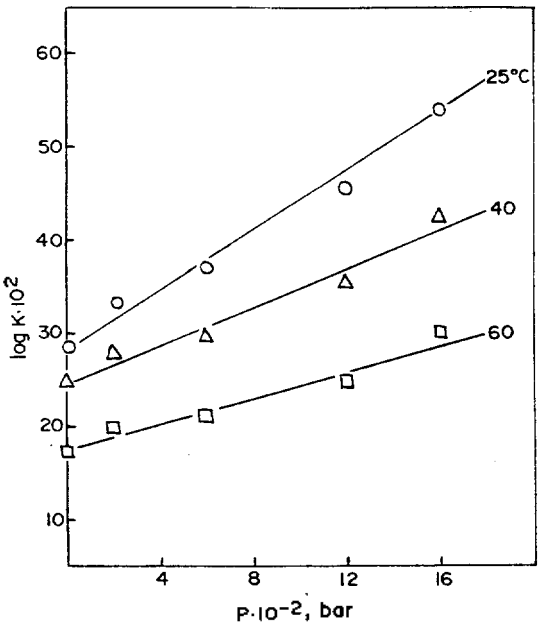

Fig. 3. Pressure denpendence of log K for the mesitylene-iodine system at several temperatures.

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 sum of the van der Waals raadii and the charge the 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.

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 ΔG and entropy of that ΔS was calculated. 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 Ketelaar[19]. Although the accuracy of the data is not great, they show a

Table 2. Thermodynamic functions[a] of $C_6H_3(CH_3)_3 \cdot I_2$ 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		390	3.64		458	4.33		504	5.70		624	6.97		737	7.23
40	1475	323	3.58	1749	401	4.31	2203	404	5.75	2701	513	6.96	2891	616	7.27
60		265	3.63		307	4.33		329	5.63		379	6.97		483	7.23
		av.	3.62		av.	4.32		av.	5.69		av.	6.97		av.	7.42

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

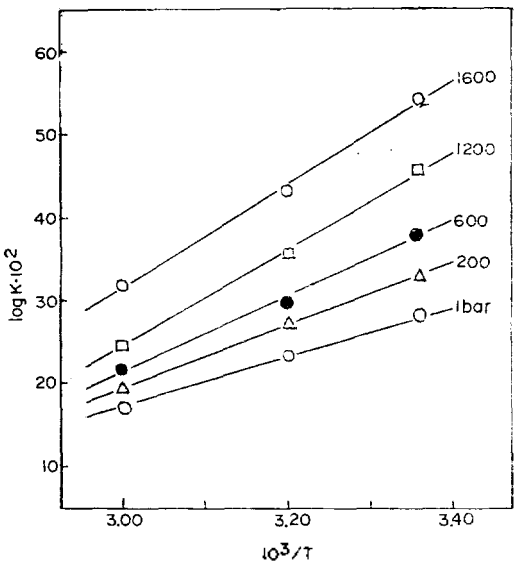

Fig. 4. Temperature dependence of log K for the mesitylene-iodine system at various pressures.

definite increase of ΔH and ΔS with pressure. There is an increase in oscillator strength at higher pressure which is paralleled by the increase in ε_{max}. And hence there is no increase in bandwidths.

Pressure, Temperature Shift and Oscillator Strength. The shift of absorption maxima and the values of oscillator strength observed at various pressures and temperatures are shown in *Table* 3. Ewald[10,11], Kwun[12,13] and Scholz[14] have reported similar shifts.

The dependence of oscillator strength on pressure for various temperatures is generally not

Table 3. Pressure and temperature shift[a] of $C_6H_3(CH_3)_3 \cdot I_2$ CT-absorption maxima and oscillator strength of $C_6H_3(CH_3)_3 \cdot I_2$ CT-bands.

Temp (°C)	Pressure (bar)	$\Delta\nu$ (cm^{-1})	$\Delta\nu'$ (cm^{-1})	$f \cdot 10^2$
25	1	0		13.8
	200	148		13.8
	600	238		14.1
	1200	367		14.2
	1600	457		14.3
40	1	0	83.7	15.2
	200	121	110	15.4
	600	204	137	15.5
	1200	305	146	15.4
	1600	387	154	15.8
60	1	0	224	16.5
	200	76.5	259	16.6
	600	166	276	16.9
	1200	280	311	17.2
	1600	344	337	17.3

[a] Red shift ($\Delta\nu$) with increasing pressure $(\nu_1 - \nu_p)_{max}$ blue shift ($\Delta\nu'$) with increasing temperature $(\nu_t - \nu_{25})_{max}$

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 measurement on a particular system. The oscillator strength f of the CT-absorption could be evaluated directly by graphical method on a wave

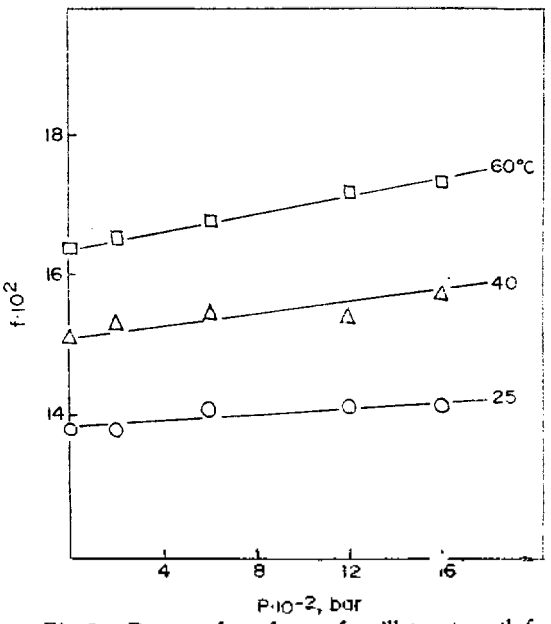

Fig 5. Pressure dependence of oscillator strength for the mesitylene-iodine system at several temperatures.

number scale. Its value was estimated from ε_{max} $\Delta\nu_{1/2}$, using the equation[20]

$$f = 4.319\times10^{-9}\ \varepsilon_{max}\Delta\nu_{1/2} = 10.36\times10^{-9}\ \varepsilon_{max}(\nu_{max}-\nu_{1/2L}) \quad (4)$$

Where $\Delta\nu_{1/2}$ is the bandwidth at $\varepsilon = \varepsilon_{max}/2$ 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*. 5. $\partial f/\partial P$ is 3.50, 3.75, 5.26×10^{-6}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 indicated a low energy for complex formation (see *Table* 3). 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 mesitylene-iodine system in *n*-hexane solution can be compared with the toluene-iodine and the xylene-iodine system in *n*-hexane investigated by Kwun[12,13] at temperatures of 25, 40 and 60°C and pressures of 1, 200, 600, 1200 and 1600 bars. The main properties are similar in all systems observed. Complex formation is markedly strongest, however, in the mesitylene system. This can be explained to be cause that the electron density is greatest by the positive inductive effect in mesitylene, as suggested by Andrews and Keefer[18] for the aromatic compounds. A similarity exists in the temperature dependence of the volume change and in the pressure dependence of the oscillator strength.

For the toluene-iodine and the xylene-iodine system, $\partial\Delta V/\partial T$ and $\partial f/\partial P$ are both positive, also it is positive for the mesitylene-iodine system. Attempts are described in the literature for correlating the electron transfer energy $h\nu_{max}$ to ΔG values of complex formation. Briegleb [21] 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 mesitylene-iodine system is shown in *Fig*. 6. The red shift of the band maximum at different pressures (*Table* 3) 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 4.4 (precise to $\pm$0.2) for each temperature. Thus for mesitylene-iodine the following relationship holds

$$\partial(h\nu_{max})/\partial P = 4.4\partial\Delta G/\partial P \quad (5)$$

For the temperature varition a linear relationship for $\nu_t-\nu_{25}$ as a function of $\Delta G_t-\Delta G_{25}$ is less obvious.

An interpretation of the expressions depends on the model used for the charge transfer complexes. If one supposes as in reference that the variation at the depth of potential in the ground state is described by ΔG, then the numerical fac-

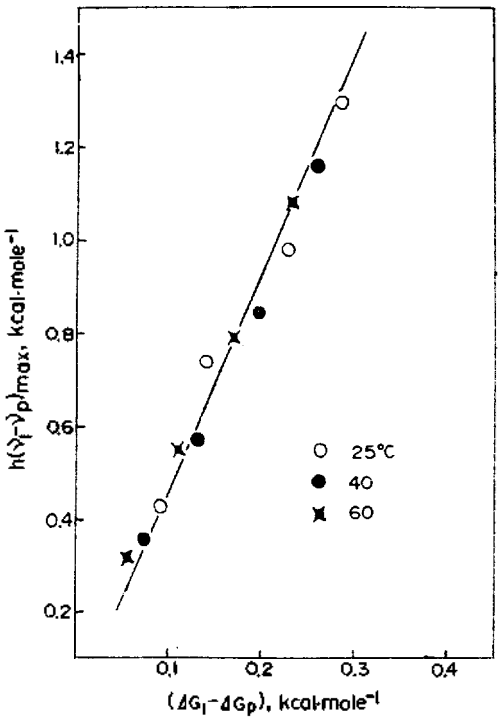

Fig. 6. Correlation between the differences of electron transfer energies $h\nu_{max}$ and differences of free energy ΔG of complex formation for pressure variation in the mesitylene–iodine system.

tors 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 bule 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[22].

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