

The Study on the Physicochemical Properties of Fluid under High Pressure (I). Effects of Pressure and Temperature on the Pentamethyl Benzene–Iodine Charge Transfer Complex in *n*-Hexane

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The stabilities of the charge transfer complexes of pentamethyl benzene with iodine in *n*-hexane have been investigated by UV-spectrophotometric measurements at 25, 40 and 60°C up to 1600 bars. The equilibrium constant of the complex formation was increased with pressure while being decreased with temperature raising. Changes of volume, enthalpy, free energy and entropy for the formation of the complexes were obtained from the equilibrium constants. The red-shift at higher pressure, the blue-shift at higher temperature, and the relation between pressure and oscillator strength have been discussed by means of thermodynamic functions. In comparison with the results in the previous studies, the absolute values of ΔV at each temperature were increased with the number of methyl groups of polymethyl benzene. However, it can be seen that both ΔH and ΔS show extreme behaviors in durene near atmospheric pressure but they are negatively increased with the number of methyl groups near 1600 bar. This order of the thermodynamic parameters may be a measure of the relative basicities of polymethyl benzenes toward iodine under each pressure, and these phenomena are explained in terms of a positive inductive effect and a steric hindrance effect of the polymethyl benzene molecule.

Introduction

In the previous studies¹⁻³ we have measured an effect of increased hydrostatic pressure on the formation constant of electron donor-acceptor complexes formed between various methylated benzenes and iodine in solution, and concluded that a large part of the effect could be explained by changes in the solvation of the donor, acceptor and complex with pressure change.

The effect of pressure on solid charge transfer complexes has been investigated by Drickamer and co-workers^{4,5}. Offen⁶ has found that the charge transfer complex formed between anthracene and *s*-trinitrobenzene absorbs a longer wave UV light (red-shift) with pressure elevation. Our early investigations of this series of the charge transfer complexes having iodine in common indicated that the stabilities of the charge transfer complexes increase in the order of benzene < toluene < xylene < durene < mesitylene. Present studies have dealt with the charge transfer complex formed between pentamethyl benzene and iodine in *n*-hexane.

Increase of pressure can affect the solution spectrum of a given charge transfer complex by changing the charge transfer energy, the oscillator strength of the charge transfer transition and the equilibrium constant of complex formation. As a rule, increased pressure causes a red-shift of the absorption in solution as in the case of solid complexes.⁴⁻⁶ Exceptional blue-shift have been observed for the same complexes in liquid and in solid solutions.^{7,8}

For the pentamethyl benzene-iodine system in *n*-hexane, UV absorption spectra were obtained over a range of pressure. The most marked change with pressure was the optical density in this system. To ascribe all of this to an increase in the transition moment predicted by Mulliken would, however, neglect the effect of pressure on the association equilibrium,



between the complex and its component molecules. A complete

analysis of the optical density observed over a range of donor and acceptor concentrations will allow one to evaluate two distinct pressure effects on the equilibrium constant, K and on the absorption coefficient, ϵ in liquid solutions. The effect on K can be due to the volume of the complex being smaller than that of its components. On the other hand, Offen and Kadhim⁶, using a solid polymer as solvent for the complexes, have considered that all the increase in optical density were due to increase in oscillator strength under those conditions.

In the present work, it was possible to evaluate K , ϵ , ΔH , ΔG and ΔS from the absorption spectra measured over a range of concentrations and at several temperatures under various pressures. The volume change ΔV which accompanies the formation of one mole of complex from its components was found from the change of K with pressure. The red-shift observed at higher pressure, the blue-shift at 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 differences of free energies, ΔG of the complex formation for the pressure variation was also discussed. The thermodynamic parameters evaluated were compared with the results in the previous studies^{1-3, 9,10} and its result was discussed in terms of the positive inductive effect and the steric hindrance effect of the polymethyl benzene molecule.

Experimental

Iodine (superpure grade, Merck, Germany) and *n*-hexane (uvasol grade, Merck, Germany) were used without further purification. Pentamethyl benzene (G. R. grade, Tokyo Kasei, Japan) was recrystallized twice from methanol and its physical properties were compared with those which appeared in the literature. The solutions of pentamethyl benzene and iodine in *n*-hexane were prepared by the general procedures. The concentrations of pentamethyl benzene were 1.53×10^{-1} , 2.23×10^{-1} , 3.37×10^{-1} and 4.38×10^{-1} mole/l⁻¹, and those of iodine were

1.36×10^{-4} , 2.21×10^{-4} and 3.06×10^{-4} mole- l^{-1} . Both concentrations were adjusted so as to keep the absorbancy within suitable limits.

The spectroscopic measurements were made as described in the previous papers¹⁻³ and high pressure optical cells were maintained at the desired temperatures (25, 40 and 60°C) by a thermostat within $\pm 0.1^\circ\text{C}$ up to 1600 bars. The absorbancies of the mixed solutions at the complex absorption maxima were usually determined in the neighborhood of 355 nm.

In order to obtain the equilibrium constant K and the absorption coefficient ϵ of equation (1), the method of Benesi and Hildebrand¹¹ has been used together with an additional factor to allow for the change of density due to the pressure and temperature variation, *i.e.*

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

in which $[A]_0$ and $[D]_0$ are the initial molar concentrations of acceptor and donor respectively, $\log(I_0/I)$ is absorbancy, A at the absorption maxima, λ_{\max} , d is the optical path length of which length was always 1.5 cm in this experiment. ρ_0 and ρ are densities of the 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 Taslimi¹². The charge transfer bands were characteristically broad and the values of λ_{\max} were estimated by taking the mean of the absorption maxima of all the measurements on a particular system. The accuracy was usually greater at higher pressure due to the greater intensity of the bands.

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 $1/[D]_0$, of which one example at 25°C is presented in Figure 1. The plots show good linearities between the two quan-

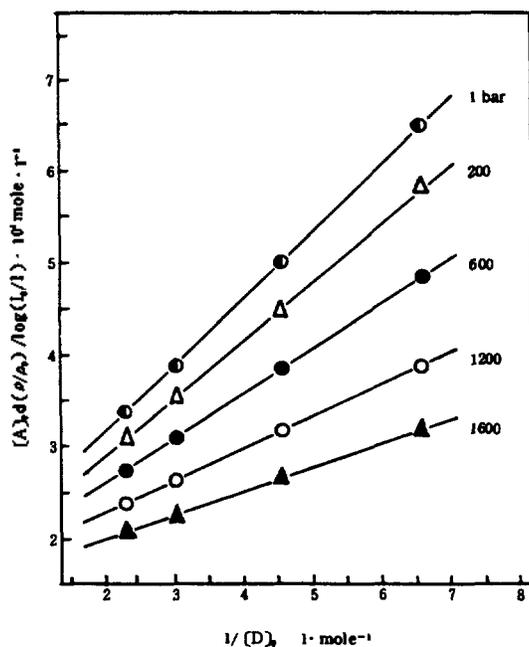


Figure 1. Plot of $[A]_0 \cdot d \cdot (\rho / \rho_0) / \log(I_0/I)$ versus $1/[D]_0$ of the pentamethyl benzene - iodine system in *n*-hexane at 25°C and at various pressures.

ties in all the systems examined. From these plots it was found that one-to-one molecular complexes are formed in solutions according to the previous work¹³. The values of K and ϵ were calculated from the slopes and the intercepts of the straight lines. The least square method was used to determine the slopes and the intercepts.

Results and Discussion

Pentamethyl Benzene - Iodine CT - Complex Formation. 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 increase with pressure at the constant temperature. On the other hand, K decreases with temperature raising at the constant pressure, but ϵ has a opposite feature. It has been found that the formation of the pentamethyl benzene-iodine CT-complex was predominant at higher pressure. The volume change ΔV associated with the formation of the CT-complex from its components can be calculated from the equilibrium constant by the following equation.

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

They are given by the slopes of lines shown in Figure 2. The volume changes and absorption maxima of the CT-complex formation are given in Table 1. The measured values of ΔV represent the change in volume when the complex is formed from its components. Therefore, the negative sign of ΔV indicates that the molar volume of the complex is smaller than sum of the molar volumes of its components. Thus, the complexes are looser at higher temperature since the volume change is found to decrease with temperature raising as shown in Table 1.

Thermodynamic Functions. The changes of standard free energy, enthalpy and entropy due to the CT-complex formation were calculated from the equilibrium constants. Since good

TABLE 1: Absorption Maxima, Equilibrium Constants, Absorption Coefficients and Volume Change of Pentamethyl Benzene-Iodine CT-complexes

Temperature (°C)	Pressure (bar)	λ_{\max} (nm)	K ($l \cdot \text{mole}^{-1}$)	ϵ ($l \cdot \text{mole}^{-1} \text{cm}^{-1}$)	$-\Delta V$ ($\text{cm}^3 \cdot \text{mole}^{-1}$)
25	1	352.8	2.38	5780	12.9
	200	354.1	2.63	5952	
	600	355.5	3.29	6135	
	1200	356.8	4.54	6369	
	1600	358.0	5.70	6667	
40	1	351.7	2.00	6098	11.4
	200	352.9	2.22	6250	
	600	353.6	2.70	6494	
	1200	354.7	3.61	6579	
	1600	355.5	4.36	6803	
60	1	350.0	1.61	6410	9.68
	200	350.8	1.77	6667	
	600	351.3	2.05	6803	
	1200	352.4	2.44	6944	
	1600	353.3	3.01	7092	

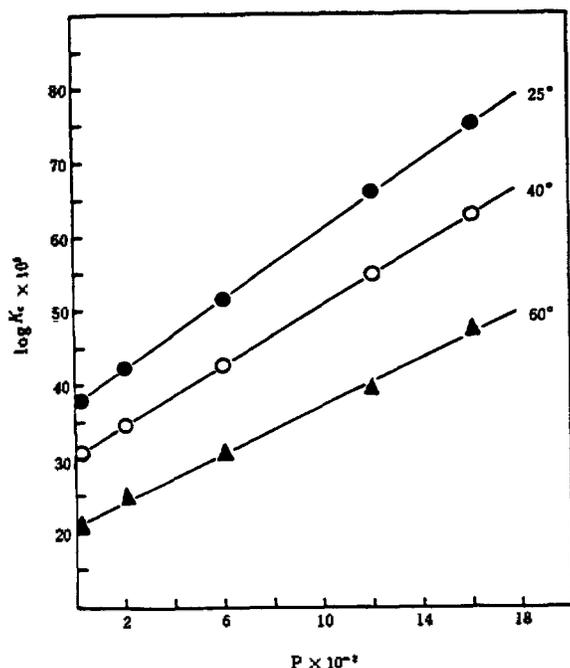


Figure 2. Pressure dependence of $\log K$ for the pentamethyl benzene - iodine charge transfer complex in *n*-hexane at several temperatures.

linearity was obtained from the plot of $\log K$ versus $1/T$ such as Figure 3, standard enthalpy change ΔH for the complex formation was calculated from the slope. Then for each temperature, standard free energy change ΔG and standard entropy change ΔS were calculated (Table 2). ΔH and ΔS do not vary with temperature, accordingly ΔG is linear function of temperature in the range considered. If the plot of $\ln K$ versus P is the quadratic fit with very small curvature at constant temperature as in the previous study³, it could be written as

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

which means that ΔG , ΔH and ΔS are assumed to be quadratic functions of pressure. Table 3 shows the 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, $\partial \Delta H / \partial P$ has to be equal to $\Delta V - T(\partial \Delta V / \partial T)$, line 8 in Table 3 equals to line 9, and line 11 equals to line 12. It can be seen that the thermodynamic properties in this work gratify, in a sense, Maxwell's relationship in the liquid solution. These relations have agreement with that in the previous work³. Although the accuracy of the data in Table 3 is not great, they show a definite decrease of ΔH , ΔG and ΔS with pressure. And

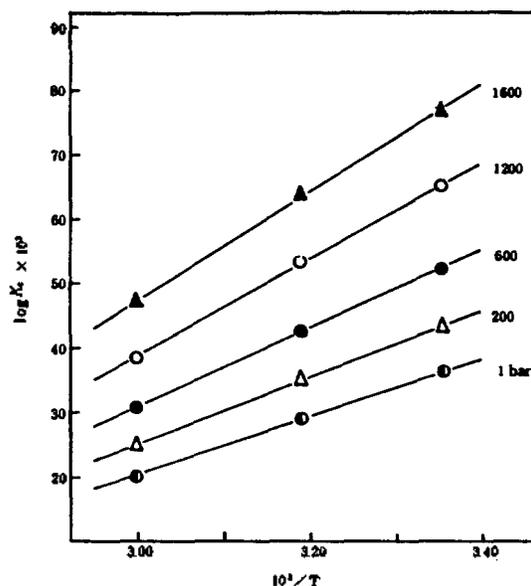


Figure 3. Temperature dependence of $\log K$ for the pentamethyl benzene - iodine charge transfer complex in *n*-hexane at various pressures

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 shifts of absorption maxima and the values of oscillator strength observed at various pressures and temperatures are summarized in Table 4. It can be seen that the red-shift increases with pressure but the blue-shift does not significantly with pressure in Table 4. The pressure dependence of red-shift at several temperatures is shown in Figure 4. The dependence of red-shift on pressure for a given temperature would indicate a small transition energy for the complex formation. Thus, it is found that the excited state, with its strong component of coulombic interaction, should have a much deeper potential energy curve and a smaller equilibrium separation at higher pressure. The oscillator strength 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 following equation.¹⁴

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

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 charge transfer absorption band. The oscillator strength shows a linear increase with pressure up to 1600 bar as shown in Figure 5. Values

TABLE 2: Thermodynamic Functions of Pentamethyl Benzene - Iodine 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		514	5.69	573	5.90		706	6.62		897	7.57		1031	8.67	
40	2209	431	5.68	2341	496	5.89	2677	618	6.58	3155	799	7.52	3616	916	8.62
60		315	5.69	378	5.89		475	6.62		591	7.59		730	8.66	
		av. 5.69		av. 5.89			av. 6.61			av. 7.56			av. 8.65		

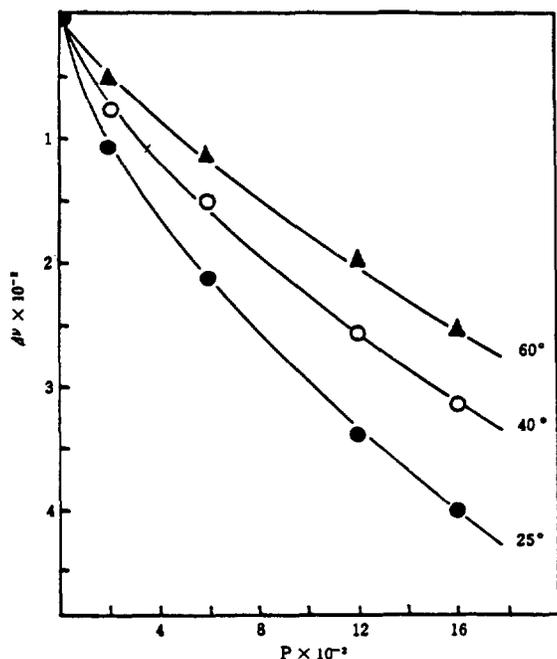
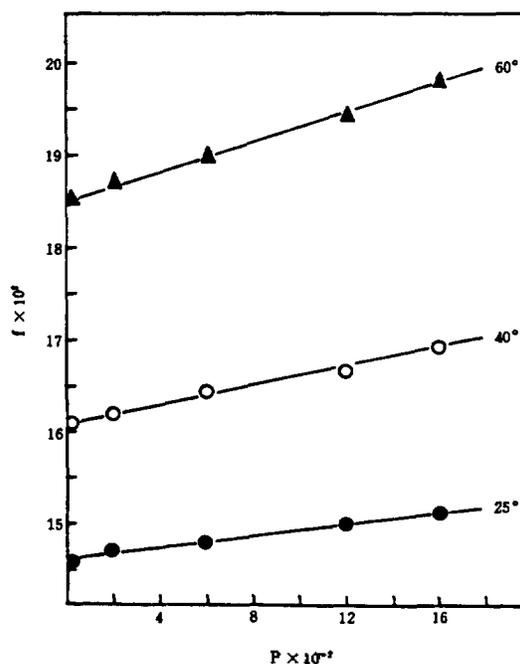
ΔH , ΔG in cal·mole⁻¹; ΔS in cal·mole⁻¹·deg⁻¹.

TABLE 3: Thermodynamic Properties for the Formation of Pentamethyl Benzene - iodine charge Transfer Complex in *n*-hexane at 25 °C and at Various Pressures

1. P (bar)	1	500	1000	1500
2. ΔV ($\text{cm}^3 \cdot \text{mole}^{-1}$)	-12.9	-12.1	-11.2	-10.4
3. $\partial \Delta V / \partial T$ ($\text{cm}^3 \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$)	9.07×10^{-2}	8.62×10^{-2}	7.69×10^{-2}	7.06×10^{-2}
4. ΔH ($\text{kJ} \cdot \text{mole}^{-1}$)	-9.29	-11.2	-13.0	-14.8
5. $\partial \Delta H / \partial P$ ($10^{-1} \text{J} \cdot \text{mole}^{-1} \cdot \text{bar}^{-1}$)	-39.5	-37.6	-35.6	-33.7
6. $\Delta V - T(\partial \Delta V / \partial T)$ ($\text{cm}^3 \cdot \text{mole}^{-1}$)	-40.0	-37.7	-34.2	-31.6
7. $\Delta U = \Delta H - P\Delta V$ ($\text{kJ} \cdot \text{mole}^{-1}$)	-9.29	-10.5	-11.8	-13.2
8. $\partial \Delta U / \partial P$ ($10^{-1} \text{J} \cdot \text{mole}^{-1} \cdot \text{bar}^{-1}$)	-27.9	-26.6	-25.0	-23.7
9. $-T(\partial \Delta V / \partial T) - P(\partial \Delta V / \partial P)$ ($\text{cm}^3 \cdot \text{mole}^{-1}$)	-27.1	-26.5	-24.6	-23.7
10. ΔG ($\text{kJ} \cdot \text{mole}^{-1}$)	-2.13	-2.85	-3.64	-4.18
11. ΔS ($\text{J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$)	-23.8	-26.6	-30.3	-35.0
12. $-\partial \Delta S / \partial P$ ($\text{J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1} \cdot \text{bar}^{-1}$)	-22.7	-26.0	-32.9	-37.4
13. $\partial \Delta S / \partial P$ ($\text{J} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1} \cdot \text{bar}^{-1}$)	-4.64×10^{-3}	-2.76×10^{-3}	-0.88×10^{-3}	-0.54×10^{-3}

TABLE 4: Pressure and Temperature Shift of $\text{C}_6\text{H}(\text{CH}_3)_5\text{I}_2$ CT-absorption Maxima and Oscillator Strength of $\text{C}_6\text{H}(\text{CH}_3)_5\text{I}_2$ CT-Bands at Various Pressures and Temperatures

Temperature (°C)	Pressure (bar)	$(\nu_1 - \nu_2)_{\text{max}}$ (cm^{-1})	$(\nu_1 - \nu_2)_{\text{max}}$ (cm^{-1})	$f \times 10^4$
25	1	0		14.6
	200	108		14.7
	600	216		14.8
	1200	318		15.0
	1600	412		15.1
40	1	0	88.6	16.1
	200	96.7	116	16.2
	600	152	151	16.5
	1200	240	166	16.7
	1600	304	196	16.9
60	1	0	226	18.5
	200	16.1	266	18.7
	600	105	337	19.0
	1200	194	350	19.4
	1600	266	372	19.8

**Figure 4.** Pressure shift of the pentamethyl benzene - iodine charge transfer complex absorption maxima in temperatures.**Figure 5.** Pressure dependence of oscillator strength for the pentamethyl benzene - iodine system in *n*-hexane at several temperatures.

of $\partial f / \partial P$ are 3.08×10^{-6} , 4.98×10^{-6} , $7.83 \times 10^{-6} \text{ bar}^{-1}$ at 25, 40 and 60 °C respectively. The dependence of the oscillator strength on pressure for a given temperature would indicate a repulsion effect between the complex components, thus, the oscillator strength increases with temperature at a given pressure and $\partial f / \partial P$ also increases with temperature raising. In order to see the correlation between $h\nu_{\text{max}}$ and ΔG for the pentamethyl benzene-iodine system, the red-shift of the band maximum at different pressures are plotted as a function of the respective change of ΔG in Figure 6. For the pressure variation the result indicates a reasonable linearity of which the slope is 1.6 for each temperature. Thus, for the pentamethyl benzene-iodine system the following relationship holds.

$$\partial (h\nu_{\text{max}}) / \partial P = 1.6 \partial (\Delta G) / \partial P \quad (6)$$

On the other hand, for the temperature variation a linear relationship for $(\nu_1 - \nu_2)_{\text{max}}$ as a function of $\Delta G_1 - \Delta G_{25}$ is less obvious. An interpretation of the expression depends on the model used for the charge transfer complexes. For instance, if one supposes

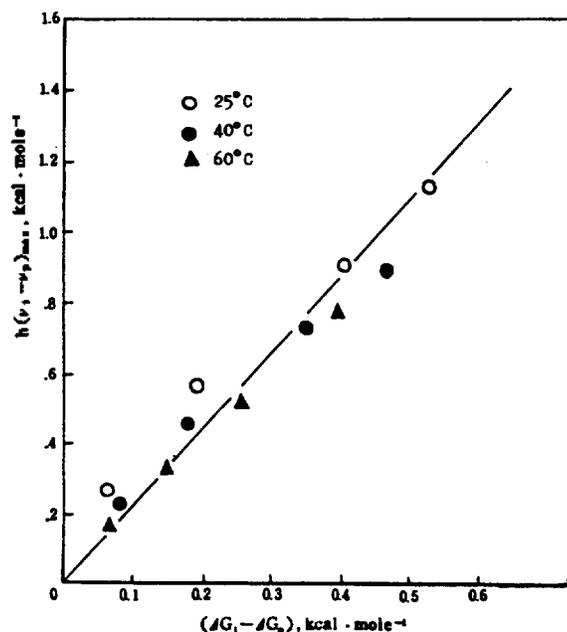


Figure 6. Correlation between the difference of electron transfer energies, $h\nu_{\max}$ and the difference of free energies, ΔG of the complex formation for pressure variation in the pentamethylbenzene-iodine system.

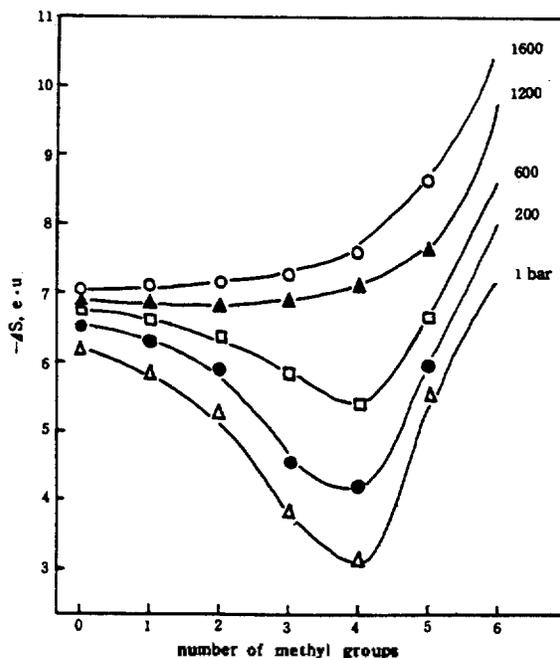


Figure 8. Variation of entropy change on the formation of polymethyl benzene-iodine charge transfer complexes in *n*-hexane at various pressures.

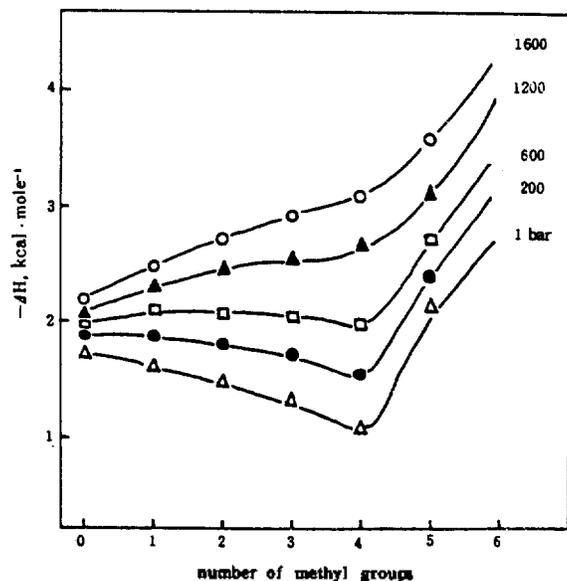


Figure 7. Variation of enthalpy change on the formation of polymethyl benzene-iodine charge transfer complexes in *n*-hexane at various pressures.

that the variation at the depth of potential in the ground state is described by ΔG , then the numerical factor in equation (6) should give an information about the shift or a deformation of the potential of the excited state.

Comparison of the Results for the Polymethyl Benzene-Iodine CT-Complex Formation. In the case of charge transfer complexes having one electron acceptor (iodine in this work) in common, the ability of the charge transfer increases as the number of methyl groups releasing electron increases in the electron donor (polymethyl benzene in this work), and is also affected by the steric hindrance effect of polymethyl benzene because it will be increased with the number of methyl groups on the benzene ring. In comparison of the plots of $\log K$ against

pressure for the various polymethyl benzene complexes^{1-3,9,10} with iodine, it is especially found that the change of $\log K$ on pressure in the case of durene will be larger than that in the case of mesitylene at high pressure because the steric hindrance effect becomes weakened with pressure elevation, while $\log K$ in the case of durene by the larger steric hindrance effect is smaller than that in the case of mesitylene near atmospheric pressure. Since the absolute value of the volume change increases with the number of methyl groups on the benzene ring^{1-3,9,10}, it can be seen that the values of ΔV may be a measure of the steric hindrance effect on the formation of the charge transfer complexes of polymethyl benzene with iodine. The variation of ΔH and ΔS with the number of methyl groups of polymethyl benzene are shown in Figure 7 and Figure 8 at various pressures respectively. From the results, it can be seen that both ΔH and ΔS have extremum behaviors in durene near atmospheric pressure but they are negatively increased with the number of methyl groups near 1600 bar. It indicates that the stabilities of the CT-complexes are affected by the positive inductive effect and by the steric hindrance effect since both of them increase with the number of methyl groups of polymethyl benzene. While the increase of steric hindrance effect with the number of methyl groups is larger than that of positive inductive effect from benzene to durene but it is opposite in the case of pentamethyl benzene near atmospheric pressure, therefore, the stability of the CT-complex is mainly affected by the positive inductive effect because the steric hindrance effect of polymethyl benzene is nearly destroyed by the strong external restraints at high pressure.

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Dipole Moment Derivatives and Infrared Intensities of SiH₄ and SiD₄

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The complete neglect of differential overlap (CNDO/2) approximate wavefunctions have been applied to select the preferred signs for the dipole moment derivatives of SiH₄ and SiD₄ in conjunction with the experimental alternatives. The apparent sign discrepancy from earlier report has been identified. The effective atomic charge for hydrogen was found to be $\chi_H/e = 0.229$, more than two times larger in comparison with the values of typical hydrocarbons like CH₄. The anomalously large effective hydrogen charge was interpreted based on a quantum mechanical model as well as the value of atom anisotropy relative to effective atomic charge.

Introduction

Of the many pioneers in molecular spectroscopy, Mulliken was possibly the first to emphasize the importance of infrared intensities¹. He recognized that understanding this kind of data is essential for solving the central problem of chemistry; that is, for establishing the relationship between the properties of a material and its structure. However, during most of the period following Mulliken's paper, only limited progress was made in interpreting infrared intensities. Based on his paper, it was taken as self-evident that an interpretive model of intensities must be founded upon the chemical bond concept. Recent efforts to resolve dipole moment derivatives into derivatives of chemical bond moments have resulted in sets of terms in which those describing the interactions between different bonds are of the same magnitudes as those defining the properties of one particular bond². Thus, unlike molecular energies, infrared intensities cannot be adequately reduced to a sum of terms that can be assigned to particular chemical bonds because of the importance of the interaction terms.

The problem of interpreting infrared intensities has improved dramatically within the last 10 years. That was because of the emergence of the concept of dipole moment derivatives as properties of the atoms in a molecule, rather than as properties of its chemical bonds. The atomic properties derived from

intensities are, then, contained in the so-called atomic polar tensors^{3,4} and effective atomic charges⁵. The atomic polar tensor for atom α in a molecule is defined as the conjugate (transposed) gradient of the molecular dipole moment vector, P , written in various notations as³

$$P_{\alpha}^{\alpha} = \nabla_{\alpha}^* P \equiv \begin{bmatrix} \partial P_x / \partial X_{\alpha} & \partial P_x / \partial Y_{\alpha} & \partial P_x / \partial Z_{\alpha} \\ \partial P_y / \partial X_{\alpha} & \partial P_y / \partial Y_{\alpha} & \partial P_y / \partial Z_{\alpha} \\ \partial P_z / \partial X_{\alpha} & \partial P_z / \partial Y_{\alpha} & \partial P_z / \partial Z_{\alpha} \end{bmatrix} \quad (1)$$

and the square of the effective atomic charge is defined as one-third of the sum of squares of the polar tensor components⁶, that is,

$$\chi_{\alpha}^2 \equiv (1/3) \nabla_{\alpha}^* P : \nabla_{\alpha} P. \quad (2)$$

This development has led to the discovery of surprising order in intensity data. The polar tensors for a few, but ubiquitous atoms like hydrogen and fluorine, seem to be transferable properties that are characteristic of these atoms to a good approximation⁷⁻¹². Furthermore, the analysis of the integrated intensities of a variety of hydrocarbons, fluorocarbons, and other materials with diverse structures revealed that the effective charges for the hydrogen and fluorine atoms in these systems fell within fairly narrow range of values^{5,13}.

Above observations encourage further testing of the atomic