

Our calculation gives good results as a whole except  $\nu_{A2}$  in translational mode. This means that there are still difficulties in a potential form for expressing the intrachain interactions.

In this paper, the asymmetric potential functions are introduced in order to reproduce the observed cell parameters and to give physically realistic surface of potential. The polar coordinates representation is used in order to describe the motions of molecules in molecular crystals. As many authors have suggested quantum effects must be included in potential functions.

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## The Study on the Physicochemical Properties of Fluid under High Pressure (II). The Effect of Pressure and Temperature on the Hexamethyl Benzene-Iodine Charge Transfer Complex in *n*-Hexane

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The effect of pressure and temperature on the stabilities of the charge transfer complexes of hexamethyl benzene with iodine in *n*-hexane has been investigated by UV-spectrophotometric measurements. In this experiment the absorption spectra of mixed solutions of hexamethyl benzene and iodine in *n*-hexane were measured at 25, 40 and 60°C under 1, 200, 600, 1200 and 1600 bar. 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 were discussed by means of thermodynamic functions. In comparison with the results in the previous studies, it can be seen that the pressure dependence of oscillator strength has a extremum behavior in durene as the variation of  $\Delta H$  or  $\Delta S$  with the number of methyl groups of polymethyl benzene near atmospheric pressure in the previous study. The shift or deformation of the potential in the ground state and in the excited state of the complexes formed between polymethyl benzene and iodine was considered from the correlation between the differences of the electron transfer energies and the differences of free energies of the complex formation for the pressure variation.

## Introduction

In part I<sup>1</sup>, we discussed the thermodynamic properties on the formation of electron donor-acceptor complexes formed between polymethyl benzene and iodine in *n*-hexane and came to conclusion that the stabilities of the charge transfer complexes having iodine in common could mainly be affected by the positive inductive effect because the steric hindrance effect of polymethyl benzene is nearly destroyed by the strong external

restraints at higher pressure.

This paper reports a study of iodine solutions under high pressures which was undertaken in an effort to learn more about molecular complexes in general and, specifically, more about the polymethyl benzene-iodine complexes. In the earlier works<sup>1-6</sup>, since the effect of pressure and temperature on the charge transfer absorption of the complexes of six polymethyl benzenes with iodine had been investigated in *n*-hexane, we have now extended our measurements to include electron donor-

acceptor complex formed between hexamethyl benzene and iodine in *n*-hexane and made a comparison on the formation of polymethyl benzene-iodine complexes as a whole.

In the case of electron donor-acceptor complex formed between polymethyl benzene and iodine, the energy levels of the ground state and the excited state should make a difference, that is, the effect of pressure on these complexes should increase if the number of methyl groups on the benzene ring increase. For complexes formed between polymethyl benzene of which the number of methyl groups is small and iodine, little change in potential is expected either during formation or on excitation and there should be only small solvent and pressure effects on the equilibrium constants and absorption maxima.

In the present work, we were able to evaluate  $K$ ,  $\epsilon$ ,  $\Delta H$ ,  $\Delta G$ ,  $\Delta S$ , etc. from the absorption spectra measured by the method in part I<sup>1</sup>. From the change of  $K$  with pressure we found the volume change  $\Delta V$  which accompanies the formation of one mole of complex from its components. The red-shift of charge transfer bands 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 at the same time, the energy levels of the ground state and the excited state of the complexes formed between polymethyl benzene and iodine are considered from the correlation between the differences of the electron transfer energies  $h\nu$  and the differences of free energies  $\Delta G$  of the complex formation for the pressure variation.

## Experimental

*n*-hexane (uvasol grade, Merck, Germany), hexamethyl benzene (ultra pure grade, Tokyo Kasei, Japan) and iodine (superpure grade, Merck, Germany) were used without further purification. The solutions of hexamethyl benzene and iodine in *n*-hexane were prepared by the general procedures. The concentrations of hexamethyl benzene which were adjusted so as to keep the absorbancies within suitable limits were 0.62, 0.92,

1.23,  $1.54 \times 10^{-1}$  mole  $\cdot$  l<sup>-1</sup> and those of iodine were 5.03, 6.02,  $7.07 \times 10^{-4}$  mole  $\cdot$  l<sup>-1</sup>. These were varied at least three fold for any one system.

The spectroscopic measurements were made as described in part I<sup>1</sup> 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 measured in the neighborhood of 370 nm.

In order to obtain the equilibrium constant  $K$  and the absorption coefficient  $\epsilon$  of the association equilibrium,  $A + D \rightleftharpoons C$ , between the complex and its components, the method of Benesi and Hildebrand<sup>7</sup> has been used together with an additional factor to allow for the change of density due to the pressure and temperature variation, *i.e.*

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

in which  $[A]_0$  and  $[D]_0$  are the initial molar concentrations of acceptor and donor respectively,  $\log(I_0/I)$  is absorbancy at the absorption maxima  $\lambda_{\text{max}}$ ,  $d$  is the optical path length of which value was always 1.1 cm in this experiment.  $\rho_0$  and  $\rho$  are densities of the solution at 25°C and 1 bar and at the experimental temperature and pressure respectively. The values of the ratios

for the solutions were derived from the results of Kuss and Taslimi<sup>8</sup>. After the values of absorbancies were measured experimentally, the quantities of  $[A]_0 \cdot d \cdot (\rho/\rho_0) / \log(I_0/I)$  evaluated were plotted against  $1/[D]_0$ . Since the plots indicated good linearities between two quantities in all the systems examined, it was found that one-to-one molecular complexes are formed in our solutions according to published work<sup>9</sup> as in part I. The least square method was used to determine the slopes and the intercepts of the straight lines.

## Results and Discussion

### The Hexamethyl Benzene-Iodine CT-Complex Formation:

The equilibrium constants in molar concentration units and absorption coefficients obtained at temperature 25, 40, 60°C and at pressure 1, 200, 600, 1200, 1600 bar on the CT-complex formation of hexamethyl benzene with iodine in *n*-hexane are summarized with the wave length of absorption maxima  $\lambda_{\text{max}}$  in Table 1. We have found an increase in  $K$  and  $\epsilon$  for the hexamethyl benzene-iodine CT-complex at high pressure as in part I<sup>1</sup>. It can be seen that there are small increase in oscillator strength at high pressure (Table 4), and thus it showed that the bandwidth decreases at high pressure. The quantitative results differ from those of Gott and Maisch<sup>10</sup>. In studying the influence of pressure and temperature on  $\lambda_{\text{max}}$ , it was found that a red-shift or a blue-shift takes place depending on whether pressure or temperature increase. Such behaviour was also reported by Ewald<sup>11,12</sup>.

The volume changes  $\Delta V$  associated with the formation of the CT-complexes from their components can be calculated from the slopes of the plots of  $\log K$  versus  $P$  such as shown in Figure 1 and are given in Table 1. The measured values of  $\Delta V$  represent the change in volume when the complex is formed from its components. Therefore, the negative sign of  $\Delta V$  indicate that

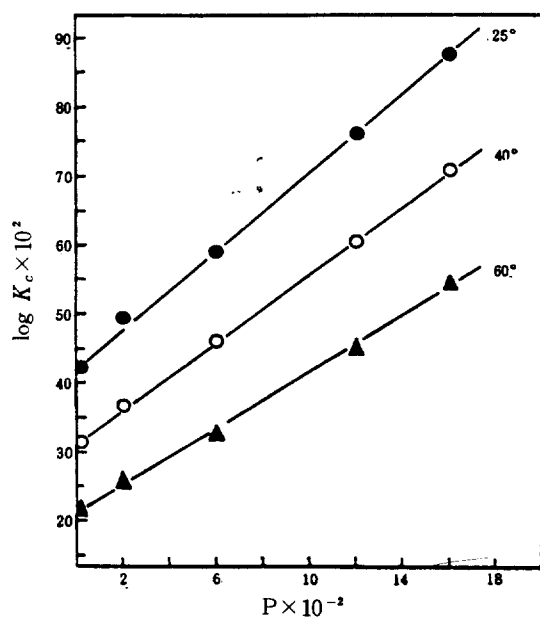


Figure 1. Pressure dependence of  $\log K$  for the hexamethyl benzene-iodine charge transfer complex in *n*-hexane at several temperatures.

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

Temperature (°C)	Pressure (bar)	$\lambda_{\max}$ (nm)	$K$ (l·mole <sup>-1</sup> )	$\epsilon$ (l·mole <sup>-1</sup> ·cm <sup>-1</sup> )	$-\Delta V$ (cm <sup>3</sup> ·mole <sup>-1</sup> )
25	1	370.6	2.67	2882	14.5
	200	371.8	3.26	2905	
	600	373.2	3.88	3067	
	1200	374.6	5.76	3145	
	1600	376.0	7.55	3205	
40	1	369.3	2.07	3058	12.3
	200	370.1	2.42	3106	
	600	370.9	2.92	3236	
	1200	372.1	4.07	3356	
	1600	373.0	5.17	3436	
60	1	367.5	1.64	3125	10.1
	200	368.1	1.84	3215	
	600	368.6	2.14	3344	
	1200	369.5	2.79	3425	
	1600	370.4	3.55	3509	

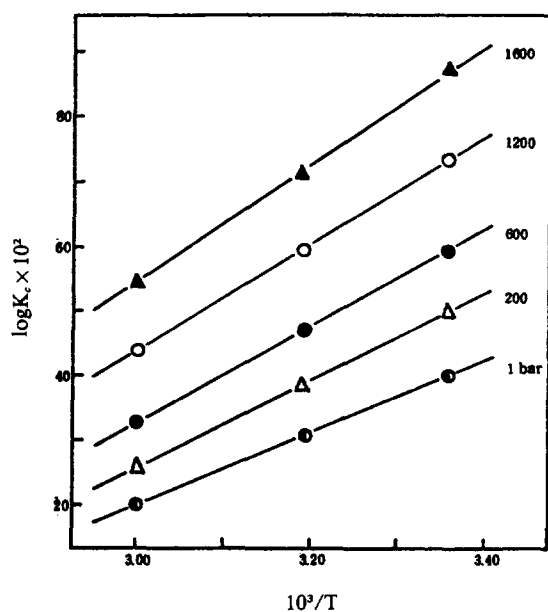


Figure 2. Temperature dependence of  $\log K$  for the hexamethyl benzene-iodine charge transfer complex in *n*-hexane at various pressures.

molar volume of the complex is smaller than sum of the molar volume of its components. Thus, the complexes are looser at higher temperature since the volume change is found to decrease with temperature raising in Table 1. 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 transfer bond length, and will not be reflected in the observed  $\Delta V$ .

The structures of some complexes are known in the solid state from the X-ray diffraction work of Wallwork<sup>13</sup>. 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<sup>14</sup> to obtain the van der Waals volumes of both the separate components and the complexes. The general agreement of  $\Delta V$  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  $\Delta V$  is connected with the magnitude of  $K$ , but exceptionally large values of  $\Delta V$  can occur where steric effects discussed in part I prevent the formation of complex.

Since good linearity was obtained from the plot of  $\log K$  versus  $1/T$  such as Figure 2, standard enthalpy changes  $\Delta H^\circ$  for the complex formation were calculated from the slopes of the lines under various pressures. Then standard free energy changes  $\Delta G^\circ$  and standard entropy changes  $\Delta S^\circ$  were calculated. The results obtained are summarized in Table 2. They show a definite increase in  $-\Delta H^\circ$ ,  $-\Delta G^\circ$  and  $-\Delta S^\circ$  with pressure. There is an increase in oscillator strength at high pressure which is paralleled by the increase in  $\epsilon_{\max}$ . If the plot of  $\log K$  versus  $P$  shown in Figure 1 is the quadratic fit with very small curvature at constant temperature as in part I<sup>1</sup>, it is sufficient to write

$$\log K = a + bP + cP^2, \quad (2)$$

which means that  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  are assumed to be quadratic functions of pressure. Table 3 shows smoothed values of thermodynamic properties at 1, 500, 1000 and 1500 bar derived from Table 2. Although the accuracy of the data in Table 3 is not great, it is found that the data obey in a sense Maxwell's relationship from a check of internal consistency as in the case of part I<sup>1</sup>.

**Pressure, Temperature Shift and Oscillator Strength:** The charge transfer bands are characteristically broad and thus  $\lambda_{\max}$  in Table 1 were estimated by taking the mean of the maxima of all the measurements on a particular system. The accuracy is usually greater at higher pressure and lower temperature due to the greater intensity of the band. The shifts of absorption maxima observed at various pressures and temperatures are given by the wave number in Table 4. The effects of pressure and temperature are clearly shown by the results. The red-shift of the charge transfer band due to increased interaction with the solvent occurs for every complexes. In Table 4, it is found that a magnitude of red-shift increases significantly with pressure but a blue-shift does a little with pressure.

The oscillator strength,  $f$ , of the charge transfer absorption

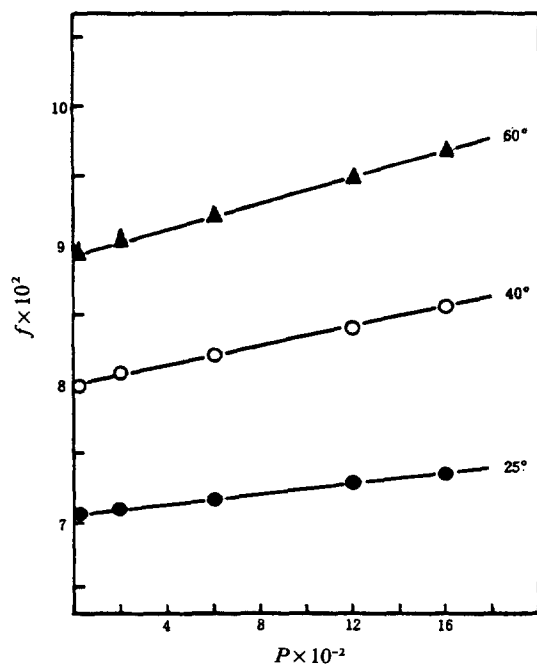
**TABLE 2: Thermodynamic Functions of Hexamethyl Benzene-Iodine CT-Complex at Various Pressures**

Temp. (°C)	Pressure (bar)														
	1			200			600			1200			1600		
	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$	$-\Delta H^\circ$	$-\Delta G^\circ$	$-\Delta S^\circ$
25	582	7.27		700	8.48		803	8.65		1037	10.24		1198	10.35	
40	2750	453	7.34	3227	550	8.55	3383	667	8.67	4089	874	10.27	4255	1022	10.32
60		327	7.27		404	8.47		501	8.65		679	10.24		839	10.35
		av.	7.29		av.	8.50		av.	8.66		av.	10.25		av.	10.34

$\Delta H^\circ$ ,  $\Delta G^\circ$  in cal·mole<sup>-1</sup>,  $\Delta S^\circ$  in cal·mole<sup>-1</sup>·deg<sup>-1</sup>

**TABLE 3: Thermodynamic Properties for the Formation of Hexamethyl Benzene-Iodine Charge Transfer Complex in *n*-Hexane at 25°C and at Various Pressures**

1. <i>P</i> (bar)	1	500	1000	1500
2. $\Delta V$ (cm <sup>3</sup> ·mole <sup>-1</sup> )	-14.5	-13.6	-12.7	-11.8
3. $\partial\Delta V/\partial T$ (cm <sup>3</sup> ·mole <sup>-1</sup> ·deg <sup>-1</sup> )	$12.6 \times 10^{-2}$	$11.9 \times 10^{-2}$	$11.0 \times 10^{-2}$	$10.2 \times 10^{-2}$
4. $\Delta H^\circ$ (kJ·mole <sup>-1</sup> )	-11.5	-14.0	-15.9	-17.4
5. $\partial\Delta H^\circ/\partial P$ (10 <sup>-1</sup> J·mole <sup>-1</sup> ·bar <sup>-1</sup> )	-54.2	-48.2	-44.1	-42.0
6. $\Delta V - T(\partial\Delta V/\partial T)$ (cm <sup>3</sup> ·mole <sup>-1</sup> )	-52.1	-49.1	-45.5	-42.2
7. $\Delta U = \Delta H^\circ - P\Delta V$ (kJ·mole <sup>-1</sup> )	-11.5	-13.3	-14.6	-15.6
8. $\partial\Delta U/\partial P$ (10 <sup>-1</sup> J·mole <sup>-1</sup> ·bar <sup>-1</sup> )	-38.2	-36.9	-34.3	-33.5
9. $-T(\partial\Delta V/\partial T) - P(\partial\Delta V/\partial P)$ (cm <sup>3</sup> ·mole <sup>-1</sup> )	-37.5	-36.4	-34.6	-33.0
10. $\Delta G^\circ$ (kJ·mole <sup>-1</sup> )	-2.47	-3.21	-3.94	-4.65
11. $\Delta S^\circ$ (J·mole <sup>-1</sup> ·deg <sup>-1</sup> )	-30.5	-36.1	-40.1	-43.0
12. $-\partial\Delta G/\partial T$ (J·mole <sup>-1</sup> ·deg <sup>-1</sup> )	-31.2	-36.5	-39.1	-41.9

**Figure 3.** Pressure dependence of oscillator strength for the hexamethyl benzene-iodine system in *n*-hexane at several temperatures.

could be evaluated directly by graphical method on a wave number scale, using the following equation<sup>15</sup>,

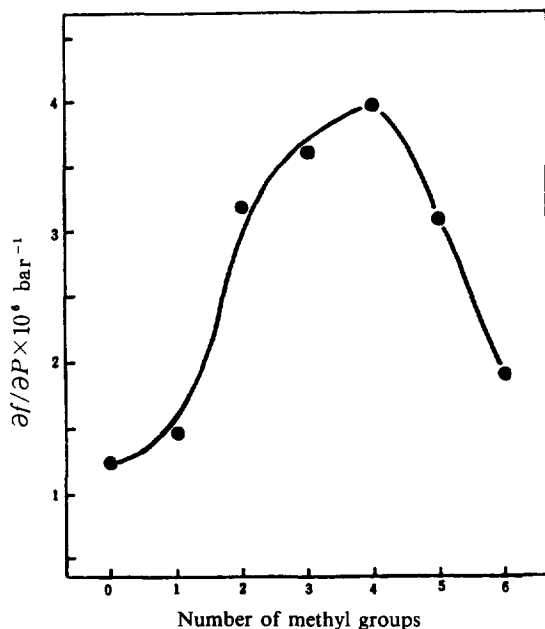
$$f = 1.036 \times 10^{-8} \cdot \epsilon_{\max} (\nu_{\max} - \nu_{\frac{1}{2}L}) \quad (3)$$

where  $\nu_{1/2L}$  is the half-height frequency at the red side of the maximum of the charge transfer absorption band. The values of oscillator strength estimated 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. Fur-

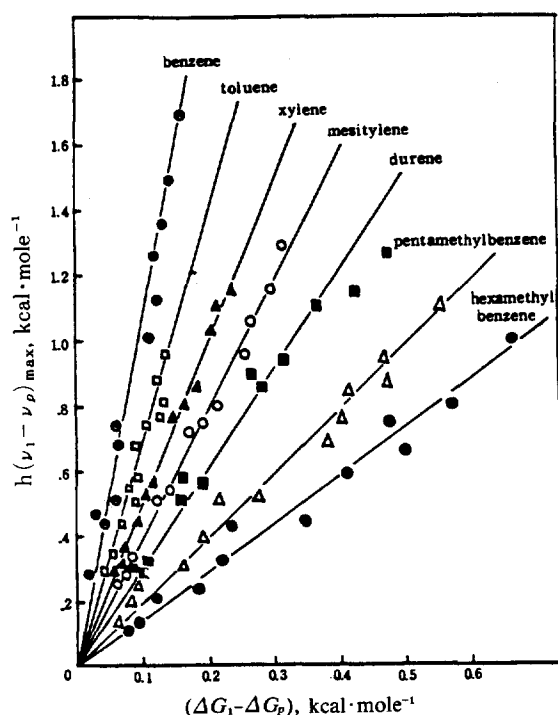
**TABLE 4: Pressure- and Temperature Shift of C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>·I<sub>2</sub> CT-absorption Maxima and Oscillator Strength of C<sub>6</sub>(CH<sub>3</sub>)<sub>6</sub>·I<sub>2</sub> CT-Bands at Various Pressures and Temperatures**

Temperature (°C)	Pressure (bar)	$(\nu_1 - \nu_p)_{\max}$ (cm <sup>-1</sup> )	$(\nu_1 - \nu_{2s})_{\max}$ (cm <sup>-1</sup> )	$f \times 10^2$
25	1	0		7.02
	200	87.1		7.09
	600	188		7.16
	1200	288		7.28
	1600	387		7.32
40	1	0	95.0	8.00
	200	58.6	124	8.08
	600	117	166	8.22
	1200	204	179	8.39
	1600	269	214	8.55
60	1	0	228	8.94
	200	44.4	270	9.05
	600	81.2	341	9.22
	1200	147	368	9.42
	1600	213	402	9.59

ther, it was found that its dependence on temperature is rather significant for a given pressure in Table 4. The oscillator strength shows a linear increase with pressure up to 1600 bars at a given temperature in Figure 3.  $\partial f/\partial P$  are 1.88, 3.34,  $3.95 \times 10^{-6}$  bar<sup>-1</sup> at 25, 40 and 60°C respectively. It is expected from  $\Delta V$  in Table 1 that a repulsive effect between the complex components will increase with temperature raising. The dependence of oscillator strength on pressure for a given temperature would indicate a repulsive effect between the complex components because  $\partial f/\partial P$  increases with temperature raising. On the other hand, the variation of  $\partial f/\partial P$  with the number of methyl groups of



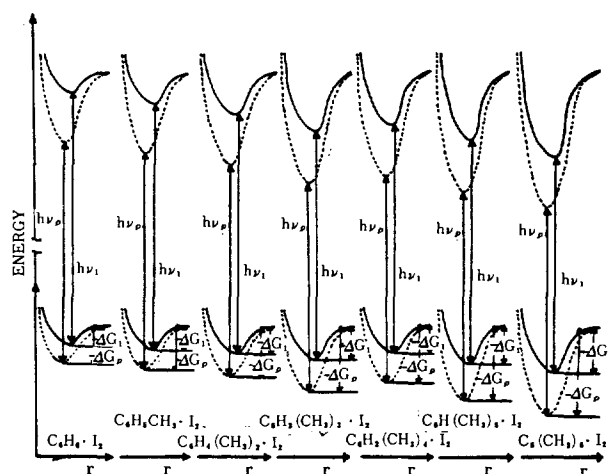
**Figure 4.** The dependence of oscillator strength on pressure with the number of methyl groups of polymethyl benzene-iodine CT-complexes at 25 °C.



**Figure 5.** Correlation between the difference of electron transfer energies,  $h\nu_{\max}$  and the difference of free energies,  $\Delta G$  of the complex formation for pressure variation in the polymethyl benzene-iodine system.

polymethyl benzene<sup>1-6</sup> is shown at 25 °C in Figure 4. From this, we can see that  $\partial f/\partial P$  has extremum behavior in durene and that it is in agreement with the variation of  $\Delta H$  or  $\Delta S$  with the number of methyl groups near atmospheric pressure<sup>1</sup>. As was expected, it was found that  $\partial f/\partial P$  could be a measure of repulsive effect between the components in the charge transfer complex.

**Correlation between Electron Transfer Energy and Free Energy :** Within the accuracy of our measurements, the red-



**Figure 6.** Schematic energy diagrams for the electron donor acceptor complex of methylated benzenes with iodine in solution, showing the effects of pressure on the free energy change,  $\Delta G$  and on the energy of charge transfer transition,  $h\nu$  of the complexes. Key: ———, atmospheric pressure; - - - - - , high pressure.

shifts of the band maxima at different pressure are plotted as a function of the respective changes of  $\Delta G$ . For the pressure variation our present and earlier<sup>1-6</sup> results indicated a reasonable linearity as shown in Figure 5. Thus for the charge transfer complexes formed between Polymethyl benzene and iodine the following relationship holds

$$\partial(h\nu_{\max})/\partial P = A \cdot \partial(\Delta G)/\partial P. \quad (4)$$

In the case of charge transfer complexes having one electron acceptor (iodine in this series) in common, the numerical factor,  $A$ , in eq. (4) was 8.6 in benzene as a electron donor and toluene 7.0, xylene 5.3, mesitylene 4.4, durene 3.3, pentamethyl benzene 1.6, hexamethyl benzene 1.3.

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  $\Delta G^{12}$ , then the numerical factor in eq.(4) should give an information about the shift or a deformation of the potential of the excited state.

The effect of pressure on the charge transfer complexes of polymethyl benzene with iodine is illustrated in the energy diagrams in Figure 6. These diagrams are not quantitative but are given to show the effect of pressure on the charge transfer energy and on the free energy of formation of the electron donor-acceptor complexes. The change of pressure will have little effect on the charge transfer energy or the stability of the complex. The solvation of the components and the complex is, however, changed by increase in pressure and this in turn increases the stability of the complex if it is more polar than its components from which it is formed. Thus the energy of the charge transfer band is affected by the change in solvation brought about by increase in pressure again only if there is a change in polarity during excitation.

These pressure effects can be understood in terms of the model suggested by Prochorow and Tramer<sup>16</sup>. The characteristic broadness of the charge transfer bands and the small energy of formation of the complexes suggest that their ground state has a shallow and broad potential energy curve. Their excited

state should have a much deeper potential energy curve and a smaller equilibrium separation under high pressure than atmospheric pressure, and hence this phenomenon is more predominant as the number of methyl groups on the benzene ring increases in Figure 6. This model can account for the sensitivity of the charge transfer band maximum to pressure changes and for the absence of broadening. This is in agreement with the observed results.

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## MNDO Studies on the Gas-Phase $S_N2$ Reaction\*

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The MNDO was found to be the most reliable semi-empirical SCF-MO method for the studies of  $S_N2$  reactions involving anion and neutral molecule. The results of our MNDO calculations on the  $S_N2$  reactions of  $\text{CH}_3\text{X} + \text{Y}^- \rightarrow \text{CH}_3\text{Y} + \text{X}^-$  where  $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{CN}, \text{CH}_3$  and  $\text{Y} = \text{F}, \text{CH}_3$  showed that the order of the leaving group ability is the reverse of the order of proton affinities. It was also found that there is no symbiosis involved in the  $S_N2$  transition state and the departure of the leaving group is relatively late in contrast to the early bond formation of the nucleophile. The Marcus equation was found to apply to the MNDO barriers and energy changes.

For many years bimolecular nucleophilic substitution ( $S_N2$ ) reaction has been one of the most extensively investigated types of reactions in chemistry. These studies have played an important role of developing ideas such as structure-reactivity relationships<sup>1</sup>, linear free energy relationships<sup>1</sup>, kinetics as a probe of mechanism<sup>2</sup> and solvent effects<sup>3</sup>. Since the pioneering works of Hughes and Ingold<sup>4</sup> numerous studies on the  $S_N2$  reaction conducted mainly in solution have been reported<sup>5</sup>. It has since been established that the reaction is first order in both nucleophile and substrate, and proceeds in one step involving concerted formation of the new bond by backside attack at carbon center and cleavage of the leaving group with inversion of configuration at the site of attack.

Recently however much interest has been focussed upon pure structure-reactivity relationships without any interfering solvent effect<sup>6</sup>. This type of studies has become possible since 1971 through the novel experimental works of gas-phase  $S_N2$  reac-

tions using ion cyclotron resonance (ICR) spectrometry<sup>7</sup>. On the theoretical side, a number of *ab initio*<sup>8</sup> and CNDO/2<sup>9</sup> MO calculations have been carried out on the  $S_N2$  reactions. These calculations were usually for the reactions proceeding in vacuo, *i.e.*, in the absence of solvent, so that direct comparisons with the experimental results of gas-phase studies are possible. However the CNDO/2 results<sup>10</sup> were in complete disagreement with the *ab initio* results<sup>11</sup>, whereas the excessive cost of computation limited the use of *ab initio* calculations; theoretical works on the  $S_N2$  reaction were mostly on simple model reactions with *ab initio* method. In practice however chemists are interested in somewhat larger molecular systems undergoing bimolecular nucleophilic substitution, and hence it is desirable to deal with the problem with an appropriate semiempirical MO method which is sufficiently reliable in reproducing essential features of the experimental results.

In this work, we have shown that MNDO method<sup>12</sup> is the most reliable semi-empirical SCF MO method for the investigation

\*Determination of Reactivity by MO Theory (Part XXXVII)