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Effect of Pressure on Iodine Complexes. II. Absorption Spectra of the Charge Transfer Bands with Diethyl Ether, Diethyl Sulfide, and Diethyl Selenide in Heptane

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Absorption spectra of the CT bands of I_2 complexes with Et_2O, Et_2S, and Et_2Se in heptane have been measured up to 4400 bar at 25 °C. The equilibrium constants and the volume changes accompanying complex formation, and the molar extinction coefficients and absorption maxima have been estimated. The volume changes were comparable with those estimated by the visible I_2 bands and by the X-ray data of the I_2 complexes in the crystalline state. In the CT bands of $Et_2S–I_2$ and $Et_2Se–I_2$ complexes inversion of shift from red to blue has been observed with increasing pressure though the CT band of $Et_2O–I_2$ complex shifted only through red. This inversion appears to be characteristic of the strong CT complex. Enhancement of the molar extinction coefficient of the CT band has been found with increasing pressure suggesting enhancement of the CT interaction between I_2 and the n-donor.

In previous papers[1,2] I_2 complexes with diethyl ether (Et_2O), diethyl sulfide (Et_2S), and diethyl selenide (Et_2Se) have been studied as an example of a n-σ complex under high pressure measuring the visible I_2 band. Enhancement of the molar extinction coefficient and the blue shift of the visible I_2 band have been observed with increasing pressure, and the decrease in bond distance between the n-donor and I_2 with increasing pressure up to 3300 bar was estimated as 0.008 nm. The I_2 complex has not only a visible I_2 band but also a charge transfer (CT) band. Then information about the pressure effect on the I_2 complex can be also found by measuring the latter band. The pressure effect on the CT band of the I_2 complexes with Et_2O, Et_2S, and Et_2Se in heptane has consequently been studied.

Experimental

The purification of reagents and the method of measuring the absorption spectra under high pressure are the same as described previously.[1,2]

Results and Discussion

Equilibrium Constants. The CT absorption spectra of the $Et_2S–I_2$ complex are shown in Fig. 1, and as can be seen the absorption spectra are free from component bands. Similar distinct CT absorption spectra have been observed in the $Et_2Se–I_2$ complex. The equilibrium constants (K) accompanying complex formation and the molar extinction coefficients (ε_{max}) of these CT bands have been estimated from the Benesi-Hildebrand equation.[2] The CT band of the $Et_2O–I_2$ complex overlaps the I_2 band in the ultraviolet region (Fig. 2). For the estimation of K and ε_{max} of the $Et_2O–I_2$ complex, a modified Benesi-Hildebrand equation has been used as previously described.[1] These results are shown in Table 1 together with the spectroscopic data.

The volume changes, ΔV, accompanying complex formation have been calculated from the pressure dependence of $\ln K$.[1,2] These are shown in Table 2. The volume changes estimated from the CT band of the I_2 complex in the present work is comparable with that previously estimated from the visible I_2 band in each complex[2] and furthermore comparable with that estimated from the X-ray data of the I_2 complex.[2]

Spectroscopic Properties. The absorption maxima (λ_{max}) of the CT bands of several I_2 complexes are

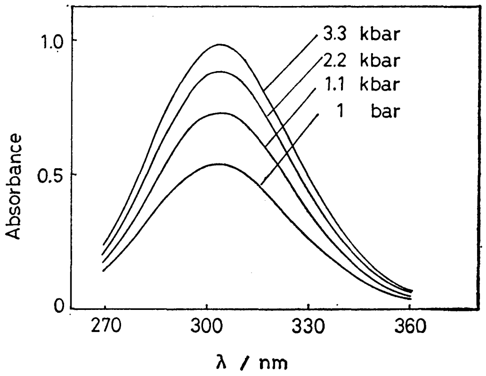

Fig. 1. CT absorption spectra of mixed solution of Et_2S and I_2 in heptane at 25 °C and various pressures. Et_2S: 2.4×10^{-3} mol dm^{-3}, I_2: 5.5×10^{-5} mol dm^{-3}. The absorptions are not corrected for compression.

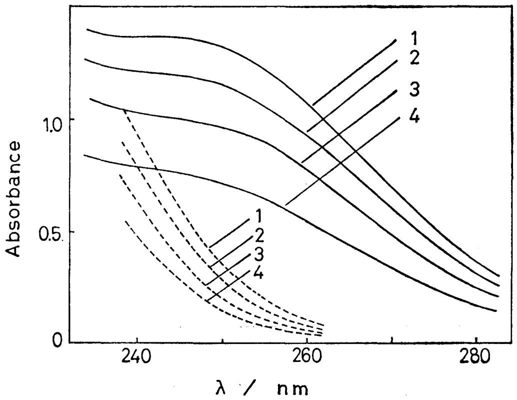

Fig. 2. CT absorption spectra of mixed solution of Et_2O and I_2 in heptane at 25 °C and various pressures. Et_2O: 0.57 mol dm^{-3}, I_2: 3.0×10^{-4} mol dm^{-3}. Dotted lines indicate absorption spectra of I_2 (3.0×10^{-4} mol dm^{-3}) in heptane. 1: 3300 bar, 2: 2200 bar, 3: 1100 bar, 4: 1 bar. The absorptions are not corrected for compression.

TABLE 1. EQUILIBRIUM CONSTANTS (K), MOLAR EXTINCTION COEFFICIENTS (ε_{max}) AND ABSORPTION MAXIMA (λ_{max}) OF VARIOUS I_2 COMPLEXES IN HEPTANE AT 25 °C

P / bar	K[a]	ε_{max} / mol^{-1} dm^3 cm^{-1}	λ_{max} / nm
Et_2O–I_2			
1	4.1±1.0[b]	7100±1200	250.8±0.5
	5.9[c]	5650[c]	252[c]
1100	6.9±1.0[b]	7200±1200	252.2±0.5
2200	8.6±1.3[b]	7200±1200	252.6±0.5
3300	10.3±1.3[b]	7200±1200	252.8±0.5
Et_2S–I_2			
1	1460±170	21600±1200	302.7±0.3
	1430[d]	29800[d]	302[d]
1100	2170±340	21900±1200	303.2±0.3
2200	3420±530	22200±1200	303.3±0.3
3300	4570±860	22600±1200	303.2±0.3
4400			302.4±0.2
Et_2Se–I_2			
1	10400±1600	31400±1000	314.2±0.3
			315[e]
1100	19000±4500	32000±1000	314.6±0.3
2200	25000±6700	33900±1000	315.0±0.3
3300	38100±8900	34400±1000	314.8±0.3
4400			314.1±0.2

a) In mole fractions. b) Mean value of K at 250 and 254 nm. c) Ref. 3. d) Ref. 4. e) Ref. 5 in CCl_4.

TABLE 2. VOLUME CHANGES (ΔV) ACCOMPANYING THE FORMATION OF I_2 COMPLEXES AT 25 °C (cm^3 mol^{-1})

	Et_2O–I_2	Et_2S–I_2	Et_2Se–I_2
ΔV_{CT}[a]	−7.5±1.0	−10.0±1.2	−13.5±3.0
ΔV_{vis}[b]	−6.7±1.0	−8.1±1.2	−14.6±4.0
ΔV_{theor}[c]	−6.4	−8.9	−9.8

a) From CT band (this work). b) From visible I_2 band (Ref. 2). c) From a theoretical estimation (Ref. 2).

shown in Table 1. In Et_2O–I_2 complex the λ_{max} values of the CT band have been estimated from the observed absorption by subtracting that of the free I_2, which has been calculated from the equilibrium constant of this complex and the molar extinction coefficient of free I_2. In Et_2O–I_2 complex λ_{max} showed a red shiftt with increasing pressure. The red shift has been generally observed in π-π complexes.[6–11] Two explanations have been proposed for the red shift of the CT band with increasing pressure. One is the enhancement of the dielectric constant of the solvent by compression.[6,11,12] This effect stabilizes the excited state of the CT complex rather than the ground state as the dipole moment of the former state is much larger than that of the latter. The other reason is the decrease in the bond distance between a donor and an acceptor,[8,9] supposing that the distance between a donor and an acceptor at the potential minimum of the ground state is larger than that of the excited state.

In Et_2S–I_2 and Et_2Se–I_2 complexes the λ_{max} of the CT band shifted to red with increasing pressure, and then to blue (Table 1). Such an unusual pressure shift from red to blue has been observed only in CT complex between hexamethylbenzene (HMB) and tetracyanoethylene (TCNE).[7,8,11] Gott and Maisch attributed the blue shift in the HMB–TCNE complex under high pressure to the onset of steric hindrance between the nitrogen atoms of TCNE and the methyl groups of HMB.[7] This explanation does not appear to be valid for Et_2S–I_2 and Et_2Se–I_2 complexes because of the absence of steric hindrance. The bond energies of these complexes in nonpolar solvents are 33, 41, and 32 kJ mol^{-1} for Et_2S–I_2,[4] Et_2Se–I_2,[5] and HMB–TCNE complexes,[13] respectively. These values are larger than those of other CT complexes (≈20 kJ mol^{-1}) which indicate normal red shifts of the CT bands with increasing pressure.[6–11] Therefore the unusual pressure shift, namely the inversion of shift with increasing pressure up to several thousand bars may be a character of the complex with strong CT interaction.

The increases in ε_{max} of the CT bands up to 3300 bar are shown in Table 3 as $\Delta\varepsilon_{obsd}$. The same magnitude of $\Delta\varepsilon_{obsd}$ value has been generally observed in π-π complexes.[7–11] The enhancement of ε_{max} of the CT band may be ascribed to the decrease in the bond distance between a donor and an acceptor with increasing pressure as the overlap integral increases due to the decrease in bond distance as expected by Mulliken,[14] implying enhancement of the CT interaction. This explanation supports the preceding conclusion, that is, a decrease in the bond distance of 0.008 nm between I_2 and an n-donor with increasing pressure up to 3300 bar.[2] Furthermore the amount of increase in the overlap integral accompanying decrease in the bond distance is expected to be larger in the stronger CT complex since the overlap integral

TABLE 3. THE INCREASES IN THE MOLAR EXTINCTION COEFFICIENTS AT THE CT ABSORPTION MAXIMA WITH INCREASING PRESSURE UP TO 3300 bar (mol^{-1} dm^3 cm^{-1})

	Et_2O–I_2	Et_2S–I_2	Et_2Se–I_2
$\Delta\varepsilon_{obsd}$	100±1200	1000±1200	3000±1000
$\Delta\varepsilon_{est}$	2200	2400	2200

$\Delta\varepsilon=\varepsilon$ (at 3300 bar) $-\varepsilon$ (at 1 bar), where ε is the molar extinction coefficient at the CT absorption maximum. The subscripts "obsd" and "est" represent the observed value in Table 1 and the estimated value from Fig. 3, respectively.

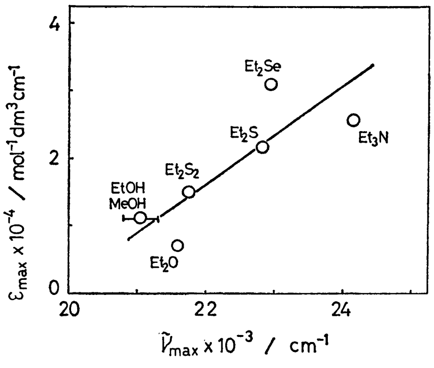

Fig. 3. Relation between ε_{max} of CT band and $\tilde{\nu}_{max}$ of visible I_2 band of I_2 complexes with n-donors at 1 bar. References 15 and 16 were utilized. $\tilde{\nu}_{max}=1/\lambda_{max}$.

increases exponentially with decrease in bond distance. This may explain the $\Delta\varepsilon_{\text{obsd}}$ values in Table 3 being larger with stronger n-donors (O<S<Se).

A relation between ε_{max} of the CT bands and λ_{max} (or $\tilde{\nu}_{\text{max}}$) of the visible I_2 bands of the I_2 complexes with n-donors is expected at 1 bar since it is established that the former values are larger and the latters are at shorter wavelengths with stronger n-donors.[15] This relation is shown in Fig. 3 with a straight line of slope 7.3 $\text{mol}^{-1}\,\text{dm}^3\,\text{cm}^{-1}/\text{cm}^{-1}$. From this slope we can estimate the increases in ε_{max} of the CT bands corresponding to the previously observed blue shifts of the visible I_2 bands, that is, 300 cm^{-1} for Et_2O–I_2 and Et_2Se–I_2 complexes and 330 cm^{-1} for Et_2S–I_2 complex with increasing pressure up to 3300 bar.[2] These blue shifts suggest enhancement of the CT interaction with increasing pressure. The results are shown in Table 3 as $\Delta\varepsilon_{\text{est}}$ and compared with the observed values. The values of $\Delta\varepsilon_{\text{est}}$ appear to be the same order of magnitude as the $\Delta\varepsilon_{\text{obsd}}$ values and this supports the hypothesis that the increase in ε_{max} of the CT band with increasing pressure is due to the enhancement of the CT interaction between I_2 and the n-donor.

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