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

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Absorption spectra of the visible I_2 band of I_2 complexes with Et_2O, Et_2S, and Et_2Se in heptane have been measured up to 3300 bar at 25 °C. The equilibrium constants and volume changes accompanying complex formation, the molar extinction coefficients and the absorption maxima have been estimated. The volume changes were found comparable with those estimated from the X-ray data of the I_2 complexes in the crystalline state. The enhancement of the molar extinction coefficient and the blue shift of the visible I_2 band with increasing pressure have been established. The results suggest a decrease in the bond distance between an n-donor and I_2, compared with the spectroscopic properties of the I_2 complex at 1 bar. The decrease has been estimated as 0.008 nm with increasing pressure up to 3300 bar.

There have been several investigations of iodine (I_2) complexes as examples of charge transfer (CT) complexes from both the experimental and theoretical point of view.[1] Pressure effects on the I_2 complexes with π-donors such as benzene, toluene, and mesitylene have been studied by Ham,[2] and Kwun and Lentz,[3] where it was concluded that the equilibrium constants accompanying complex formation increased with increasing pressure. There has yet been no investigation of I_2 complexes with n-donor such as ether or amines under high pressure.

In the study of the I_2 complex at 1 bar, not only a CT band but also a I_2 band in the visible region (visible I_2 band) has been reported.[1] The I_2 band shifts to blue (to shorter wavelength) very largely with complex formation, and the shift is larger with stronger n-donors. Thus the blue shift in the visible I_2 band has been a useful indication of CT interaction. Furthermore, the molar extinction coefficients of the visible I_2 bands increase with stronger n-donors. Consequently the investigation of the visible I_2 bands of the I_2 complexes with n-donors under high pressure has been interesting. Recently by measuring the visible absorption spectra pressure effect on I_2 complex with diethyl ether (Et_2O) in heptane has been studied.[4] The present report is an extention of the work using diethyl sulfide (Et_2S) and diethyl selenide (Et_2Se) as n-donors in heptane.

Experimental

The purification of I_2 and heptane has been described in a preceding paper.[4] Et_2S (Wako Pure Chemical Co., Ltd.) was dried with calcium chloride and fractionally distilled, bp 91—92 °C (lit,[5] bp 92 °C). Et_2Se was synthesized by the method of Bird and Challenger,[6] n_D^{20} 1.4790, bp 107—108 °C (lit,[7,8] n_D^{20} 1.4768, bp 108 °C). The method of measuring the absorption spectra under high pressure has been described in a preceding paper.[4]

Results and Discussion

The absorption spectra of the Et_2S–I_2 complex in Fig. 1 show an isosbestic point at 490 nm. The absorption band at 522 nm decreases and at 438 nm increases with increasing pressure. The former band has been ascribed as free I_2 (I_2 in heptane) and the latter the complexed I_2 with Et_2S.[6] In the Et_2Se–I_2 complex absorption spectra similar to Fig. 1 were observed with an isosbestic point at 470 nm. The absorption spectra of the Et_2O–I_2 complex have been described previously.[4]

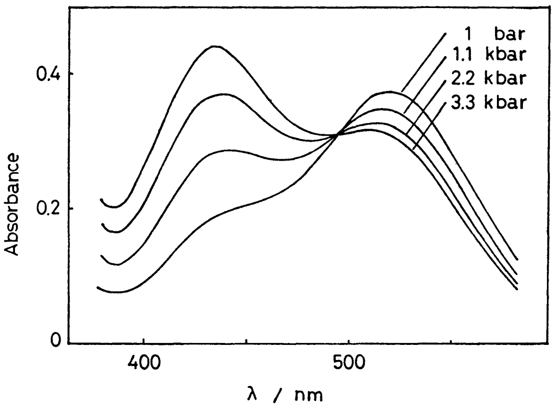

Fig. 1. Visible I_2 absorption spectra of mixed solution of Et_2S and I_2 in heptane at 25 °C and various pressures. Et_2S: 1.4×10^{-3} mol dm^{-3}, I_2: 5.0×10^{-4} mol dm^{-3}. The absorptions are not corrected for compression.

Equilibrium Constants. The equilibrium constants accompanying complex formation and the molar extinction coefficients have been estimated by the Benesi-Hildebrand equation[10]

$$\frac{X_A}{A} = \frac{V}{K\varepsilon l}\frac{1}{X_D} + \frac{V}{\varepsilon l}, \qquad (1)$$

where K is the equilibrium constant in mole fractions accompanying complex formation, A the absorbance of the mixed solution of I_2 and donor, ε the molar extinction coefficient of the complex, l the path length, X_A and X_D the initial mole fractions of I_2 and donor, respectively, and V the molar volume of the solution which has been assumed to be equal to that of the solvent under each pressure.[11] The value of the initial concentration of I_2 in units of mol dm^{-3} ($[I_2]$) used by Benesi and Hildebrand[10] depends on the pressure. The value in mole fraction units (X_A) has been utilized in Eq. 1 with the following relation:

$$X_A = [I_2]V. \qquad (2)$$

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
Free $I_2$$^{b)}$			
1		900±30	522.0±0.5
1100		900±30	520.5±0.5
2200		900±30	519.5±0.5
3300		900±30	518.0±0.5
Et_2O–I_2			
1	6.1±1.0$^{c)}$	980±60	462.5±1.5
	5.9$^{d)}$	950$^{d)}$	462$^{d)}$
1100	8.4±1.2$^{c)}$	980±60	460.0±1.5
2200	11.0±1.2$^{c)}$	980±60	458.0±1.5
3300	12.1±1.6$^{c)}$	980±60	456.0±1.5
Et_2S–I_2			
1	1320±210	1820±70	438.0±0.5
	1430$^{e)}$	1960$^{e)}$	435$^{d)}$
1100	2010±670	1830±70	435.5±0.5
2200	2480±600	1970±70	433.5±0.5
3300	3360±1200	2120±70	432.0±0.5
Et_2Se–I_2			
1	6600±900	2730±60	435.5±0.5
			436$^{f)}$
1100	13500±6000	2780±60	433.0±0.5
2200	20900±10000	2930±60	431.5±0.5
3300	26300±11000	3020±60	430.0±0.5

a) In mole fraction units. b) I_2 in heptane. c) Ref. 4. d) Ref. 9. f) Ref. 13, in CCl_4.

The values of K and ε have been evaluated from the intercept and the slope of the plot of X_A/A *vs.* $1/X_D$, the results of which are shown in Table 1 together with the spectroscopic data.

The volume changes, ΔV, accompanying formation of the I_2 complexes have been calculated from the following equation and the slopes of the ln K *vs.* P plot as shown in Table 2:

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

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
$\Delta V_{vis}$$^{b)}$	−6.7±1.0$^{c)}$	−8.1±1.2	−14.6±4.0
$\Delta V_{theor}$$^{b)}$	−6.4$^{c)}$	−8.9	−9.8

a) From visible I_2 band and Eq. 3. b) From Eq. 4. c) Ref. 4.

In the preceding paper[4] the volume change accompanying the formation of the Et_2O–I_2 complex was estimated from Eq. 4, assuming that the I_2 complex is formed along the axis of cylinder having a radius equal to the van der Waals radius for the iodine atom:

$$\Delta V = (\pi r^2 \Delta d) N_A, \tag{4}$$

where N_A is Avogadro's number, r the radius of the cylinder, and Δd the contraction of the cylinder accompanying complex formation estimated by the following equation:

$$\Delta d = d_X - (d_D + d_A), \tag{5}$$

where d_X is the bond distance of the complex estimated from the X-ray data of the crystal, and d_D and d_A are van der Waals radii for the donor atom (O) and the acceptor atom (I), respectively. In the same manner the volume changes for the Et_2S–I_2 and Et_2Se–I_2 complexes have been estimated with the bond distance for 1,4-dithiane–I_2[14] and 1,4-diselenane–I_2[15] complexes in the crystal for d_X, van der Waals radii[16] of the sulfur and selenium atoms for d_D, and van der Waals radius of the iodine atom for d_A and r, the results of which are shown in Table 2. These values are comparable with those estimated from the pressure dependence of the equilibrium constants.

Spectroscopic Properties. Absorption maxima (λ_{max}) of the visible I_2 band are shown in Table 1. The values of λ_{max} for free I_2 were determined directly from the observed absorption. In the Et_2S–I_2 and Et_2Se–I_2 complexes, these were determined from the observed absorptions under the condition that $X_D \gg X_A$, where the absorption of free I_2 could be neglected. The λ_{max} values of the Et_2O–I_2 complex have been estimated from the observed absorption by subtracting the absorption of the free I_2 calculated from the equilibrium constant of the Et_2O–I_2 complex and the molar extinction coefficient of free I_2. All of the λ_{max} values shifted to blue with increasing pressure; Ham failed to observe any blue shift in the visible absorption spectra of I_2 in heptane up to 2000 bar.[2] The molar extinction coefficients (ε_{max}) of the visible I_2 band at λ_{max} increased with increasing pressure in Et_2S–I_2 and Et_2Se–I_2 complexes (Table 1). In the Et_2O–I_2 complex and free I_2, however, ε_{max} was not enhanced.

The pressure effect of the increase in ε_{max} accompanying the blue shift of λ_{max} is similar to the property of I_2 complexes with n-donors at 1 bar as shown in Fig. 2, where the value of ε_{max} is larger in the I_2 complex whose λ_{max} is at shorter wavelength. Mulliken and Person explained this as follows.[1] The visible I_2 band corresponds to the excitation of an electron from the π_g MO to the σ_u MO of I_2 molecule. Since the latter MO is strongly antibonding, the size of the σ_u MO must be larger than that of the π_g MO. When the I_2 molecule, coupled with a donor in a I_2 complex, is excited by absorption of visible light, its suddenly swollen size ($\sigma_u \leftarrow \pi_g$) increases the repulsion energy between I_2 and the donor, which causes the blue shift of the visible I_2 band. The shift should be greater, the more compact the I_2 complex. The enhanced intensity of the visible I_2 band is presumably explained in terms of the increased mixing of the excited state of the visible I_2 band with the higher excited states of the I_2 complex, as a result of the shift of the excited state of the visible I_2 band to higher energy. Such a explanation may be suited for the pressure effects on the I_2 complex, that is, the blue shift of λ_{max} and the enhancement of ε_{max} of the visible I_2 band, implying a decrease in the bond distance between I_2 and the n-donor.

The values of the slope in Fig. 2 have been estimated to be 0.01, 0.12, 0.81, and 0.95 $mol^{-1}\ dm^3\ cm^{-1}/cm^{-1}$ at band maxima of free I_2, Et_2O–I_2, Et_2S–I_2, and Et_2Se–

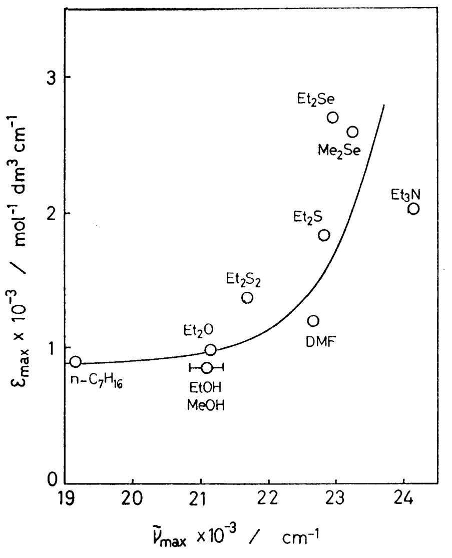

Fig. 2. Relation between ε_{max} and $\tilde{\nu}_{max}$ at visible I_2 band of I_2 complexes with n-donors at 1 bar. References 1 and 17 were utilized. $\tilde{\nu}_{max}=1/\lambda_{max}$.

TABLE 3. THE INCREASES IN THE MOLAR EXTINCTION COEFFICIENTS AT λ_{max} OF VISIBLE I_2 BANDS WITH INCREASING PRESSURE UP TO 3300 bar (mol^{-1} dm^3 cm^{-1})

	Free I_2	Et_2O–I_2	Et_2S–I_2	Et_2Se–I_2
$\Delta\varepsilon_{obsd}$	0	0	300	290
$\Delta\varepsilon_{est}$	1.4	36	267	285

$\Delta\varepsilon=\varepsilon_{max}$ (at 3300 bar) $-\varepsilon_{max}$ (at 1 bar). The subscripts "obsd" and "est" represent the observed value in Table 1 and the estimated one from Fig. 2, respectively.

I_2 complexes, respectively. The blue shifts of the visible I_2 bands with increasing pressure up to 3300 bar have been estimated as 140 cm^{-1} for free I_2, 300 cm^{-1} for Et_2O–I_2 and Et_2Se–I_2 complexes, and 330 cm^{-1} for Et_2S–I_2 complex from Table 1. The amount of increase in ε_{max} corresponding to the blue shift of the visible I_2 band with increasing pressure up to 3300 bar may be estimated from the slope of the curve in Fig. 2. These values shown in Table 3 are comparable with the observed ones. This result may support that Mulliken's explanation is suited for the pressure effect on I_2 complexes.

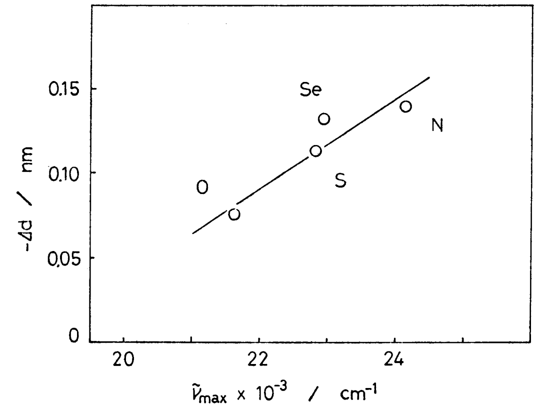

Fig. 3. Relation between $-\Delta d$ and $\tilde{\nu}_{max}$ of visible I_2 bands with several n-donors at 1 bar. O: Et_2O–I_2, S: Et_2S–I_2, Se: Et_2Se–I_2, N: Me_3N–I_2, Δd: see Eq. 5. For the estimation of Δd, van der Waals radii[16] of O, S, Se, N, and I atoms and X-ray data of 1,4-dioxane–I_2 (O),[18] 1,4-dithiane–I_2 (S),[14] 1,4-diselenane–I_2 (Se),[15] and Me_3N–I_2 (N)[19] complexes in their crystals were utilized.

In I_2 complexes with n-donors at 1 bar, it has been found that the decreases in distance between the n-donors and I_2 accompanying complex formation are larger with stronger n-donors.[14,15,18,19] These values are also related to the absorption maxima of the visible I_2 bands in Fig. 3, suggesting the blue shift of the visible I_2 band by the increase in the repulsion force between a n-donor and I_2. The value of $-\Delta d$ in Fig. 3 represents a decrease in the interatomic distance between an n-donor atom and an iodine atom accompanying formation of the I_2 complex (refer to Eq. 5). A linear relation between $-\Delta d$ and the absorption maxima ($\tilde{\nu}_{max}$) of the visible I_2 band has been obtained, and the slope has been estimated to be 2.7×10^{-5} nm/cm^{-1}. The blue shift of 300 cm^{-1} in the visible I_2 band of Et_2Se–I_2 complex with increasing pressure up to 3300 bar has been observed. The value of $-\Delta d$ corresponding to this blue shift may be estimated as 0.008 nm from the slope in Fig. 3.

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