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Interaction between Pyrazine and Halomethanes. I. Complex Formation between Pyrazine and Halomethanes at Room Temperature

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The absorption spectrum of pyrazine has been studied at room temperature in various mixed solvents of cyclohexane and halomethanes such as carbon tetrachloride, chloroform and dichloromethane. With increasing concentration of halomethane, the singlet-singlet (S-S) and singlet-triplet (S-T) n→π* absorptions decrease in intensity and become structureless, whereas the S-S π→π* absorption remains essentially unchanged. The observations are attributed to the complex formation between pyrazine and halomethanes involving the non-bonding electrons in pyrazine. From the concentration and temperature dependences of the n→π* absorption spectra, the equilibrium constants, enthalpy and entropy changes have been obtained for the complex formation in all the systems studied. The equilibrium constants obtained from the S-S and S-T n→π* absorptions are in good agreement with each other.

As is well known, the electronic spectra of organic compounds exhibit solvent effects. Burawoy,1) Kasha,2) and McConnell3) proved that the solvent effect is useful for characterization of the π→π* and n→π* transitions, showing that the latter transition generally undergoes a blue shift in polar solvents. Brealey and Kasha4) studied the blue shift of the n→π* absorption spectra of benzophenone and pyridazine in hydroxylic mixed solvents, and attributed it to the hydrogen bonding between the solutes and the hydroxylic components of the solvents. But Pimentel5) suggested that the Franck-Condon principle is significant in the blue shift. Krishna and Goodman6) reported, on the solvent effects in the n→π* absorption and n←π* phosphorescence spectra of pyrazine and 2,5-dimethylpyrazine in EPA glass, that the weak hydrogen bonding and Franck-Condon strain resulting therefrom are operative. Baba *et al.*7) examined the solvent effects on the absorption and fluorescence spectra of diazines, and discussed the dipole moments in the (n,π*) excited states. Recently, Zalewski *et al.*8) observed the absorption, fluorescence, and phosphorescence spectra of pyrazine in such matrices as durene, benzene, and cyclohexane, focusing on the nature of the first (n,π*) excited state.

The present paper deals with the S-S and S-T n→π* absorption spectra of pyrazine, which show a blue shift and a blurred structure in the presence of the halomethanes, carbon tetrachloride, chloroform, and dichloromethane. In view of the molecular symmetry of pyrazine and the nonpolar nature of carbon tetrachloride, the blue shift in carbon tetrachloride can not be interpreted in terms of the ground and excited state dipole moments. We here report evidence for the 1 : 1 complex formation between pyrazine and the halomethanes, and the related thermodynamic data obtained.

Carbon tetrachloride as solvent often gives rise to specific interaction with organic compounds such as benzene and pyrazine particularly at low temperatures, that is, to anomalous changes in the absorption and emission spectra.9–13) In addition, carbon tetrachloride is known to form complexes as an electron acceptor not only with aromatic hydrocarbons14–16) such as benzene, mesitylene, and hexamethylbenzene, but also with amines17–19) such as triethylamine, butylamine, and triphenylamine.

Experimental

Pyrazine and all the solvents used were obtained from Wako Pure Chem. Ind., Ltd. Pyrazine was purified by repeated sublimation under vacuum. Cyclohexane (super special grade) was treated several times with a 200-mesh activated silica-gel column, and the benzene contained as an impurity was eliminated. Chloroform (absorption spectro grade) was passed several times just prior to use through a column packed with aluminium oxide Woelm basic (ICN Pharmaceutical Co.) in order to remove the ethanol contained as stabilizer. Carbon tetrachloride and dichloromethane (Dotite spectrosol) were used as received.

The absorption spectra were measured with a Shimadzu UV-200 spectrophotometer, equipped with a temperature-regulated cell holder adapted for the 1-cm cells. Circulating water of a constant temperature maintained the holder temperature constant to an accuracy of ±0.5°. The temperature was monitored with a thermocouple attached to the reference cell and displayed on a recorder throughout each measurement run. A pair of matched 1-cm fused silica cells were used for the S-S n→π* absorption, and a pair of matched 5-cm cells for the S-T n→π* absorption.

Results and Discussion

Pyrazine has three different absorptions in the ultraviolet region. One is the S-S π→π* absorption in the region of 250—270 nm, and the others are the S-S and S-T n→π* absorptions in the regions of 310—330 nm and 360—380 nm, respectively. Figures 1 and 2 show the latter two absorption spectra in cyclohexane and in three different halomethanes: carbon tetrachloride, chloroform, and dichloromethane. The spectra in the halomethanes, as in ethanol, are considerably blue-shifted and the vibrational structures are quite blurred compared to those in cyclohexane. The phenomenon is particularly prominent in chloroform and dichloromethane. On the contrary, the π→π* absorption spectra in the halomethanes show only a slight red shift and the vibrational structure remains

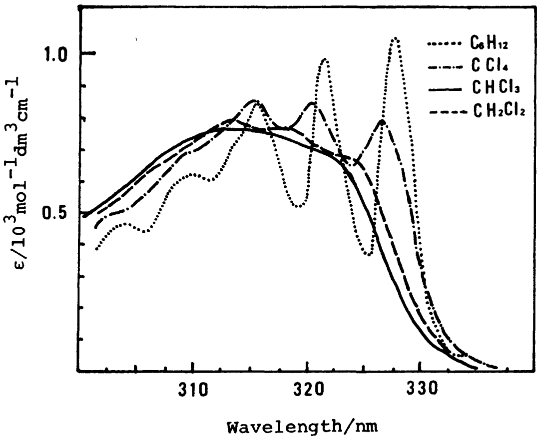


Fig. 1. S-S n→π^* absorption spectra of pyrazine in cyclohexane (······), carbon tetrachloride (·—·—), chloroform (——), and dichloromethane (------).

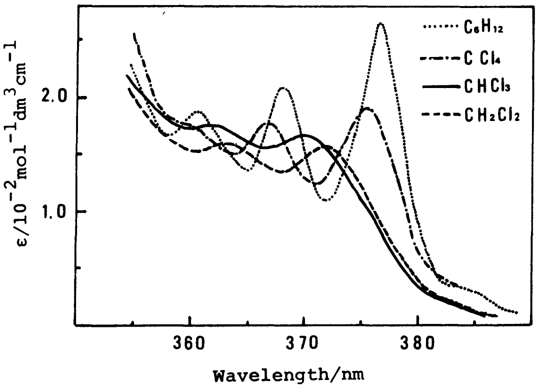


Fig. 2. S-T n→π^* absorption spectra of pyrazine in cyclohexane (······), carbon tetrachloride (·—·—), chloroform (——), and dichloromethane (----).

essentially the same as that in cyclohexane. These findings indicate that pyrazine undergoes a specific interaction with the halomethanes through its nonbonding electrons.

In order to study the interaction quantitatively, the S-S and S-T n→π^* absorptions were investigated in detail in ternary systems consisting of pyrazine, the halomethanes, and cyclohexane, where the concentration of pyrazine was kept constant and those of the halomethanes were varied. For the convenience of discussion, the ternary system containing carbon tetrachloride, for example, will be referred to as the carbon tetrachloride system. The S-S and S-T n→π^* absorption spectra thus obtained for the carbon tetrachloride system are shown in Figs. 3 and 4, respectively. Similar results have been observed for the chloroform and dichloromethane systems. With any one of the halomethanes, when the concentration of halomethane is relatively low, there always appear isosbestic points in a family of absorption curves, as can be seen in Figs. 3 and 4, suggesting formation of a 1 : 1 complex between pyrazine and the halomethane.

The equilibrium constant K of the complex formation can be determined from the S-S absorption data through the following relation, subject to the condition $[D]_0 \ll [A]_0$:

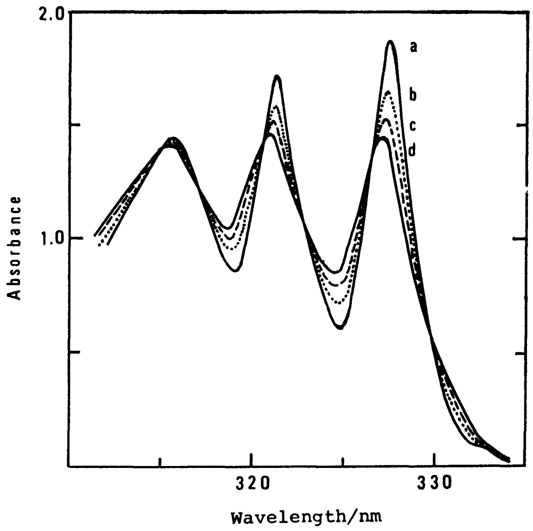


Fig. 3. S-S n→π^* absorption spectra of pyrazine in the carbon tetrachloride–cyclohexane mixed solvents at 20 °C. Concentration of pyrazine: 1.654×10^{-3} mol dm^{-3}. Concentration of carbon tetrachloride: (a) 0, (b) 1.200, (c) 2.401, (d) 3.601 mol dm^{-3}.

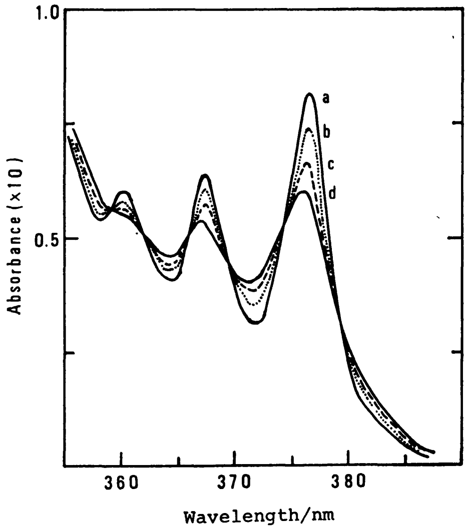
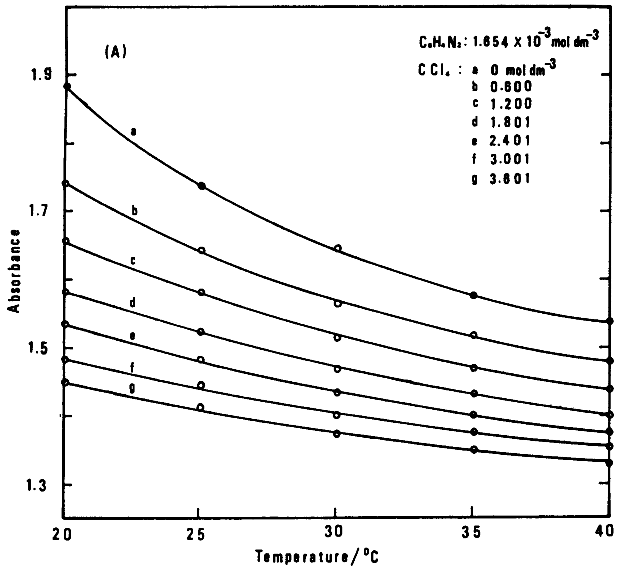


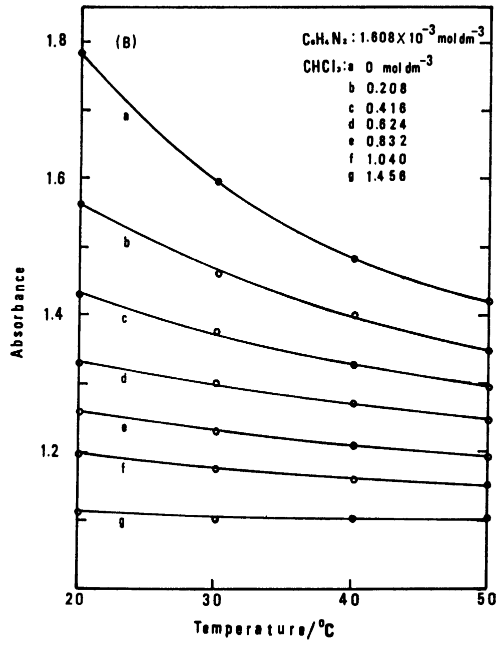
Fig. 4. S-T n→π^* absorption specrta of pyrazine in the carbon tetrachloride–cyclohexane mixed solvents. Concentration of pyrazine: 0.622 mol dm^{-3}. Concentration of carbon tetrachloride: (a) 0, (b) 0.999, (c) 3.075, (d) 6.225 mol dm^{-3}.

$$d = (1/K)(\varepsilon_D[D]_0 - d)/[A]_0 + \varepsilon_C[D]_0, \qquad (1)$$

where $[D]_0$ and $[A]_0$ are the initial molar concentrations of the donor, pyrazine, and the acceptor, halomethane, d is the absorbance measured with 1-cm optical path, and ε_D and ε_C are the molar extinction coefficients of the free and complexed donor, respectively; the ε_D values were actually determined in cyclohexane. The apparent ε_D value decreases with increasing temperature, owing to the appearance of the hot band around 333 nm in the S-S n→π^* absorption region. Therefore, in order to accurately evaluate the temperature dependence of the equilibrium constant K, we adopted the ε_D values measured at the corresponding temperatures. The concentrations of pyrazine used were 1.654×10^{-3}

mol dm^{-3} for the carbon tetrachloride system, and 1.608×10^{-3} mol dm^{-3} for the chloroform and dichloromethane systems, while the concentrations of halomethane covered the ranges of 0.600—3.601, 0.208—1.456, and 0.461—1.384 mol dm^{-3} for the carbon tetrachloride, chloroform, and dichloromethane systems, respectively. In order to estimate the heat of formation ΔH (the enthalpy change) and the entropy change ΔS, measurements were made at the following temperatures: 20, 25, 30, 35, and 40 °C for the carbon tetrachloride system; 20, 30, 40, and 50 °C for the chloroform system; 20, 30, 40, and 48 °C for the dichloromethane system. We monitored the absorption intensities at 327.5 nm and, if possible, those at 321.5 nm, corresponding to the first and second bands, respectively. Figure 5 shows the data thus obtained at 327.5 nm; the corresponding data at 321.5 nm are quite similar. From the K values estimated at the above-mentioned different temperatures, the ΔH values could be evaluated by means of the van't Hoff equation. The plots of d vs. $(\varepsilon_D[D]_0-d)/[A]_0$ and $-\ln K$ vs. $1/T$ gave fairly good straight-line relationships for any of the ternary systems studied, as exemplified in Figs. 6 and 7. The numerical results thus obtained in the S-S n→π* absorption region are listed in Table 1, together with those in the S-T region to be described in the following paragraph. The thermodynamic data in Table 1 are found to fall in the ranges of magnitude expected for the molecular complexes.[20]





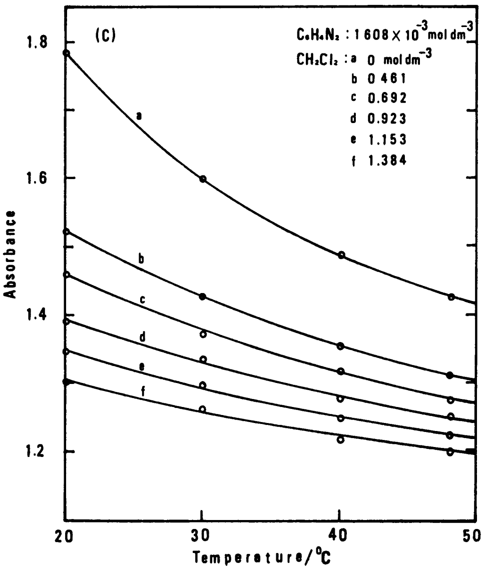


Fig. 5. Temperature dependence of the S-S n→π* absorption monitored at 327.5 nm in the (A) carbon tetrachloride, (B) chloroform, and (C) dichloromethane systems.

For the S-T n→π* absorption, the concentrations of pyrazine used were fairly high because of its very low molar extinction coefficient: they were 0.622, 0.620, and 0.619 mol dm^{-3} for the carbon tetrachloride, chloroform, and dichloromethane systems, respectively. The halomethane concentrations covered the ranges of

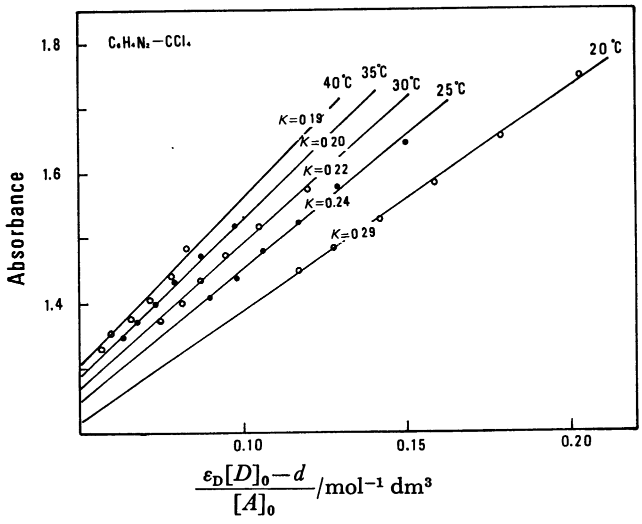


Fig. 6. Temperature dependence of the equilibrium constant K in the carbon tetrachloride system on the basis of the results in Fig. 5(A).

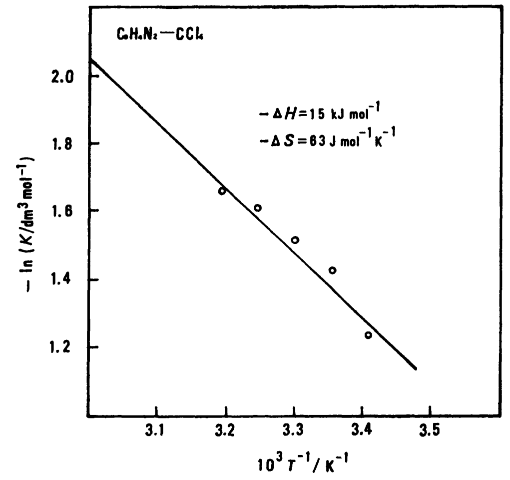


Fig. 7. Evaluation of the enthalpy and entropy changes in the carbon tetrachloride system.

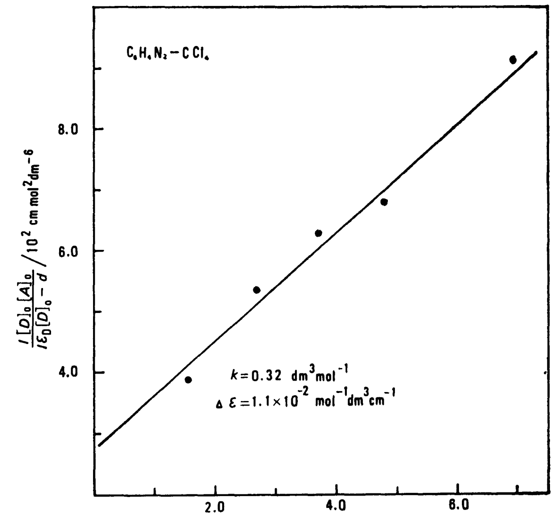


Fig. 8. Evaluation of the equilibrium constant by means of the modified Drago-Rose equation, Eq. 2, from the S-T n→π* absorption data obtained at 376 nm in the carbon tetrachloride system.

0.999—6.225, 0.244—2.493, and 0.326—1.244 mol dm^{-3} for the carbon tetrachloride, chloroform, and dichloromethane systems, respectively. Consequently, the relative concentrations of pyrazine and halomethanes no longer satisfy the condition $[D]_0 \ll [A]_0$. Therefore, the following modified Drago-Rose equation[21] was employed instead of Eq. 1:

$$\frac{l[D]_0[A]_0}{l\varepsilon_D[D]_0-d} = \frac{[D]_0+[A]_0}{\varepsilon_D-\varepsilon_C} + \frac{1}{K(\varepsilon_D-\varepsilon_C)}, \qquad (2)$$

where l is the optical path-length in cm. Equation 2 is applicable to the equilibrium system of relatively small K. The S-T n→π* absorption was studied only at room temperature (20—23 °C), since the 5-cm cells used did not fit the temperature-regulated cell holder. Figure 8 shows the plot of $(l[D]_0[A]_0)/(l\varepsilon_D[D]_0-d)$ *vs.* $[D]_0+[A]_0$, which gives a good straight-line fit. Here, the value of ε_D is 2.64×10^{-2} mol^{-1} dm^3 cm^{-1}, the molar extinction coefficient obtained at 376 nm in cyclohexane. The K's thus derived are listed in Table 1. Regarding Table 1, it should be emphasized that nearly the same values of K were obtained from the two different absorption regions, that is, the S-S and S-T n→π* absorption regions, and that the ε_C values listed as footnotes are in fairly good agreement with those in the

TABLE 1. THERMODYNAMIC QUANTITIES FOR A 1 : 1 COMPLEX FORMATION OF PYRAZINE WITH HALOMETHANES

	$K^{a)}$ mol^{-1} dm^3	$-\Delta H$ kJ mol^{-1}	$-\Delta S$ J mol^{-1} K^{-1}
CCl_4-system			
S-S absorption			
327.5 nm$^{b)}$	0.29^a 0.24^b 0.22^c 0.19^d	15	63
S-T absorption			
376 nm$^{b)}$	0.32^e		
$CHCl_3$-system			
S-S absorption			
327.5 nm$^{b)}$	1.04^a 0.73^c 0.56^d 0.47^f	23	78
321.5 nm$^{b)}$	1.06^a 0.76^c 0.58^d 0.43^f		
S-T absorption			
376 nm$^{b)}$	0.90^e		
CH_2Cl_2-system			
S-S absorption			
327.5 nm$^{b)}$	0.84^a 0.68^c 0.59^d 0.54^g	13	44
321.5 nm$^{b)}$	0.72^a 0.65^c 0.58^d 0.52^g		
S-T absorption			
376 nm$^{b)}$	0.69^e		

a) The K values cited above were obtained at the following temperatures: *a*: 20 °C, *b*: 25 °C, *c*: 30 °C, *d*: 40 °C, *e*: 20—23 °C, *f*: 50 °C, *g*: 48 °C. b) The ε_c values obtained at 327.5 nm are 635, 400, and 560 mol^{-1} dm^3 cm^{-1} for the carbon tetrachloride, chloroform, and dichloromethane systems, while those at 321.5 nm are 613 and 676 mol^{-1} dm^3 cm^{-1} for the latter two systems. Those at 376 nm are *ca.* 1.5×10^{-2} mol^{-1} dm^3 cm^{-1} for the first system, and *ca.* 1.1×10^{-2} mol^{-1} dm^3 cm^{-1} for both the latter two systems.

pure halomethanes.

The results of the absorption measurements can be summarized as follows: (1) When the solvent is changed from hydrocarbon to halomethane, the pyrazine absorption due to the S-S $\pi \rightarrow \pi^*$ transition does not undergo any substantial change, showing only a slight red shift and a little increase in intensity. (2) On the other hand, the S-S and S-T $n \rightarrow \pi^*$ absorptions exhibit remarkable changes, indicating specific interaction of the non-bonding electrons of pyrazine with the halomethanes. (3) By use of the cyclohexane–halomethane mixed solvents, reasonable values could be obtained for the equilibrium constant in the 1 : 1 complex formation between pyrazine and the halomethanes.

In the case of the carbon tetrachloride system, the complex is most probably of the charge-transfer type, whereas in the chloroform and dichloromethane systems, the complexes may be due to charge transfer, hydrogen bonding, or to a combination of both of them. In this connection, we have undertaken a study of the phosphorescence spectra in the ternary systems investigated in this work, and obtained some significant results concerning the charge transfer nature of the complexes. These will be discussed in a separate, subsequent paper.[22)]

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