Interaction between Pyrazine and Halomethanes. II. Effects of Halomethanes on the Phosphorescence of Pyrazine at 77 K

Tatsuaki KUROI,* Yasuhiko GONDO,** Masamichi KUWABARA,**
Ryoichi SHIMADA,** and Yoshiya KANDA**

Chemical Institute, Faculty of Education, Oita University, Dannoharu, Oita 870-11
***Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812*

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The phosphorescence and phosphorescence excitation spectra of pyrazine have been studied at 77 K in various mixed solvents of cyclohexane and halomethanes such as carbon tetrachloride, chloroform, and dichloromethane. When the halomethane concentration was low (below 10^{-2} mol dm^{-3}), only the cyclohexane-phase phosphorescence was observed at 77 K; the lower energy components of the well-known doublet band series in the cyclohexane-phase phosphorescence were found to decrease in intensity relative to the higher energy components, with increasing concentration of halomethane. When the halomethane concentration was raised to a range higher than 10^{-1} mol dm^{-3}, where the complex formation between pyrazine and the halomethanes was confirmed through absorption spectroscopy,[1] new phosphorescence bands appeared in the 373—375 nm region for all the systems studied. With further increase of the halomethane concentration, the new bands decreased in intensity or disappeared, and the phosphorescence approached to those in the pure halomethanes. Comparison of the absorption and phosphorescence excitation spectra shows that the new phosphorescence bands result from the 1 : 1 pyrazine–halomethane complexes. The possibility of hydrogen-bonding species formation with chloroform and dichloromethane has been discussed in the light of the phosphorescence spectra studied in the ethanol–cyclohexane mixed solvents.

The phosphorescence spectrum of pyrazine has been extensively studied in various crystalline matrices, rigid glasses, neat crystals, and in the vapor phase.[2–11] One of the unresolved problems is the anomalous phosphorescence of pyrazine observed by Shimada[2] in carbon tetrachloride matrix at 90 K. The phosphorescence shows doublet band-series structure, suggesting the existence of two different kinds of emitters with a separation of 290 cm^{-1}.[3,11] To explore the nature of the doublet structure, McDonald *et al.*[8] investigated the phosphorescence and absorption of pyrazine in carbon tetrachloride and in neat crystals at 77 K. From comparison of the phosphorescence and absorption spectra, they attributed the higher-energy components with origin at 377.4 nm to molecular pyrazine and the lower-energy components with origin at 381.4 nm to microcrystals of pyrazine. It should be noted that their measurements were restricted to concentrations higher than 10^{-4} mol dm^{-3}. In carbon tetrachloride at 77 K, the doublet band-series structure has been found to persist even at a concentration as low as 10^{-7} mol dm^{-3}, where the molecular aggregates or microcrystals are quite unlikely to occur. The anomalous phosphorescence should thus be attributed to a specific interaction between pyrazine and carbon tetrachloride. Such a specific interaction between pyrazine and the halomethanes, carbon tetrachloride, chloroform, and dichloromethane, is the main subject of this work. In order to examine the possibility of hydrogen-bond formation of pyrazine with chloroform and dichloromethane, we have also studied in detail the effect of ethanol on the phosphorescence of pyrazine.

Experimental

Pyrazine and all the solvents used were obtained from Wako Pure Chem. Ind., Ltd. The purification of the chemicals was described in the preceding paper.[1]

Measurements of the phosphorescence and phosphorescence excitation spectra were carried out with a Shimadzu RF-502 spectrophotofluorometer equipped with a cylindrical sector. The slit widths of 0.4 and 1.0 nm were adopted for the excitation and analyzing monochromators, respectively. It is often pointed out that the structures of the low-temperature spectra depend on the method of sample cooling. In this study, rapid cooling was adopted in order to diminish the possibility of formation of molecular aggregates in the course of cooling, since we intended to compare the results in this study with those of the preceding room-temperature study on the complex formation.[1]

Results and Discussion

General Remarks. In order to study the effect of the halomethanes on the phosphorescence spectrum of pyrazine, we have studied the ternary systems consisting of pyrazine, halomethane, and cyclohexane, where the halomethane is carbon tetrachloride, chloroform, or dichloromethane. For the convenience of discussion, the ternary system containing carbon tetrachloride, for example, will be referred to as the carbon tetrachloride system, following the preceding paper.[1] For comparison, we have also studied the ternary system containing ethanol in place of halomethane; this will be referred to as the ethanol system.

Phosphorescence of Pyrazine in Cyclohexane Matrix at 77 K. The phosphorescence spectrum of pyrazine in cyclohexane matrix at 77 K was observed and reexamined as a reference spectrum in some detail to determine the excitation-wavelength and solute-concentration dependences. Figure 1 shows the variation of the phosphorescence spectra with increasing wavelength of the excitation in the S-S $n \rightarrow \pi^*$ absorption region. The general spectral appearance is quite similar to that reported previously.[3] As is seen in Fig. 1, the pyrazine phosphorescence consists of a doublet band-series structure, in which the origins are located at 377 and 378 nm for the higher and lower energy components, respectively. In addition, we could observe separately the excitation spectra for the higher and lower energy

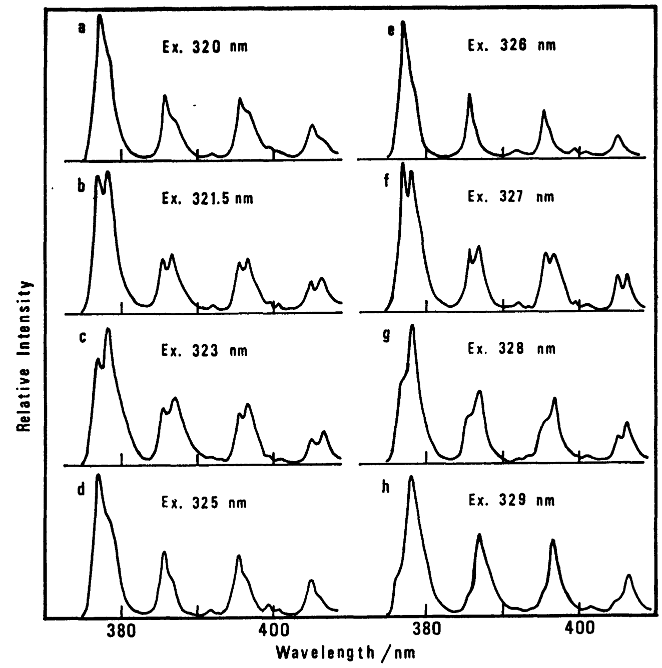

Fig. 1. Excitation-wavelength dependence of the phosphorescence spectrum of pyrazine in cyclohexane matrix at 77 K. Concentration of pyrazine: 1.647 × 10^{-4} mol dm^{-3}.

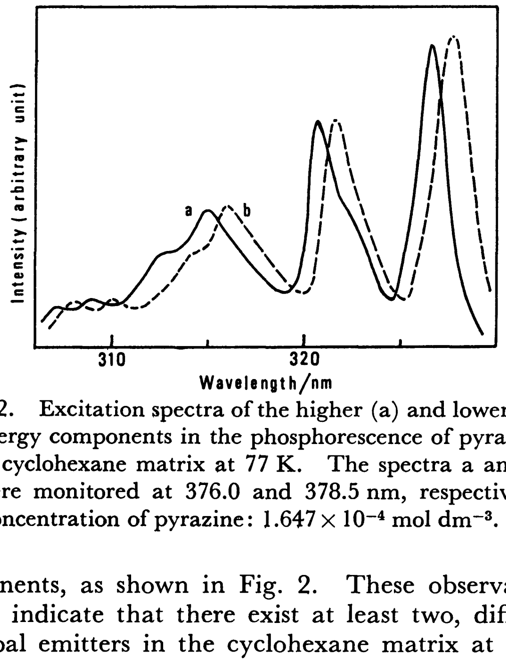

Fig. 2. Excitation spectra of the higher (a) and lower (b) energy components in the phosphorescence of pyrazine in cyclohexane matrix at 77 K. The spectra a and b were monitored at 376.0 and 378.5 nm, respectively. Concentration of pyrazine: 1.647 × 10^{-4} mol dm^{-3}.

components, as shown in Fig. 2. These observations clearly indicate that there exist at least two, different principal emitters in the cyclohexane matrix at 77 K. For the concentrations of pyrazine in the range of 10^{-7}—10^{-4} mol dm^{-3}, the phosphorescence spectrum remained essentially unchanged. Accordingly, we conclude that, in a cyclohexane solution of the order of 10^{-4} mol dm^{-3}, microcrystals or molecular aggregates are not formed at 77 K, contrary to the statement of McDonald *et al.*[8]

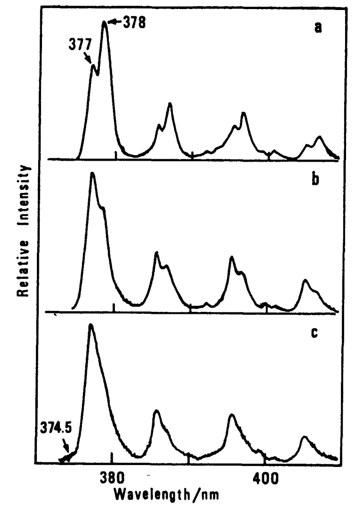

Fig. 3. Spectral changes of the pyrazine phosphorescence excited at 324 nm with the concentration variation of carbon tetrachloride from 10^{-3} to 10^{-1} mol dm^{-3} in the carbon tetrachloride–cyclohexane mixed solvents at 77 K. Concentration of pyrazine: 1.647 × 10^{-4} mol dm^{-3}. Concentration of carbon tetrachloride: (a) 1.494 × 10^{-3}, (b) 1.494 × 10^{-2}, (c) 1.494 × 10^{-1} mol dm^{-3}.

Phosphorescence of Pyrazine in the Ternary System Consisting of Pyrazine, Carbon Tetrachloride, and Cyclohexane at 77 K. Figure 3 shows the effect of carbon tetrachloride on the phosphorescence spectra of pyrazine excited at 324 nm; the relative intensities of the lower and higher energy components, both inherent to the cyclohexane-phase phosphorescence as given in Fig. 1, show a systematic change for the carbon tetrachloride concentrations ranging from the order of 10^{-3} to 10^{-1} mol dm^{-3}; namely, with increasing carbon tetrachloride concentration, the lower energy components of the cyclohexane-phase phosphorescence decrease in relative intensity compared to the higher energy ones. As the concentration of carbon tetrachloride was increased to 10^{-1} mol dm^{-3}, a new phosphorescence band appeared around the 374—375 nm region as a very weak shoulder, and the spectral structure became rather obscure. Quite similar spectral changes were also observed for various excitation wavelengths other than 324 nm in the S-S $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ absorption regions. Therefore, it may be concluded that the doublet band series in the cyclohexane-phase phosphorescence depends not only on the excitation wavelength (Fig. 1), but also on the concentration of carbon tetrachloride (Fig. 3).

On the other hand, when the carbon tetrachloride concentration was increased up to just the same concentrations (in the range 0.562—9.233 mol dm^{-3}) as those used in the preceding paper on the complex formation,[1] the phosphorescence exhibited some complicated and interesting spectral features, as shown in Fig. 4; the pyrazine concentration was kept constant at 1.647 × 10^{-4} mol dm^{-3}. Such phosphorescence results strongly depend on the excitation wavelengths as well as the carbon tetrachloride concentrations. The excitations at 310, 323, and 324 nm show that the shoulder band in the 374—375 nm region grows with increasing concentration of carbon tetrachloride in the range of 0.5 to 2.0 mol dm^{-3}. In the preceding paper,[1] this concentration range was found to be the most suitable for the observation of the complex formation between pyrazine and carbon tetrachloride. Thus, the shoulder band in the 374—375 nm region seems to have a close connec-

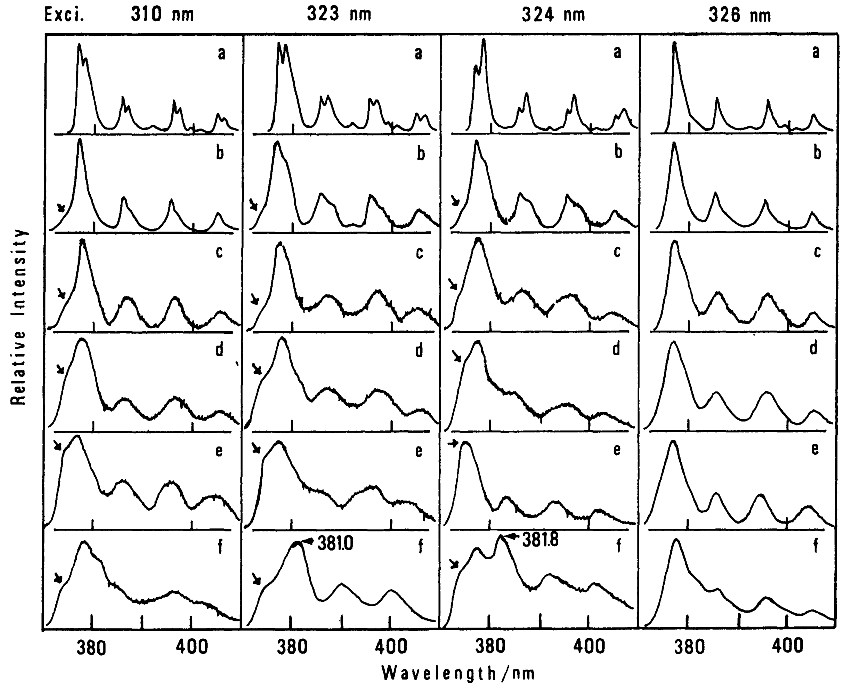

Fig. 4. Spectral changes of the pyrazine phosphorescence in the carbon tetrachloride–cyclohexane mixed solvents at 77 K excited at various wavelengths with the concentration variation of carbon tetrachloride over the range closely related to the complex formation. Concentration of pyrazine: 1.647×10^{-4} mol dm^{-3}. Concentration of carbon tetrachloride: (a) 0, (b) 0.517,(c) 1.022, (d) 1.530, (e) 2.048, (f) 9.223 mol dm^{-3}.

tion with the 1 : 1 charge-transfer complex. At the much higher concentrations, as is seen particularly in the phosphorescence spectra excited at 323 and 324 nm in Fig. 4, the 375-nm band is weaker and then there appears the doublet band-series structure with the origins at 378 and 382 nm, characteristic of the phosphorescence spectrum of pyrazine in carbon tetrachloride matrix at 77 K.

The phosphorescence excitation spectra monitored at the 375-, 378-, and 382-nm bands exhibit the first bands at 324.6, 327, and 330 nm, respectively, as shown in Fig. 5. Thus, the excitation spectra disclose that there are three principal kinds of phosphorescent species in the cyclohexane–carbon tetrachloride mixed solvents at 77 K, when the carbon tetrachloride concentrations are higher than *ca.* 0.5 mol dm^{-3}. Since the excitation spectrum responsible for 375-nm phosphorescence band is in good accord with the blue-shifted absorption spectrum of pyrazine observed in carbon tetrachloride at room temperature,[1)] we suggest that the species giving rise to the 375-nm band is the 1 : 1 charge-transfer complex; the phosphorescence of the 375-nm species is much lower in intensity compared with those of the other species.

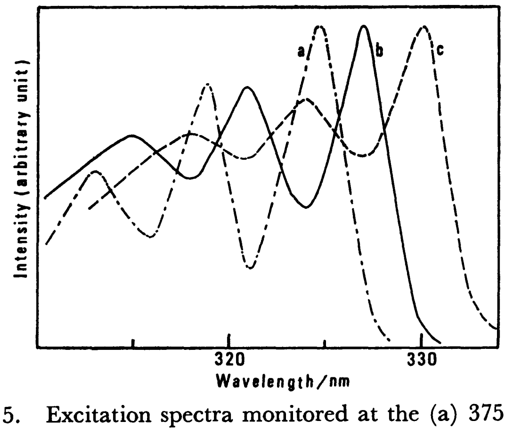

Fig. 5. Excitation spectra monitored at the (a) 375, (b) 378, and (c) 382 nm bands of the phosphorescence of pyrazine in the carbon tetrachloride–cyclohexane mixed solvents at 77 K. Concentration of pyrazine: (a) 1.647×10^{-4}, (b) and (c) 1.444×10^{-4} mol dm^{-3}. Concentration of carbon tetrachloride: (a) 1.530 mol dm^{-3}, (b) and (c) 90 vol%.

Phosphorescence of Pyrazine in the Ternary System Consisting of Pyrazine, Chloroform, and Cyclohexane at 77 K. Excitation-wavelength and chloroform-concentration dependences were also studied for the chloroform system in which the chloroform concentration was varied over the range 10^{-3}—1 mol ~~dm~~$^{-3}$. Figure 6 shows the phosphorescence spectra excited at 323 nm; with increasing chloroform concentration, the lower energy components of the cyclohexane-phase phosphorescence decrease in relative intensity compared to the higher energy ones; this result is similar to the case of the carbon tetrachloride system. In this system, one can already see new phosphorescence bands, with the origin at 374.5 nm, at the chloroform concentrations of the order of 10^{-2} mol dm^{-3}. This is consistent with the results of the preceding study on the complex formation; the equilibrium constant for the chloroform

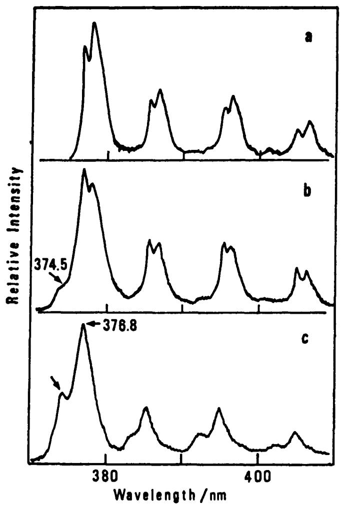

Fig. 6. Spectral changes of the pyrazine phosphorescence excited at 323 nm with the concentration variation of chloroform from 10^{-3} to 10^{-1} mol dm^{-3} in the chloroform–cyclohexane mixed solvents at 77 K. Concentration of pyrazine: 1.647×10^{-4} mol dm^{-3}. Concentration of chloroform: (a) 1.458×10^{-3}, (b) 1.458×10^{-2}, (c) 1.458×10^{-1} mol dm^{-3}.

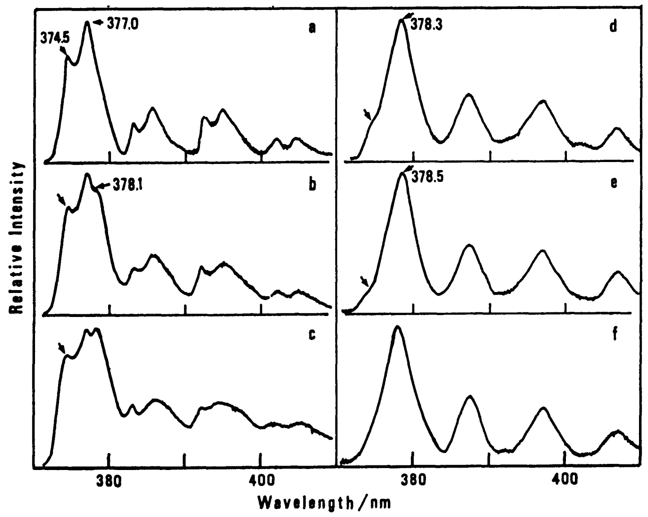

Fig. 7. Spectral changes of the pyrazine phosphorescence in the chloroform–cyclohexane mixed solvents at 77 K excited at 324 nm with the concentration variation of chloroform over the range closely related to the complex formation. Concentration of pyrazine: 1.647 $\times 10^{-4}$ mol dm^{-3}. Concentration of chloroform: (a) 0.219, (b) 0.292, (c) 0.365, (d) 0.693, (e) 0.924, (f) 1.155 mol dm^{-3}.

system is greater than that for the carbon tetrachloride system.[13]

In just the same range of chloroform concentration, 0.2—1.0 mol dm^{-3}, as that studied for the observation of the complex formation,[1] the phosphorescence showed remarkable spectral variations with excitation wavelength and chloroform concentration. The spectra excited at 324 nm are the most typical, and are shown in Fig. 7. In the chloroform concentration of 0.219 mol dm^{-3}, as is seen in Fig. 7, a new phosphorescence band-series with the origin at 374.5 nm clearly appears, while the lower energy components of the cyclohexane-phase phosphorescence completely disappear. With the chloroform concentration of 0.292 mol dm^{-3}, another new phosphorescence band-series, which is quite different both from the 374.5-nm band-series and from the lower energy components of the cyclohexane-phase phosphorescence, begins to appear around 378 nm, while the higher energy components of the cyclohexane-phase phosphorescence eventually disappear with increasing chloroform concentration. When the chloroform concentration is raised to 0.462 mol dm^{-3}, either the 323- or the 324-nm excitation gives exclusively the two new band-series with the origins at 374.5 and 378 nm. With further increase of the chloroform concentration, the intensity of the 374.5-nm band-series decreases; at the concentration of 1.155 mol dm^{-3}, the spectrum is close to that characteristic of the chloroform matrix at 77 K. The new band-series with the origin at 378 nm can thus be attributed to the chloroform-phase phosphorescence in the mixed solvent at 77 K.

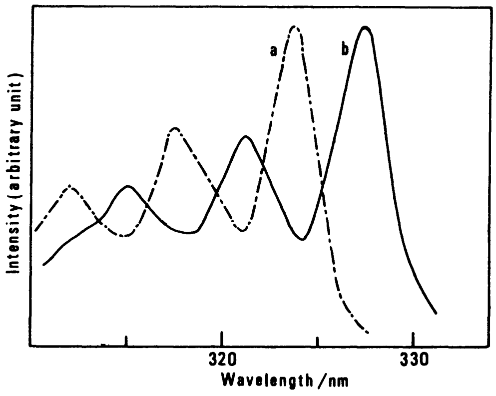

Fig. 8. Excitation spectra of the pyrazine phosphorescence monitored at (a) 373 and (b) 378 nm for the chloroform–cyclohexane mixed solvents at 77 K. Concentration of pyrazine: 8.564×10^{-4} mol dm^{-3}. Concentration of chloroform: 0.462 mol dm^{-3}.

Figure 8 shows the phosphorescence excitation spectra monitored at 373 and 378 nm for the chloroform concentration of 0.462 mol dm^{-3}; the two phosphorescence band-series with the origins at 374.5 and 378 nm are evidently attributable to different emitters. The excitation spectrum responsible for the 374.5-nm phosphorescence band is also blue-shifted in accord with the blue-shifted absorption spectrum in chloroform at room temperature, quite similarly to the case of the carbon tetrachloride system. It should also be noted that the 374.5-nm phosphorescence band-series appears with the strongest intensity in just the same range of chloroform concentration as that suitable for the observation of the 1 : 1 complex formation.[1]

Phosphorescence of Pyrazine in the Ternary System Consisting of Pyrazine, Dichloromethane, and Cyclohexane at 77 K. Figure 9 shows the changes of the phosphorescence spectrum of pyrazine with the increase of the dichloromethane concentration from 10^{-3} to 10^{-1} mol dm^{-3}. In quite a similar manner to the cases of the carbon

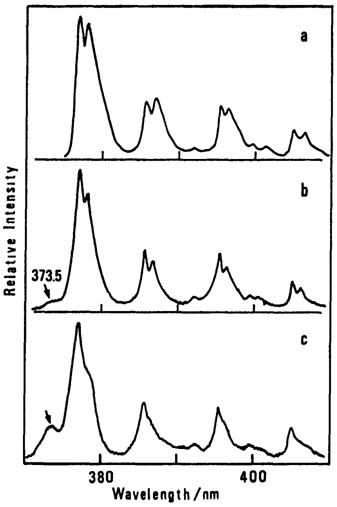

Fig. 9. Spectral changes of the pyrazine phosphorescence excited at 323 nm with the concentration variation of dichloromethane from 10^{-3} to 10^{-1} mol dm^{-3} in the dichloromethane–cyclohexane mixed solvents at 77 K. Concentration of pyrazine: 1.647×10^{-4} mol dm^{-3}. Concentration of dichloromethane: (a) 2.046×10^{-3}, (b) 2.046×10^{-2}, (c) 2.046×10^{-1} mol dm^{-3}.

tetrachloride and chloroform systems, the lower energy components of the cyclohexane-phase phosphorescence decrease with increasing concentration of dichloromethane. At the dichloromethane concentration of 2.0×10^{-2} mol dm^{-3}, a new phosphorescence band appears around 373.5 nm, as in the case of the chloroform system; this reflects the fact that nearly the same equilibrium constants for the complex formation are obtained in both systems at room temperature.[13]

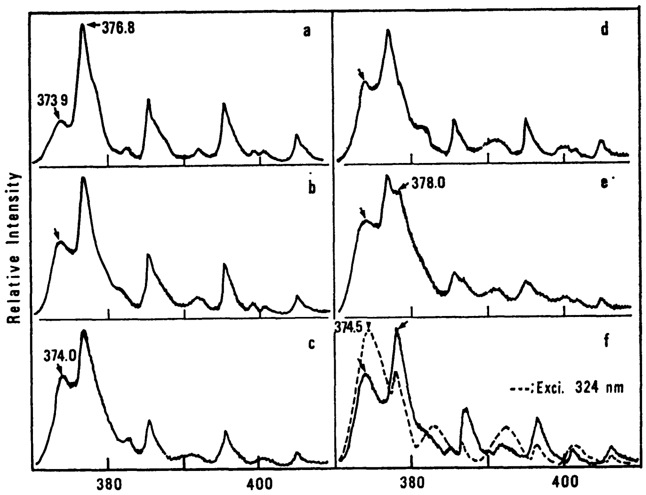

Fig. 10. Spectral changes of the pyrazine phosphorescence in the dichloromethane–cyclohexane mixed solvents at 77 K excited at 323 and/or 324 nm with the concentration variation of dichloromethane over the range closely related to the complex formation. Concentration of pyrazine: 1.444×10^{-4} mol dm^{-3}. Concentration of dichloromethane: (a) 0.255, (b) 0.511, (c) 0.766, (d) 1.021, (e) 1.277, (f) *ca.* 14 mol dm^{-3}.

Figure 10 shows the spectral changes of the phosphorescence excited at 323 and/or 324 nm with the increase of the dichloromethane concentration over just the same range as that studied on the complex formation.[1] At the concentration of 1.277 mol dm^{-3}, another new phosphorescence band appears as a shoulder at 378 nm. As in the cases of the carbon tetrachloride and chloroform systems, the new band is attributed to the dichloromethane-phase phosphorescence in the mixed solvent. In the dichloromethane concentration of about 14 mol dm^{-3}, either the 323-nm or the 324-nm excitation, even with very narrow slit width, no longer gives the higher energy components of the cyclohexane-phase phosphorescence, but gives exclusively the two new phosphorescence band-series mentioned above. The 374-nm band is somewhat dependent on the excitation wavelengths, as is seen in Fig. 10 (f); the 323- and 324-nm excitations give the bands at 373.8 and 374.5 nm, respectively. The excitation spectra monitored at 374 and 378 nm are quite similar to those of the carbon tetrachloride and chloroform systems; the excitation spectrum responsible for the 374-nm phosphorescence band is in accord with the blue-shifted absorption spectrum of pyrazine in dichloromethane at room temperature. Consequently, the 374-nm phosphorescence band can also be closely related to the 1 : 1 complex formation observed in the preceding study.[1]

Phosphorescence of Pyrazine in the Ternary System Consisting of Pyrazine, Ethanol, and Cyclohexane at 77 K. It is generally accepted that pyrazine in the ground state forms a hydrogen bond with ethanol. The ethanol system has been studied in order to examine whether the complexes in the chloroform and dichloromethane systems are of the charge-transfer type or the hydrogen-bonding one. Figure 11 shows the spectral changes of the phosphorescence excited at 323 nm with the increase of the ethanol concentration from 10^{-3} to 10^{-1} mol dm^{-3};

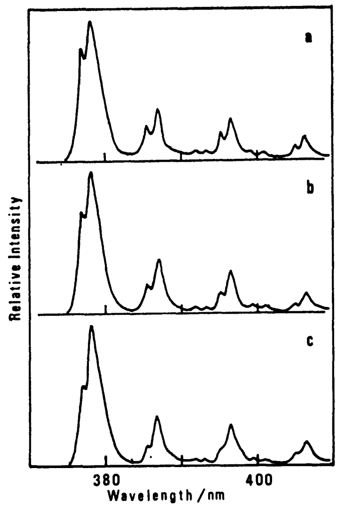

Fig. 11. Spectral changes of the pyrazine phosphorescence excited at 323 nm with the concentration variation of ethanol from 10^{-3} to 10^{-1} mol dm^{-3} in the ethanol–cyclohexane mixed solvents at 77 K. Concentration of pyrazine: 1.647×10^{-4} mol dm^{-3}. Concentration of ethanol: (a) 2.018×10^{-3}, (b) 2.018×10^{-2}, (c) 2.018×10^{-1} mol dm^{-3}.

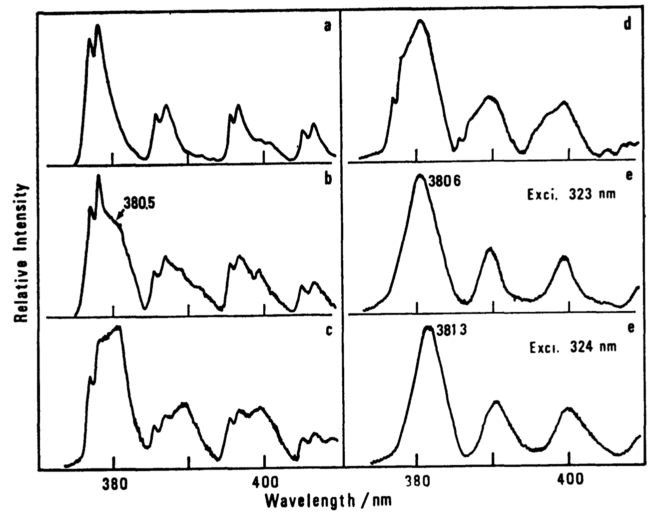

Fig. 12. Phosphorescence spectra of pyrazine excited at 323 and/or 324 nm in the ethanol–cyclohexane mixed solvents at 77 K. Concentration of pyrazine: 1.647×10^{-4} mol dm^{-3}. Concentration of ethanol: (a) 0.404, (b) 0.605, (c) 1.009, (d) 1.715 mol dm^{-3}, and (e) 90 vol%.

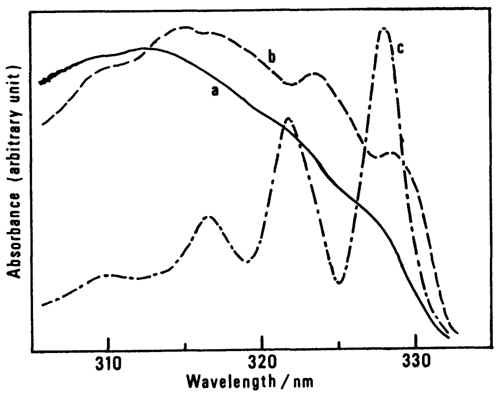

Fig. 13. Absorption and phosphorescence excitation spectra of pyrazine in the ethanol-containing mixed solvents. The absorption spectra a and b were obtained at room temperature and 77 K, respectively, in the mixed solvent of 93 vol% ethanol and 7 vol% methylcyclohexane. The excitation spectrum c monitored at 378 nm was obtained in the mixed solvent of 90 vol% ethanol and 10 vol% cyclohexane. Concentration of pyrazine: (a) and (b) 1.156×10^{-3}, (c) 1.647×10^{-4} mol dm^{-3}.

quite contrary to the cases of the halomethane systems, the lower energy components of the cyclohexane-phase phosphorescence increase in intensity relative to the higher energy ones with increasing ethanol concentration. Figure 12 shows the phosphorescence spectra at the ethanol concentrations ranging from 0.404 to 1.715 mol dm^{-3}. In contrast to the halomethane systems, the ethanol system shows no bands at wavelengths shorter than the higher energy components of the cyclohexane-phase phosphorescence. At ethanol concentrations higher than 0.605 mol dm^{-3}, new bands appear with their origin in the region 380—381 nm. Since the new phosphorescence bands are characteristic of the phosphorescence of pyrazine in ethanol glass at 77 K, they are attributed to the ethanol-phase phosphorescence in the mixed solvent. At a much higher ethanol concentration, 90% by volume, only the ethanol-phase phosphorescence has been observed, as shown in Fig. 12.

In order to examine the phosphorescence efficiences in the hydrogen bonding species, the phosphorescence excitation spectrum, curve c in Fig. 13, has been observed and compared with the absorption spectrum. The absorption spectrum of pyrazine in ethanol at room temperature loses some vibrational structure with blue shift of the spectrum due to hydrogen bonding; this is shown in Fig. 13 as curve a. The absorption spectrum at 77 K, curve b in Fig. 13, exhibits vibrational structure as shoulders at wavelengths longer than the vibrational bands observed in hydrocarbon solvents at room temperature. The absorption spectrum at 77 K is very similar to that observed at the same temperature by Krishna *et al.*[14] The phosphorescence excitation spectrum is apparently different from the absorption spectrum at 77 K. A comparison of the excitation and absorption spectra at 77 K indicates that the phosphorescence in ethanol at least mainly comes from the species which have vibrational structure in the absorption spectrum at 77 K. Therefore, it may be concluded that most of the hydrogen bonding species have very low phosphorescence efficiencies.

Krishna *et al.* proposed that the hydrogen bond was broken in the excited state, and hence the observed phosphorescence spectrum was consistent with the absence of hydrogen bonding in the triplet state; they did not perform any excitation spectrum measurement, however. Combining the results of Krishna *et al.* with our observations, the phosphorescence of pyrazine in ethanol at 77 K is thought to be emitted chiefly from the non-hydrogen bonding species, while the pyrazine molecules are modified by specific interactions such as cohesive forces between the solvent molecules or between the solute and solvent molecules. Thus, the phosphorescence bands observed around the region 373—374 nm in the chloroform and dichloromethane systems would not be attributed to hydrogen bonding species, but to the 1 : 1 charge-transfer complex species.

Origin of the New Phosphorescence Bands in the 373—375 nm Region. With the same halomethane concentrations as those suitable for the observation of the complex formation,[1] every halomethane system exhibits new phosphorescence bands with the origin in the 373—375 nm region; these are obviously different from the normal phosphorescence bands in the pure halomethane at 77 K. The 373—375 nm phosphorescence bands appear most clearly at the following halomethane concentrations: 2.048 mol dm^{-3} for the carbon tetrachloride system (Fig. 4, curve e; excited at 324 nm), 0.365 mol dm^{-3} for the chloroform system (Fig. 7, curve c; excited at 324 nm), and 0.766—1.021 mol dm^{-3} for the dichloromethane system (Fig. 10, curves c and d; excited at 323 nm). It has been previously established that the equilibrium constants for the complex formation increase in the order of carbon tetrachloride, dichloromethane, and chloroform systems.[13] Accordingly, the chloroform and dichloromethane systems start to exhibit the new 373—375 nm bands at relatively low halomethane concentrations ($\approx 10^{-2}$ mol dm^{-3}) compared to the carbon tetrachloride system, as is seen in curve b of Fig. 6 and curve b of Fig. 9, respectively.

In addition, the excitation spectra of the 373—375 nm bands are blue-shifted in accord with the blue-shifted absorption spectra in the halomethane systems at room temperature. It should be emphasized that the results of the chloroform and dichloromethane systems are quite similar to those of the carbon tetrachloride system where no hydrogen-bonding species occurs. In contrast to the halomethane systems, the ethanol system exhibits no new phosphorescence bands in the 373—375 nm region. As for the relative intensities of the two well-known band series in the cyclohexane-phase phosphorescence of pyrazine, the halomethane systems show changes opposite to those in the ethanol system, with the increase of the halomethane and ethanol concentrations from 10^{-3} to 10^{-1} mol dm^{-3}, as is seen in Figs. 3, 6, 9, and 11. Thus, the halomethane effects on the phosphorescence of pyrazine differ from those of ethanol, and in particular the hydrogen-bonding species are independent of the appearance of the new 373—375 nm bands. In view of these observations, it is concluded that the new phosphorescence bands observed in the 373—375 nm region in the halomethane systems result from the 1 : 1 charge-transfer complexes.

References

1) Preceding paper in this series: Part I, T. Kuroi, Y. Gondo, M. Kuwabara, R. Shimada, and Y. Kanda, *Bull. Chem. Soc. Jpn.*, **54**, 2243 (1981).

2) L. Goodman and M. Kasha, *J. Mol. Spectrosc.*, **2**, 58 (1958).

3) R. Shimada, *Spectrochim. Acta*, **17**, 14 (1961).

4) M. A. El-Sayed and G. W. Robinson, *Mol. Phys.*, **4**, 273 (1961).

5) L. M. Logan and I. G. Ross, *J. Chem. Phys.*, **43**, 2903 (1965).

6) W. R. Moomaw and M. A. El-Sayed, *J. Chem. Phys.*, **45**, 3890 (1966).

7) W. R. Moomaw and M. A. El-Sayed, *J. Chem. Phys.*, **48**, 2502 (1968).

8) R. J. McDonald, L. M. Logan, I. G. Ross, and B. K. Selinger, *J. Mol. Spectrosc.*, **40**, 137 (1971).

9) I. Suzuka and M. Ito, *Bull. Chem. Soc. Jpn.*, **45**, 2323 (1972).

10) C. J. Marzzacco and E. F. Zalewski, *J. Mol. Spectrosc.*, **43**, 239 (1972).

11) E. F. Zalewski, D. S. McClure, and D. L. Narva, *J. Chem. Phys.*, **61**, 2964 (1974).

12) M. Kuwabara, Master of Science Thesis, Kyushu University, March 1973.

13) For example, the equilibrium constants for complex formation at 20 °C are 0.29, 1.04, and 0.84 dm^3 mol^{-1} for the carbon tetrachloride, chloroform, and dichloromethane systems, respectively; see Ref. 1.

14) V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **33**, 381 (1960).