Emission Studies of Pyrazine in the Gas Phase

Kenichiro Nakamura[1]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received September 30, 1970*

Abstract: The emission of pyrazine in the gas phase has been studied. Pyrazine emits both fluorescence and phosphorescence, and their yields are determined to be $(1.74 \pm 0.08) \times 10^{-3}$ and $(1.70 \pm 0.08) \times 10^{-3}$ at 313 nm, respectively. Both emission yields decrease with decreasing wavelength of excitation and are zero in the $\pi-\pi^*$ band. However, the ratio of fluorescent yield to phosphorescent yield is independent of the exciting wavelength. Pyrazine emits phosphorescence when sensitized by benzene and can be used for triplet yield measurements of benzene. This sensitized-phosphorescence method for pyrazine shows the benzene triplet yield to be 0.69 ± 0.07 at (252 ± 1) nm.

Emission and spectroscopic studies of pyrazine (1,4-diazine) in the solid and liquid phases have been discussed by many authors.[2-4] However, few studies are reported for pyrazine in the gas phase and no emission yield of pyrazine in the gas phase has been reported. In this paper both triplet and singlet emission yields of pyrazine have been determined, and the sensitized emission from pyrazine is also discussed.

Electronic states of pyrazine have been calculated by many authors.[2b,5-8] Pyrazine has two absorption bands, an $n-\pi^*$ and a $\pi-\pi^*$ transition.[5,9] Goodman[2a] has found a weak absorption ($f = 10^{-6}$–10^{-7}) at 370 nm in pyrazine and assigns it to a spatially allowed electronic dipole transition. He[3] has also calculated the rates of radiationless transitions, internal conversion, and intersystem crossing, and shows that the fast intersystem crossing in pyrazine is due to the $S(n-\pi^*)$ (30,175 cm^{-1}) $\rightarrow$ $T(\pi-\pi^*)$ transition (28,238 cm^{-1}). Phosphorescent emission comes from the lowest triplet state, $T(n-\pi^*)$ (26,545 cm^{-1}), after internal conversion $T(n-\pi^*) \leftarrow T(\pi-\pi^*)$. Intersystem crossing in pyrazine is sufficiently fast[4] to give a triplet yield of almost unity, as determined by the biacetyl method.[10]

Pyrazine is a relatively stable compound compared to biacetyl, which emits phosphorescence but also dissociates at short wavelengths and at higher temperatures.[11,12] Both isomerization and polymer formation have been found in previous photochemical investigations of pyrazine.[13] The quantum yields of these processes are negligibly small in the $n-\pi^*$ band but are of the order of 10^{-2} in the $\pi-\pi^*$ band.

Experimental Section

Aldrich Chemical Co. pyrazine, purified, was recrystallized seven times from its ether solution. A Perkin-Elmer F-11 flame ionization capillary gas chromatograph operated at 60° with an MBMA 125-cm column showed no impurity peak after the recrystallizations (impurity in the recrystallized sample was estimated to be less than one part in 10^6). The recrystallized pyrazine was stored in the dark at low temperature.

The emission cell and optical systems employed in this study were the same as described in the previous paper.[14] The samples were excited by a Hanovia 1 KW Hg–Xe lamp through a Jarrell-Ash 0.25-m monochromator with 2-mm slits (band pass of 7.2 nm). Emission spectra were detected by the EMI 6255B photomultiplier through a Jarrell-Ash 0.75-m spectrometer with 2-mm slits (band pass of 1.6 nm).

Emission yields of pyrazine were determined by a relative method where the fluorescent yield of benzene was used as a standard. The value of the fluorescent yield of benzene is taken as 0.183 at 253 nm in this paper.[15] The spectral responses of the RCA 935 phototube used for measurement of transmitted light and of the EMI 6255B used for detection of emission were obtained by comparison with a Charles M. Reeder, Inc. thermocouple, Model RBL-500.

Results and Discussion

The absorption spectrum of pyrazine vapor has been measured by Halverson and Hirt,[16] and a detailed vibrational analysis is given by Ito, *et al.*[17] However, no spectra of pyrazine vapor together with extinction coefficients are shown in those papers. In order to obtain the radiative lifetime of pyrazine vapor, the absorption spectrum has been measured; the results are shown in Figure 1. A mean wave number of 32,200 cm^{-1} and an integrated extinction coefficient of 1.61×10^6 mol^{-1} l. cm^{-1} in the $n-\pi^*$ band are calculated from this figure. The radiative lifetime computed from these data is 210 nsec. With $Q_f = 1.7 \times 10^{-3}$ (which will be discussed later), the true lifetime of the first excited singlet of pyrazine is 0.36 nsec.

The emission spectrum of pyrazine at 3 Torr is shown in Figure 2. In the solid phase at low temperature pyrazine shows a very weak singlet emission and a strong triplet emission.[2b,4] Goodman[3] has reported that the quantum yields of fluorescence and phosphorescence of pyrazine in *n*-pentane–methylcyclohexane (1:2) at 77°K are 0.0006 and 0.30, respectively. However, it is seen from Figure 2 that the intensity of

---

(1) Supported by the Robert A. Welch Foundation.

(2) (a) L. Goodman and M. Kasha, *J. Mol. Spectrosc.*, **2**, 58 (1958); (b) L. Goodman, *ibid.*, **6**, 109 (1961).

(3) M. J. Cohen and L. Goodman, *J. Chem. Phys.*, **46**, 713 (1967).

(4) M. H. El-Sayed, *ibid.*, **36**, 573 (1962); **38**, 2834 (1963).

(5) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

(6) R. McWheeny and T. E. Reacock, *Proc. Phys. Soc., London, Sect. A*, **70**, 41 (1957).

(7) L. Goodman and R. W. Harrell, *J. Chem. Phys.*, **30**, 1131 (1959).

(8) K. K. Innes, J. P. Byrne, and I. G. Ros, *J. Mol. Spectrosc.*, **22**, 125 (1967).

(9) F. Halverson and R. C. Hirt, *J. Chem. Phys.*, **19**, 711 (1951).

(10) K. Nakamura and W. Roebke, to be submitted for publication.

(11) H. Ishikawa and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **84**, 1502 (1962); *J. Chem. Phys.*, **37**, 583 (1962).

(12) J. Lemaire, *J. Phys. Chem.*, **71**, 2053 (1967).

(13) F. Lahmani, N. Ivanoff, and M. Magat, *C. R. Acad. Sci., Ser. C*, **283**, 1005 (1966); M. Magat, N. Ivanoff, F. Lahmani, and M. Pileni, *J. Chim. Phys.*, 212 (1970), conference on nonradiative transitions, Paris, May 1969.

(14) K. Nakamura, *J. Chem. Phys.*, **53**, 998 (1970).

(15) W. A. Noyes, Jr., W. A. Mulac, and D. A. Harter, *ibid.*, **44**, 2100 (1966).

(16) F. Halverson and R. C. Hirt, *ibid.*, **17**, 1165 (1949).

(17) M. Ito, R. Shimada, T. Kuraishi, and W. Mizushima, *ibid.*, **26**, 1508 (1957).

Table I. Emission Yields of Pyrazine at 3 Torr

	Exciting wavelength, nm				
	326.7	313.0	300.0	290.0	280.0
Φ_f	1.73×10^{-3}	1.74×10^{-3}	1.29×10^{-3}	0.84×10^{-3}	0
Φ_p	1.66×10^{-3}	1.70×10^{-3}	1.28×10^{-3}	0.84×10^{-3}	0
Φ_f/Φ_p	1.05	1.03	1.01	1.00	

fluorescent emission in the gas is almost as strong as that of the phosphorescence emission. This fact is mainly due to the self-quenching of phosphorescence in the gas phase. The true lifetime of singlet pyrazine is much shorter than the time between collisions in the gas phase, while that of the triplet state is longer. Therefore, collisions have an effect on the triplet state but not on the singlet state, and only the intensity of phosphorescence is decreased in the gas phase.

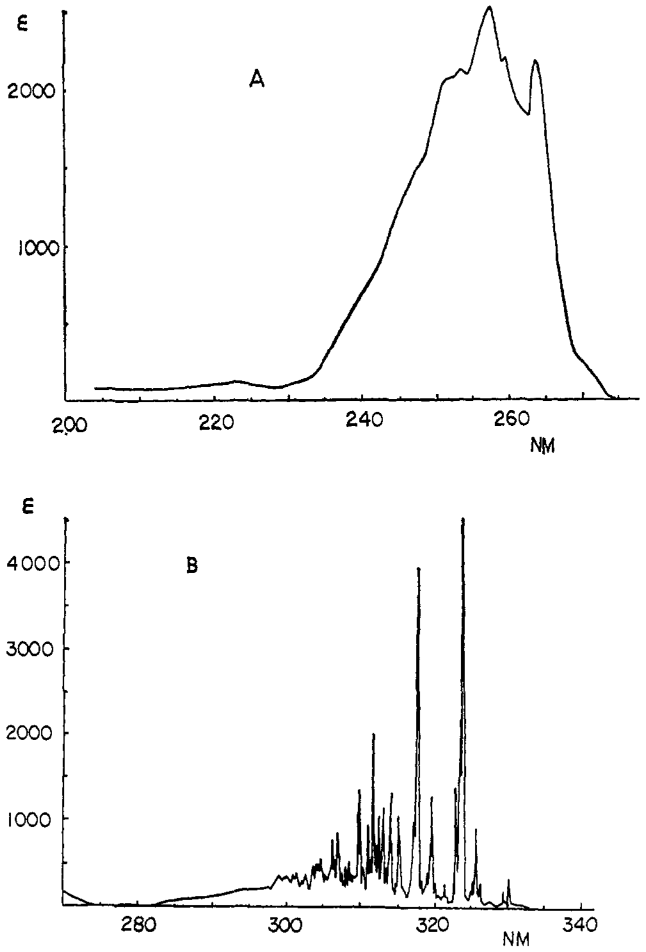

Figure 1. Absorption spectrum of pyrazine at 1 Torr and 27°. The ordinate is the extinction coefficient in mol^{-1} l. cm^{-1}: A, π–π^* region; B, n–π^* region.

The addition of *cis*-butene-2 to pyrazine strongly quenches the phosphorescence. As shown by Figure 2, the phosphorescence is completely quenched by the addition of 100 Torr of *cis*-butene-2. Oxygen has the same effect on the pyrazine emission. It is known that oxygen also quenches the fluorescence of molecules.[18–20] However, the natural lifetime of singlet pyrazine is so short that no quenching of the fluorescence is observed.

Quantum yields of singlet and of triplet emission from pyrazine are shown in Table I. The ratio of fluorescence to phosphorescence, Φ_f/Φ_p, is about unity and independent of the exciting wavelength. Both emission yields decrease with increase of energy of excitation, and no emission could be seen in the π–π^* absorption region. It is well known that an Hg–Xe lamp has no emission at 253 nm because of self-absorption of mercury vapor. Therefore, the emission yield is not strictly accurate because the fluorescent yield of benzene at 253 nm was used for a standard. Some errors are involved in the data shown in Table I, but they should not be important.

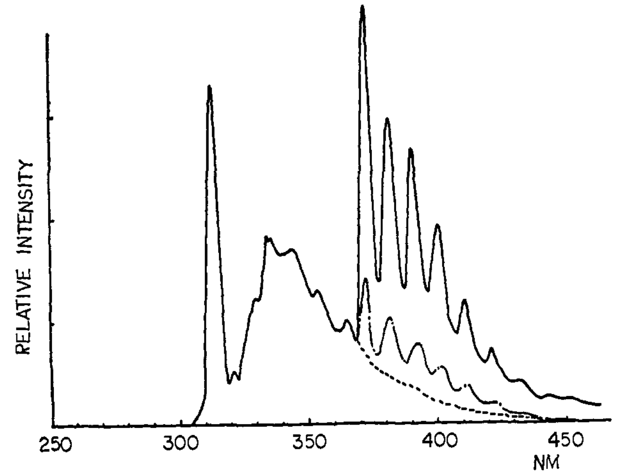

Figure 2. Emission spectrum of pyrazine at 3 Torr, excited at 313 nm. The sharp peak at 313 nm is due to the scattering light: ———, 3 Torr of pyrazine; — — —, 3 Torr of pyrazine + 10 Torr of oxygen; - - - -, 3 Torr of pyrazine + 100 torr of *cis*-butene-2.

Benzene-sensitized emission of pyrazine is shown in Figure 3. Benzene at 20 Torr with 0.1 Torr of pyrazine was excited at 253 nm. The absorption coefficient of pyrazine is very large, as is seen in Figure 1. Therefore, the low pressure of pyrazine vapor still gives a small amount of absorption. However, since the excitation of pyrazine at 253 nm leads to no emission, it can be concluded that the phosphorescence bands seen at long wavelengths in Figure 3 are due to energy transfer from triplet benzene to triplet pyrazine. The addition of isobutane, which efficiently causes vibrational relaxation,[21] to pure pyrazine excited at 253 nm does not lead to any emission. Therefore, the triplet emission from pyrazine in this figure does not come from the direct absorption of pyrazine but from an energy-transfer process. However, in the following calculation of triplet yields, correction is made for this small

(18) A. Morikawa and R. J. Cvetanović, *J. Chem. Phys.*, **52**, 3237 (1970).

(19) C. S. Burton and W. A. Noyes, Jr., *ibid.*, **49**, 1705 (1968).

(20) M. Comtet, *J. Amer. Chem. Soc.*, **92**, 5308 (1970).

(21) C. S. Parmenter and M. W. Schyler, *J. Chem. Phys.*, **52**, 92 (1970).

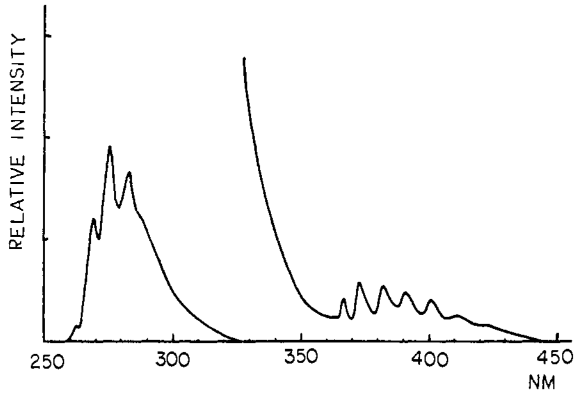

Figure 3. Benzene-sensitized emission of pyrazine excited at 253 nm; benzene pressure, 20 Torr; pyrazine pressure, 0.1 Torr. The sensitivity of the photomultiplier for measurements in the long-wavelength region is 50 times greater than that in the short-wavelength region.

amount of absorption by pyrazine. No sensitized fluorescence from pyrazine could be observed, although strong bands from the fluorescent emission of benzene were superimposed on the same region as that of pyrazine fluorescence.

The benzene-sensitized emission of pyrazine can be described as follows.

$$\mathrm{B} + h\nu \longrightarrow {}^1\mathrm{B} \qquad (1)$$

$${}^1\mathrm{B} \longrightarrow \mathrm{B} + h\nu \qquad (2)$$

$${}^1\mathrm{B} \longrightarrow {}^3\mathrm{B} \qquad (3)$$

$${}^1\mathrm{B} + \mathrm{P} \longrightarrow \mathrm{B} + {}^1\mathrm{P}_\mathrm{v} \qquad (4)$$

$${}^3\mathrm{B} \longrightarrow \mathrm{B} \qquad (5)$$

$${}^3\mathrm{B} + \mathrm{P} \longrightarrow \mathrm{B} + {}^3\mathrm{P} \qquad (6)$$

$${}^1\mathrm{P}_\mathrm{v} \longrightarrow \mathrm{X} \qquad (7)$$

$${}^3\mathrm{P} \longrightarrow \mathrm{P} + h\nu \qquad (8)$$

$$\longrightarrow \mathrm{X} \qquad (9)$$

B and P are benzene and pyrazine molecules, respectively, and ${}^1\mathrm{P}_\mathrm{v}$ is a pyrazine molecule in an upper singlet state in a high vibrational level. It should be noted that ${}^1\mathrm{P}_\mathrm{v}$ must be the upper state of the π–π^* transition. Reactions 7 and 9 represent internal conversion or isomerization.

The fluorescent yield of benzene in the presence of pyrazine is

$$Q_\mathrm{f} = k_2/(k_2 + k_3 + k_4(\mathrm{P})) \qquad (10)$$

and in the absence of pyrazine

$$Q_\mathrm{f}^0 = k_2/(k_2 + k_3) \qquad (11)$$

The triplet yield of benzene monitored by the triplet emission of pyrazine is

$$\Phi_6 = \frac{k_6(\mathrm{P})}{k_5 + k_6(\mathrm{P})}\frac{k_3}{k_2 + k_3 + k_4(\mathrm{P})} = \frac{k_8 + k_9}{k_8}Q_\mathrm{P} \qquad (12)$$

where Φ_6 is the yield of reaction 6 and Q_P is the emission yield from the triplet state of pyrazine when it is sensitized by benzene. $k_8/(k_8 + k_9)$ is the fraction of the triplet pyrazine molecules which emit phosphorescence. Also, $k_6(\mathrm{P})$ must be large compared to k_5.

$$Q_\mathrm{P} = \frac{k_8}{k_8 + k_9}\frac{k_6(\mathrm{P})}{k_5 + k_6(\mathrm{P})}\frac{k_3}{k_2 + k_3 + k_4(\mathrm{P})} \qquad (13)$$

If $Q_\mathrm{P}^0 = k_8/(k_8 + k_9)$, and if when pure pyrazine absorbs radiation all molecules which do not fluoresce cross over to the triplet state (the identical assumption that is made in the biacetyl method)

$$\Phi_\mathrm{t}^0 = (Q_\mathrm{P}/Q_\mathrm{P}^0)(Q_\mathrm{f}^0/Q_\mathrm{f}) \qquad (14)$$

where Φ_t^0 is in this case the true triplet yield of benzene, *i.e.*, without pyrazine present.

Within experimental error, $Q_{\mathrm{f}'}^0 = Q_\mathrm{P}^0$, where $Q_{\mathrm{f}'}^0$ is the fluorescent yield of pure pyrazine; hence, one could write

$$\Phi_\mathrm{t}^0 = (Q_\mathrm{P}/Q_{\mathrm{f}'}^0)(Q_\mathrm{f}^0/Q_\mathrm{f}) \qquad (15)$$

where (15) is the true triplet yield of pure benzene.

Since $Q_\mathrm{P}^0 = 1.7 \times 10^{-3}$, $Q_\mathrm{P} = 0.96 \times 10^{-3}$, and $Q_\mathrm{f}^0/Q_\mathrm{f} = 1.23$ when benzene at 20 Torr is used in the presence of 0.1 Torr of pyrazine.

$$\Phi_\mathrm{t}^0 = (0.96/1.7)(1.23) = 0.69 \pm 0.07 \qquad (16)$$

where the limit of error is a rough estimate. Any error in the fluorescent yield of benzene used as a standard is not included. Phosphorescent and fluorescent yields of pyrazine are both very low and this tends to reduce the accuracy. However, since they are nearly equal instead of differing by a factor of nearly 60 as in biacetyl,[14] relative values are more easily determined. Agreement of (15) with values reported by Cundall is satisfactory.[22]

Two other facts must be kept in mind. (a) Reaction 4 is assumed to lead to a π–π^* transition in pyrazine and hence to no singlet emission. (b) An Hg–Xe high-pressure lamp was used so that there is no emission between 252.9 and about 258 nm. Thus the triplet yield of benzene should be slightly lower than at 253.6 nm. Systematic errors in Q_P tend to cancel since $Q_{\mathrm{f}'}^0, = Q_\mathrm{P}^0$. The low phosphorescent yield in the gas phase compared to that in a glassy matrix is of interest. This is not an unusual phenomenon. Benzene, for example, shows no phosphorescence in the gas phase but a strong one in a glassy matrix. A good explanation of these facts is not apparent.

Acknowledgment. The author wishes to thank Professor W. A. Noyes, Jr., for reviewing this manuscript and for many helpful suggestions. This work was supported by a grant to W. Albert Noyes, Jr., by the Robert A. Welch Foundation. A grant from the Camille and Henry Dreyfus Foundation was helpful for the purchase of supplies.

---

(22) R. B. Cundall, K. Cunnicliff, and A. J. R. Voss, Joint Annual Meeting of the Chemical Society and the Royal Institute of Chemistry, Nottingham, April 1969; R. B. Cundall and W. Tippett, *Trans. Faraday Soc.*, 66, 350 (1970).