Cadmium (5^3P_1)-Photosensitized Luminescence of Some Compounds Containing Two Functional Groups

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The cadmium (5^3P_1)-sensitized luminescence of some aliphatic compounds which have two functional groups have been studied under the conditions of steady-state illumination at temperatures between 473 and 573 K. It was found that 1,2-dimethoxyethane (DMOE), 2-methoxyethylamine (2-MOEA), and 3-methoxypropylamine (3-MOPA) have two emission bands (wavelengths at the peaks of these bands are about 400 and 455 nm for DMOE and about 460 and 500 nm for 2-MOEA and 3-MOPA), while 2-aminoethanol (2-AEA) and 3-amino-1-propanol (3-APA) do not have any emission band. These two bands were assigned to two kinds of 1 : 1 exciplex (cyclic and acyclic ones) between an excited cadmium atom and a substrate molecule. From the temperature dependence of the emission intensity ratios of these bands, the enthalpy changes (ΔH°) of the equilibrium between two exciplexes were evaluated. The values of ΔH° are correlated to the energy differences between the wavelengths of two emission bands.

In spite of several comprehensive studies concerning the photosensitized luminescence by excited mercury[1,2] and cadmium[3—5] atoms of aliphatic amines, alcohols, and ethers, there have been almost no studies of compounds containing more than two hetero atoms. Recently, we have observed two emission bands in the cadmium-sensitized reaction of some aliphatic diamines.[6—9] From the temperature and pressure dependences of the emission intensities of these two emission bands, we have concluded that these bands can be assigned to two kinds of 1 : 1 exciplex between an excited cadmium atom and a diamine molecule. From the structure of the diamines, which give two emission bands, the short- and long-wavelength bands were assigned to the acyclic and cyclic exciplexes, respectively.[6,7]

In the present study, the cadmium-photosensitized luminescence of some other compounds which have two hetero atoms was investigated.

Experimental

1,2-Dimethoxyethane (DMOE), 2-methoxyethylamine (2-MOEA), 3-methoxypropylamine (3-MOPA), 2-aminoethanol (2-AEA), and 3-amino-1-propanol (3-APA) were obtained from commercial sources (G. R. grade). DMOE was used after drying with calcium hydride and repeated trap-to-trap distillation. The amino compounds were used after drying with potassium hydroxide and repeated trap-to-trap distillation. The cadmium metal used was of high purity (99.9999%).

The experimental apparatus and the procedures for the measurements of resonance radiation at 326.1 nm and the sensitized luminescence were similar to those used previously.[6,7]

The 326.1 nm resonance line from a spiral cadmium discharge lamp made of Pyrex glass placed in a furnace kept at 523 K was used to excite ground-state Cd atoms in the cell to the 5^3P_1 state. The resonance radiation at 326.1 nm and the sensitized luminescence in the visible region were monitored with a Hitachi spectrophotometer (model 139) equipped with a photomultiplier tube (Hamamatsu R446).

Results

Figure 1 shows the emission spectra obtained in the cadmium-photosensitized reaction of DMOE at some temperatures between 473 and 573 K. These spectra were corrected for the wavelength dependence of the sensitivity of the detection system. The spectra were adjusted to the same total intensity. The profiles have an isosbestic point at about 410 nm. This is a characteristic of the superposition of just two basic functions which have the same intensity at the isosbestic wavelength. As shown in Fig. 1, DMOE shows two emission bands. The broken lines show a separation of the two bands for the spectrum at 503 K. The position and shape of the short-wavelength band (band I) are adjusted to those of the bands reported for aliphatic ethers,[3,10] and the long-wavelength band (band II) was

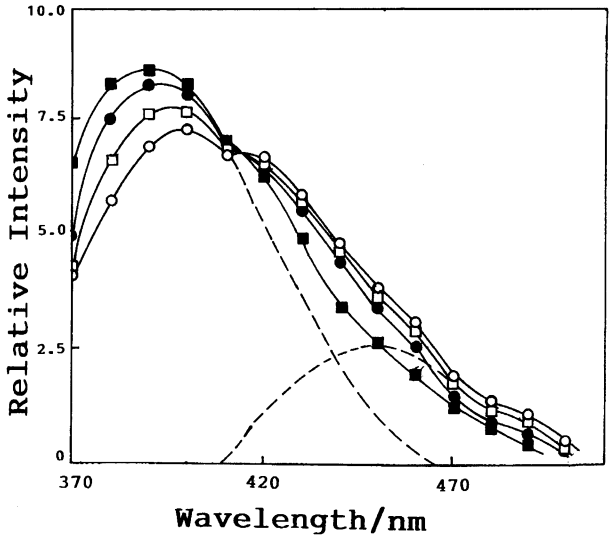

Fig. 1. Sensitivity-corrected emission spectra for the cadmium-photosensitized luminescence of DMOE at 473 (○), 503 (□), 533 (●), and 563 K (■).

obtained by subtracting band I from the total spectrum. The intensity of band I increases, and that of band II decreases with increasing temperature. These findings show that the two bands can be ascribed to two different exciplexes (exciplex A for band I and B for band II) and that the equilibrium between two exciplexes shifts from B to A with the temperature.

2-MOEA and 3-MOPA also show two emission bands at about 460 and 500 nm (Fig. 2). The position and shape of the short-wavelength band is similar to those of the emission bands reported for aliphatic amines.[3,4,11] For 2-MOEA and 3-MOPA the emission band at about 400 nm (assigned to the exciplex concerning with an *O*-atom) was not observed. The temperature dependences of the intensities of the emission bands were found to be similar to those for DMOE.

Figure 3 shows the pressure dependences of the ratios of the integrated intensities of the two emission bands, I(band II)/I(band I). As Fig. 3 shows, the ratios are independent of the pressure of the substrates. This shows that two exciplexes have the same composition as mentioned previously for some diamines.[7—9] From an analogy with the diamines, the acyclic and cyclic exciplexes were assigned to the short- and long-wavelength bands, respectively. For 2-AEA and 3-APA, no emission was observed.

In order to estimate the quenching efficiencies of the 326.1 nm resonance radiation by substrates, the intensity of the 326.1 nm resonance line was measured at various substrate pressures. The quenching rate constants were estimated using Stern–Volmer plots by a previously described method,[7—9] and are listed in Table 1.

The quantum yields of the luminescence were determined by comparing the integrated intensities of the emission bands with that for ammonia under conditions which give a complete quenching of the resonance line (the quantum yield for ammonia was reported to be 0.67[4]). The quantum yields obtained at 503 K are listed in Table 1, together with the wavelengths of the peaks of the bands.

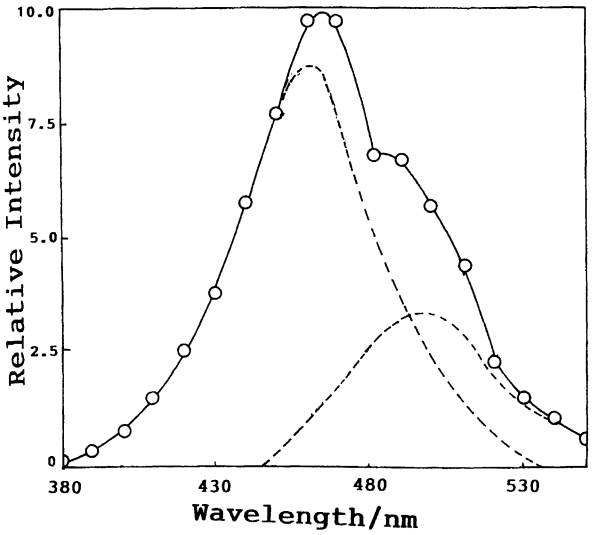

Fig. 2. Sensitivity-corrected emission spectrum for the cadmium-photosensitized luminescence of 3-MOPA at 503 K.

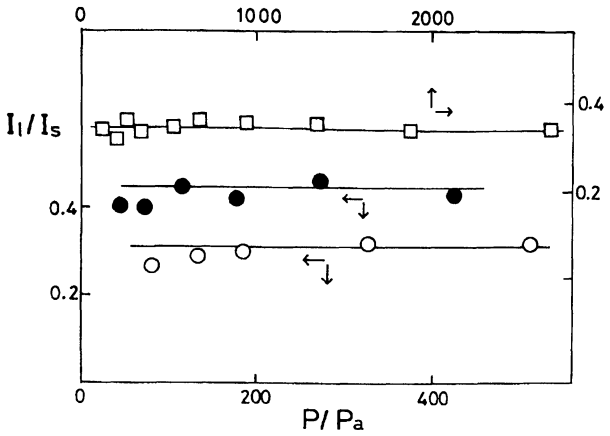

Fig. 3. Pressure dependence of the ratios of the integrated intensities of the two emission bands for DMOE (□), 2-MOEA (●), and 3-MOPA (○).

Table 1. Quenching Rate Constants of the 326.1 nm Resonance Line, Peak Wavelengths of Emission Bands, and Quantum Yields of Luminescence

	k_Q	Band I		Band II	
Compounds	cm^3 $molecule^{-1}$ s^{-1}	λ/nm	ϕ	λ/nm	ϕ
DMOE	0.022±0.001	400	0.049	455	0.017
2-MOEA	0.59±0.01	460	0.18	500	0.078
3-MOPA	1.38±0.06	460	0.17	500	0.027
2-AEA	1.27±0.05				
3-APA	1.85±0.05				

Discussion

In order to explain the experimental results, the following set of reactions is proposed:

$$Cd(^1S_0) + h\nu(326.1\ nm) \rightarrow Cd(^3P_1) \quad I \qquad (1)$$

$$Cd(^3P_1) \rightarrow Cd(^1S_0) + h\nu(326.1\ nm) \quad k_2 \qquad (2)$$

$$Cd(^3P_1) + MO \rightarrow CdMO^* \quad k_3 \qquad (3)$$

$$Cd(^3P_1) + MO \rightarrow c\text{-}CdMO^* \quad k_4 \qquad (4)$$

$$Cd(^3P_1) + MO \rightarrow \text{other reactions} \quad k_5 \qquad (5)$$

$$CdMO^* + MO \rightleftharpoons c\text{-}CdMO^* + MO \quad k_6, k_{-6} \qquad (6), (-6)$$

$$CdMO^* \rightarrow Cd(^1S_0) + MO + h\nu(\text{band I}) \quad k_7 \qquad (7)$$

$$c\text{-}CdMO^* \rightarrow Cd(^1S_0) + MO + h\nu(\text{band II}) \quad k_8 \qquad (8)$$

Here, MO represents the substrate, CdMO* stands for an exciplex which fluoresces, producing band I, while c-CdMO* stands for another exciplex which fluoresces to produce band II. As discussed in a previous paper,[8]

the production of $Cd(^3P_0)$ is not involved in the above-mentioned reaction mechanism. The independence of the intensities of the sensitized luminescence of the substrate pressure in the high-pressure region suggests that the quenching processes of the exciplexes by substrates can also be ignored. A similar lack of exciplex quenching processes by diamine was confirmed for *N,N,N'N,'*-tetramethyl-1,3-propanediamine (TMPDA) based on the finding that the decay rates of the sensitized luminescence did not depend on the diamine pressure.[8]

The quenching rate constant for DMOE is almost the same as that for diethyl ether, while those for 2-MOEA and 3-MOPA are similar to those for aliphatic amines, such as ethylamine, propylamine, and butylamine.[3] In addition, no emission band concerning the *O*-atom was observed for 2-MOEA and 3-MOPA, as mentioned above. These results show that an excited cadmium atom predominantly attacks the *N*-atom for amino compounds. This is consistent with the fact that the quenching efficiencies for the ethers are much smaller than those for the amines.

The following equations for the intensities of the exciplex emissions at high pressures of the substrates, where the cadmium resonance radiation is completely quenched and the intensities of the emissions are constant, were derived by a steady-state treatment based on the assumption that a fast equilibrium between two exciplexes is attained:

$$I(\text{band I}) = I(\frac{k_3 + k_4}{k_Q})(\frac{k_{-6}k_7}{k_6k_8 + k_{-6}k_7}) \quad (9)$$

and

$$I(\text{band II}) = I(\frac{k_3 + k_4}{k_Q})(\frac{k_6k_8}{k_6k_8 + k_{-6}k_7}). \quad (10)$$

Here, I(band I) and I(band II) are the integrated intensities of bands I and II; I is the intensity of the 326.1 nm resonance radiation absorbed by cadmium atoms; k_Q is the quenching rate constant, $k_Q = k_3 + k_4 + k_5$. The equilibrilum constant (K) between two exciplexes is expressed by

$$K = \frac{k_6}{k_{-6}} = (\frac{I(\text{band II})}{I(\text{band I})})(\frac{k_7}{k_8}). \quad (11)$$

In a previous paper,[8] it was shown that a simulation of the temporal profiles for the two emission bands gave the result that $k_7 = k_8 = 1.9 \times 10^5$ s^{-1} for TMPDA. Since we have no information concerning the values of k_7 and k_8 for DMOE, 2-MOEA, and 3-MOPA, it was assumed that the values of k_7/k_8 for these compounds are also equal to unity as a first approximation. Although the k_7 and k_8 values should depend on the kind of substrate, they may be expected to vary in a somewhat similar manner to one another, since the two exciplexes have similar electronic structures. The values of K can be calculated form Eq. 11 using the ratios of I(band I)/I(band II) obtained at various temperatures.

The values of $\Delta H°$ and $\Delta S°$ for the equilibrium between the two exciplexes were obtained from the slopes and intercepts of the straight-line plots of ln K vs. $1/T$ (shown in Fig. 4), and are listed in Table 2, together with the K values at 503 K. The values of K depend directly on the values of k_7/k_8, while $\Delta H°$ depends on its temperature dependence. It is difficult to see how the values of k_7 and k_8 would vary with the temperature. Since the ratio of k_7/k_8 is the ratio of the rate constants for two similar radiation processes, this ratio is expected to little depend on the temperature. Although the values of K and $\Delta S°$ obtained here are only approximate, the values of $\Delta H°$ seem to be more reliable.

As is shown in Table 2, the values of $\Delta H°$ for DMOE, 2-MOEA, and 3-MOPA are considerably larger (less negative) than those for 1,2-ethanediamine (EDA) and 1,3-propanediamine (PDA). This shows that the attachment of the second ligand atom (*O*-atom) to an excited cadmium atom for DMOE, 2-MOEA, and 3-MOPA is less exohermic than that (*N*-atom) for EDA and PDA. This result is consistent with the fact that the energy differences ($\Delta\nu$) between the two emission bands for DMOE, 2-MOEA, and 3-MOPA are smaller than those for EDA and PDA (Table 2). It was also observed that the red shift of the emission band from the resonance line upon the formation of exciplexes of an excited cadmium atom with amines is larger than that with alcohols and ethers. These are consistent with the observation that the first and second ligand binding energies for the transition-mental ions are generally larger for ammonia than those for water.[12]

The energy differences calculated from the wavelengths of the two emission bands are larger than those estimated from the temperature dependence of the emission intensity ratios. This difference can be attributed to the difference in the potential energies of

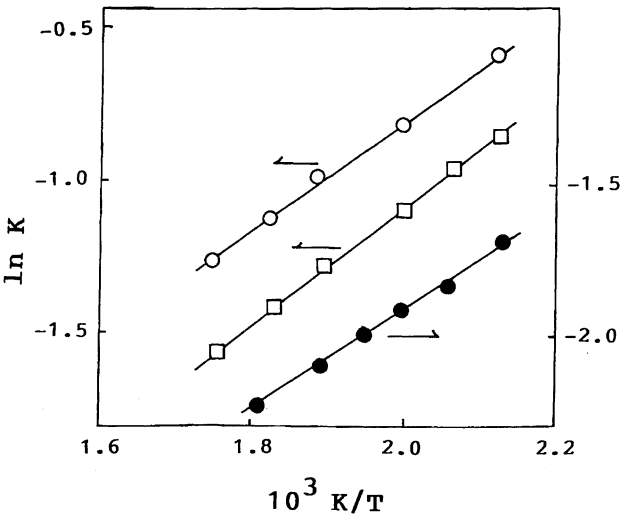

Fig. 4. Plots of ln K against $1/T$ for the equilibrium between cyclic and acyclic exciplexes for DMOE (□), 2-MOEA (○), and 3-MOPA (●).

Table 2. Values of K, $\Delta H°$, $\Delta S°$, and $\Delta\tilde{\nu}$

Compounds	K (at 503 K)	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}	$\Delta\tilde{\nu}$/cm^{-1}
EDA	6.8	−34.7	−53	4200
PDA	3.9	−34.5	−57	4040
DMOE	0.34	−18.2	−45	3020
2-MOEA	0.45	−15.8	−38	1740
3-MOPA	0.16	−14.6	−44	1740

EDA; 1,2-ethanediamine. PDA; 1,3-propanediamine.

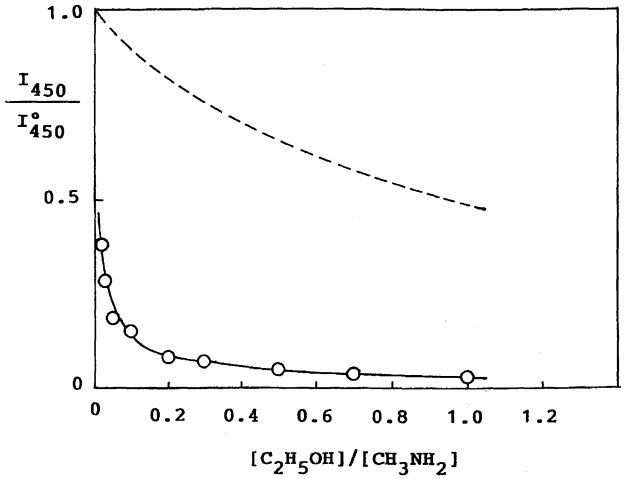

Fig. 5. Effect of added ethanol on the emission intensity for the cadmium-photosensitized luminescence of methylamine. The broken line shows the relative intensity calculated using the quenching rate constants reported for methylamine and ethanol.[3)]

the ground states for the configurations corresponding to two types of exciplex. The potential-energy surface of the ground state for a cyclic configuration must be more repulsive than that for an acyclic one.

Since the quenching efficiencies for amines are considerably larger than those for alcohols, and the quenching efficiencies obtained for 2-AEA and 3-APA are similar to those for amines, the initial attack of an excited cadmium atom to 2-AEA and 3-APA must be to an amino group. Although the emission band from an exciplex concerning and N-atom is expected to be observed, as mentioned above, no emission band was obtained for 2-AEA and 3-APA. In order to determine the reason why no emission was observed for amino alcohols, we examined the effect of the addition of ethanol on the emission intensity at 450 nm of the cadmium-photosensitized luminescence of methylamine. As Fig. 5 shows, the emission intensity decreases drastically with increasing ethanol pressure. This indicates that ethanol effectively quenches the luminescence of amine (the decrease in the emission intensity is much steeper than that expected by the competitive quenching of the triplet cadmium atoms by methylamine and ethanol). Since diethylether hardly quenches the emission, a hydroxyl group seems to play an important role in this quenching. Although it seems to be interesting to know whether ethanol suppresses the formation of an exciplex or breaks the exciplex, we could not reach any conclusion. And although the origin of this quenching effect remains an open question, similar effects must completely quench the emission for 2-AEA and 3-APA.

References

1) L. F. Philips, *Acc. Chem. Res.*, **7**, 135 (1974).
2) A. B. Callear, *Chem. Rev.*, **87**, 355 (1987).
3) T. Tsunashima and S. Sato, *Rev. Chem. Intermed.*, **2**, 201 (1979).
4) S. Yamamoto and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 1382 (1975).
5) H. Umemoto, S. Tsunashima, and S. Sato, *Bull. Chem. Soc. Jpn.*, **51**, 1951 (1978).
6) S. Yamamoto, M. Itami, Y. Sueishi, and N. Nishimura, *Chem. Lett.*, **1990**, 1109.
7) S. Yamamoto, Y. Sueishi, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **64**, 3335 (1991).
8) H. Umemoto, K. Kuwahara, T. Ohnuma, A. Masaki, and S. Yamamoto, *J. Chem. Soc., Faraday Trans.*, **87**, 2897 (1991).
9) S. Yamamoto, T. Sakata, and N. Nishimura, *J. Chem. Soc., Faraday Trans.*, **89**, 703 (1993).
10) S. Yamamoto, K. Tanaka, and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 2172 (1975).
11) S. Yamamoto, M. Yasunobu, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **54**, 3677 (1981).
12) P. J. Marinelli and R. R. Squires, *J. Am. Chem. Soc.*, **111**, 4101 (1989).