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Cadmium (5^3P_1)-Photosensitized Luminescence of Some Aliphatic Diamines

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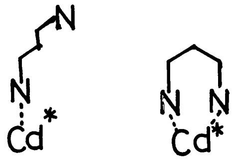
The cadmium(5^3P_1)-photosensitized luminescence of some aliphatic diamines was studied by a steady-illumination method at temperatures between 230 and 330 °C. It was found that 1,2-ethylenediamine, *N,N,N′,N′*-tetramethyl-1,2-ethylenediamine, 1,3-propanediamine, and *N,N,N′,N′*-tetramethyl-1,3-propanediamine have two emission bands (wavelengths at the peaks of these bands are about 450 and 550 nm), while *N,N,N′,N′*-tetramethylmethanediamine, *N,N′*-dimethylpiperazine, and triethylenediamine have only a short-wavelength band. From the temperature and pressure dependences of the emission intensities of the two bands, it had been concluded previously that these bands could be assigned to two kinds of 1 : 1 exciplexes between an excited cadmium atom and a diamine molecule. From the temperature dependence of the equilibrium constants between the two exciplexes which had been obtained from the ratio of the emission intensities of the two bands, the enthalpy and entropy changes of the equilibrium were evaluated. The cyclic exciplexes assigned to the long-wavelength band have smaller enthalpies and entropies than do the noncyclic exciplexes assigned to the short-wavelength band.

It is well known that excited triplet cadmium[1-4] and mercury[5,6] atoms react with the some compounds which contain a nitrogen or an oxygen atom (NH_3, H_2O, aliphatic amines, alcohols, and ethers) to form exciplexes, and that these exciplexes fluoresce. Recently, we have studied the cadmium-photosensitized reactions of some aliphatic diamines.[7] Two emission bands were observed in the blue and green regions for *N,N,N′,N′*-tetramethyl-1,2-ethylenediamine (TMEDA) and *N,N,N′,N′*-tetramethyl-1,3-propanediamine (TMPDA), while only a short-wavelength band was observed for *N,N′*-dimethylpiperazine (DMP) and triethylenediamine (TEDA). From the temperature and pressure dependences of the emission intensities of these two bands, we have concluded that these bands can be assigned to two kinds of 1:1 exciplexes between an excited cadmium atom and a diamine molecule. The cyclic and noncyclic exciplexes which are shown in Scheme 1 were suggested for the long- and short-wavelength bands respectively. DMP and TEDA can not form cyclic exciplexes because of their rigid structures.



Scheme 1.

In the present study, the equilibrium constants between the two exciplexes were determined over the temperature range 230—330 °C, from which the enthalpy and entropy changes of the equilibrium can be estimated. The present paper reports on details conserning the cadmium-photosensitized luminescence of diamines and the quenching of the 326.1 nm resonance radiation by them.

Experimental

The experimental apparatus and the procedures for the measurements of resonance radiation at 326.1 nm and sensitized luminescence were similar to those used previously.[7,8] A part of the vacuum line was constructed using greaseless stopcocks in order to prevent any adhesion of sample gases to stopcock grease. A cylindrical quartz cell (17 mm in internal diameter and 20 cm in length) was kept in an electric furnace, the temperature of which was varied from 230 to 330 °C. A spiral cadmium discharge lamp made of Pyrex glass was placed in another furnace kept at 250 °C. The 228.8 nm resonance line was completely absorbed by the Pyrex glass. The visible lines from the lamp were removed with a glass band-pass filter (Toshiba, UV-D33S). The 326.1 nm resonance line was used to excite Cd($^3P_1$) atoms from cadmium vapor in the cell. The resonance radiation at 326.1 nm and the sensitized luminescence were monitored with a Hitachi spectrophotometer (Model 139). The wavelength dependence of the sensitivity of the monochromator-photomultiplier combination was determine by using standard fluorescence solutions of quinine sulfate and *N,N*-dimethyl-*m*-nitroaniline.[9]

N,N,N′,N′-Tetramethylmethanediamine (TMMDA), 1,2-ethylenediamine (EDA), TMEDA, 1,3-propanediamine (PDA), TMPDA, DMP, and TEDA were obtained from commercial sources (G. R. grade). These diamines were used after drying by potassium hydroxide and repeated trap-to-trap distillation. The cadmium metal used was of high-purity grade (99.9999%).

Results

Figure 1 shows the emission spectra obtained in the cadmium-photosensitized reaction of DMP and PDA at various temperatures between 230 and 300 °C. These spectra were corrected for the wavelength dependence of the sensitivity of the detection system. As is shown in Fig. 1, two emission bands are evident for PDA (broken lines show a separation of two bands for the spectra at 230 °C). The spectra for the PDA obtained at 230, 260, and 300 °C were adjusted to the same total intensity at two peaks. The profiles have an isosbestic point. The intensity of the short-wavelength band (band I) increases and that of the long-wavelength band (band II) decreases with increasing temperature. DMP shows one emission

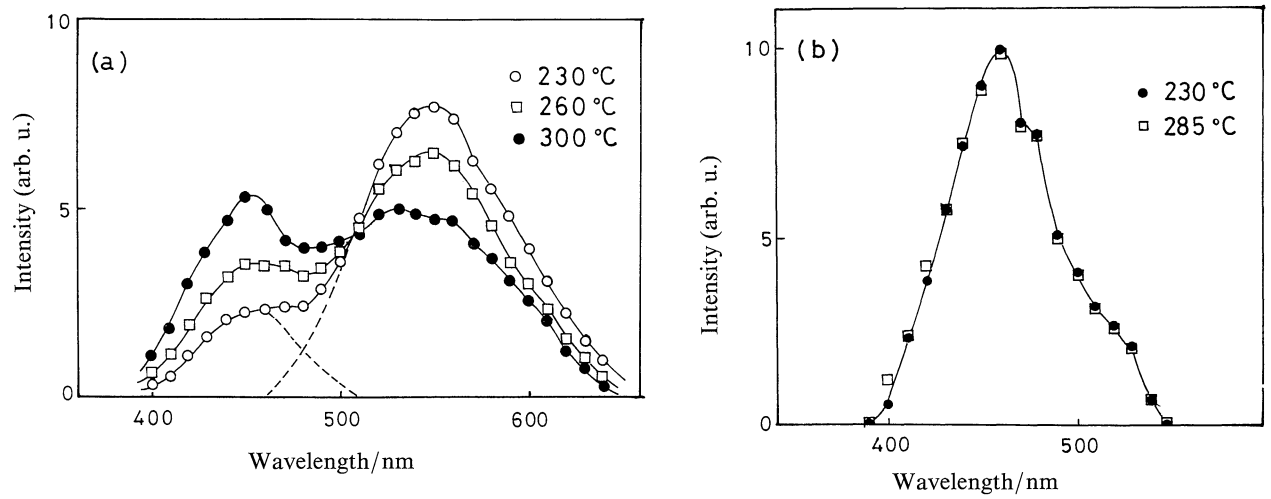


Fig. 1. Emission spectra for cadmium-photosensitized luminescence of PDA (a) and DMP (b).

Table 1. Half-Quenching Pressure for Quenching of 326.1 nm Resonance Radiation, Wavelength at Peak of Emission Bands, and Quantum Yield of Luminescence

Diamine	$P_{1/2}$	λ/nm		Quantum yield	
	Pa	Band I	Band II	Band I	Band II
TMMDA	66.0±2.6	480	—	0.24	—
EDA	8.9±0.1	460	570	0.040	0.27
TMEDA	11.1±0.2	460	550	0.020	0.16
PDA	12.7±0.2	450	550	0.044	0.17
TMPDA	15.5±0.2	452	570	0.040	0.17
DMP	12.0±0.2	460	—	0.060	—
TEDA	10.3±0.2	442	—	0.29	—

band and the spectrum is independent of temperature. EDA, TMEDA, and TMPDA have two emission bands and the temperature dependences of their emission spectra are very similar to that for PDA, while TMMDA and TEDA have only the short-wavelength band and their spectra are also independent of the temperature, like that for DMP. The position and shape of band I of EDA, TMEDA, PDA, and TMPDA are similar to those of the bands of TMMDA, DMP, and TEDA, and of the bands reported for the Cd(^{3}P$_1$)-aliphatic amine systems. Band II has not been reported for other systems.

The quantum yields of the luminescence were determined by comparing the integrated intensity of the emission bands with that for ammonia under the same conditions. The quantum yield of the luminescence for ammonia was reported to be 0.67.[1,2] The quantum yields obtained at 230 °C are listed in Table 1.

In order to estimate the efficiencies of quenching of the 326.1 nm resonance radiation, the emission intensity at 326.1 nm was measured at various pressures of diamines. Stern–Volmer plots for some diamines are shown in Fig. 2. The half-quenching pressures obtained from the slope of the straight lines in Fig. 2 are listed in Table 1. The measurements were carried out in the absence of any buffer gas. It is not necessary to take into account the effect of pressure broadening, since the pressures of the diamines were very low.

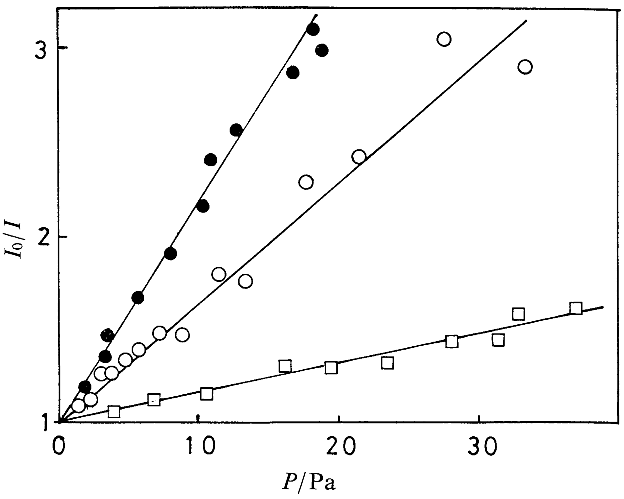


Fig. 2. Stern-Volmer plots for quenching of resonance radiation by EDA (●), TMPDA (○), and TMMDA (□) at 230 °C.

The pressure dependences of the relative intensities at the peaks of the emission bands for PDA are shown in Fig. 3. Slightly different pressure dependence from those presented in a previous letter[7] was obtained by using greaseless stopcocks in this study. As Fig. 3 shows, the intensities increase rapidly with increasing PDA pressure in the low-pressure region, and then leveled off to a constant value. The intensities are constant at higher pressures than 200 Pa (I_{440}/I_{550}=0.28). The pressure dependence of the relative emission intensity at 450 nm is very similar to that at 550 nm. Similar pressure dependences of the emission intensities of the two bands were obtained for EDA, TMEDA, and TMPDA.

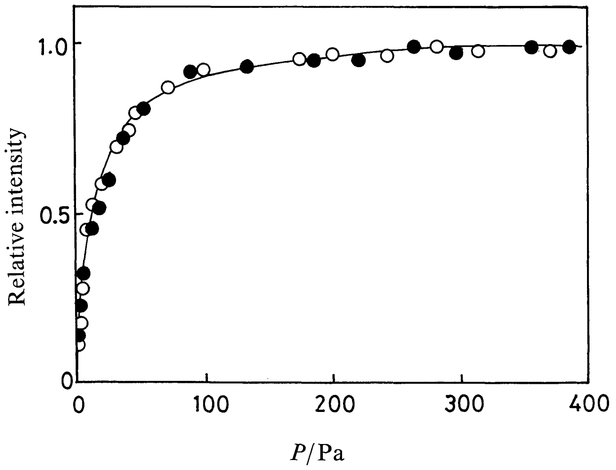


Fig. 3. Pressure dependences of emission intensities at 450 (○) and 550 nm (●) for PDA at 230 °C.

Discussion

In a previous letter[7] we concluded that the two emission bands can be assigned to two kinds of 1:1 exciplexes between an excited cadmium atom and a diamine molecule from the pressure and temperature dependences of the emission intensities of the two bands as well as the dependence of the emission intensities on the intensity of the exciting light. From the temporal profiles of the intensities of the two emission bands and that of the 326.1 nm resonance radiation measured for TMPDA under pulsed excitation conditions, it has been suggested that two exciplexes are formed directly from $Cd(^3P_1)$, and that there are collision-induced mixing processes between these exciplexes.[10] The following reaction scheme has been proposed:

$$Cd(^1S_0) + h\nu(326.1\ \text{nm}) \longrightarrow Cd(^3P_1) \qquad (1)\ I^0$$

$$Cd(^3P_1) \longrightarrow Cd(^1S_0) + h\nu(326.1\ \text{nm}) \qquad (2)\ k_2$$

$$Cd(^3P_1) + DA \longrightarrow CdDA^* \qquad (3)\ k_3$$

$$Cd(^3P_1) + DA \longrightarrow CdDA^{**} \qquad (4)\ k_4$$

$$Cd(^3P_1) + DA \longrightarrow \text{other reactions} \qquad (5)\ k_5$$

$$CdDA^* + DA \rightleftharpoons CdDA^{**} + DA \qquad (6)(-6)\ k_6,\ k_{-6}$$

$$CdDA^* \longrightarrow Cd(^1S_0) + DA + h\nu(450\ \text{nm}) \qquad (7)\ k_7$$

$$CdDA^{**} \text{ — } Cd(^1S_0) + DA + h\nu(550\ \text{nm}). \qquad (8)\ k_8$$

Here, DA represents a diamine, CdDA* stands for an exciplex which fluoresces band I, while CdDA** stands for another exciplex which fluoresces band II. As has been discussed in a previous paper,[10] it was concluded that the production of $Cd(^3P_0)$ is a minor process for the Cd/TMPDA system from the finding that the decay profile of the resonance radiation is consistent with the quenching rate constant determined from the slope of the Stern–Volmer plot. If $Cd(^3P_0)$ is produced and the equilibration between $Cd(^3P_1)$ and $Cd(^3P_0)$ is rapid, as in the Cd/ammonia system,[4] the slope of the Stern–Volmer plot should correspond to the population-weighted sum of the quenching rate constants of the $^3P_1$ and $^3P_0$ states, while the rate constant determined by the decay profiles of the resonance radiation must be equal to the weighted average; there must be a difference by a factor of more than two between the weighted sum and the weighted average at 500 K. The minor production of $Cd(^3P_0)$ in this system can be attributed to the large quenching efficiency of TMPDA. The production of $Cd(^3P_0)$ is not involved in the above-mentioned reaction mechanism, since the other diamines used also had large quenching efficiencies.

A steady-state treatment leads to the following equation:

$$\frac{I_0}{I} = 1 + \frac{k_Q}{k_2}[DA], \qquad (9)$$

where I_0 and I represent the intensities of the resonance radiation (defined as $k_2\ [Cd(^3P_1)]$) in the absence and presence of diamines, respectively; k_Q is the quenching rate constant: $k_Q = k_3 + k_4 + k_5$. The Stern–Volmer plots given in Fig. 3 are expressed by this equation.

In a previous paper[10] the value of $4.0 \times 10^5\ s^{-1}$ for k_2 (the effective radiation lifetime of $Cd(^3P_1)$ is somewhat lengthened by radiation imprisonment) was used in a simulation of temporal profile of the resonance radiation in the cadmium–TMPDA system at 230 °C. From the half-quenching pressures, the values of k_Q can be estimated; they are listed in Table 1.

The following equations for the intensities of the exciplex emissions are derived by the steady-state treatment based on the assumption that fast equilibrium between two exciplexes is attained:

$$I_s = \alpha k_7[CdDA^*] = \alpha I^0 \frac{(k_3 + k_4)[DA]}{k_2 + k_Q[DA]} \frac{k_6 k_7}{(k_6 + k_{-6})(k_7 + k_8)}, \qquad (10)$$

$$I_l = \beta k_8[CdDA^{**}] = \beta I^0 \frac{(k_3 + k_4)[DA]}{k_2 + k_Q[DA]} \frac{k_6 k_8}{(k_6 + k_{-6})(k_7 + k_8)}, \qquad (11)$$

where I_s and I_l are the emission intensities at the peaks of bands I and II, I^0 is the intensity of the 326.1 nm resonance radiation absorbed by cadmium atoms, and α and β are proportional factors between the total emission intensities of bands I and II and the intensities at the peaks. As was mentioned above, the emission intensities at the peaks of bands I and II level off to constant values at high pressures. If I_s^∞ and I_l^∞ denote the constant intensities at high pressures, the following equation is obtained:

$$\frac{I_s}{I_s^\infty}=\frac{I_l}{I_l^\infty}=\frac{k_Q[\mathrm{DA}]}{k_2+k_Q[\mathrm{DA}]}. \tag{12}$$

The solid line in Fig. 3 shows the values calculated according to Eq. 12 by using the values of k_2 and k_Q shown above. The calculated values are in good agreement with the observed ones within the limits of experimental error. Similar good agreements between the calculated and experimental values were obtained for other diamines. This demonstrates that the above reaction scheme and the assumption mentioned above are reasonable.

The equilibrium constant, K, between two exciplexes is expressed by

$$K=\frac{[\mathrm{CdDA}^{**}]}{[\mathrm{CdDA}^{*}]}=\frac{\alpha}{\beta}\,\frac{k_7}{k_8}\,\frac{I_l}{I_s}. \tag{13}$$

The ratios of α/β were obtained for the four diamines which show the two emission bands at some temperatures by comparing the values of I_l/I_s to the ratios of the integrated intensities of the emission bands (Table 2), and found to be independent of the temperature. Since both k_7 and k_8 are the rate constants for radiation processes, the ratio k_7/k_8 must be independent of the temperature. In a previous paper,[10] it was shown that a simulation of the temporal profiles of the two emission bands gave the results that $k_7=k_8=1.9\times10^5\ \mathrm{s}^{-1}$ for TMPDA. Since we have no information concerning the values of k_7 and k_8 for other diamines, it is assumed that the values of k_7/k_8 for other diamines are also equal to unity as a first approximation. Although the k_7- and k_8-values should depend on the kind of diamine, they may be expected to vary in a somewhat similar manner to one another, since the two exciplexes for EDA, TMEDA, PDA, and TMPDA have similar structures, respectively (as will be shown later, the enthalpy changes between the two exciplexes are very similar for these diamines). The values of K can be obtained by Eq. 13 at various temperatures for EDA, TMEDA, PDA, and TMPDA. The values of ΔH° and ΔS° were obtained from the slopes and the intercepts of the straight lines between $\ln K$ and $1/T$ shown in Fig. 4 and are listed in Table 2, together with the K-values at 230 °C.

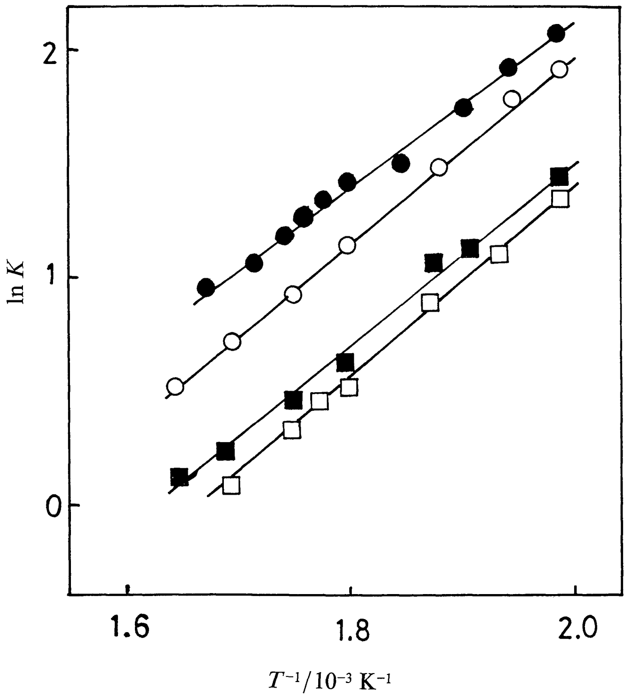


Fig. 4. Plots of $\ln K$ against $1/T$. EDA (○), TMEDA (●), PDA (□), and TMPDA (■).

Table 2. Values of k_Q, α/β, K, ΔH°, and ΔS°

Diamine	$10^{10}\,k_Q$ / $\mathrm{cm^3\,mol^{-1}\,s^{-1}}$	α/β	K[a)]	ΔH° / $\mathrm{kJ\,mol^{-1}}$	ΔS° / $\mathrm{J\,Kmol^{-1}}$
TMMDA	0.51±0.02	—	—	—	—
EDA	3.8 ±0.1	0.82	6.8	−34.7±0.5	−53±1
TMEDA	3.0 ±0.1	0.84	8.0	−30.8±0.5	−44±1
PDA	2.6 ±0.1	0.87	3.9	−34.5±0.6	−57±1
TMPDA	2.2 ±0.1	0.56	4.3	−33.7±0.5	−55±1
DMP	2.8 ±0.1	—	—	—	—
TEDA	3.3 ±0.1	—	—	—	—

a) At 230 °C.

In conclusion, the exciplexes for the long-wavelength bands have a smaller enthalpy and entropy than do the exciplexes for the short-wavelength bands. This results seem to give another kind of evidence that the former are cyclic, because of the general tendency that cyclic compounds have smaller entropy than do chain compounds.[11] The energy differences between the two exciplexes obtained above are smaller than the energy differences between the wavelengths of the peaks of the two emission bands (about 48 kJ mol^{-1}). This shows that the potential energy surfaces of the ground state for the cyclic exciplexes must be more repulsive than that for the noncyclic exciplexes; this is shown schematically in Fig. 5.

Callear et al.[12,13] observed two emission bands in mercury(6^3P_0)-t-butylamine and diethylamine systems. They pointed out that the short-wavelength band is due to the HgA* monomer, and that the long-wavelength band can be assigned to the $\mathrm{HgA_2}^*$ dimer. Although they did not described the structures of the dimers, two amine molecules may attach directly to an excited mercury atom. If this is the case, the $\mathrm{HgA_2}$ dimers are closely related to the cyclic exciplexes observed in the present study. Indeed, both species have a common feature of having long-wavelength bands. More experimental work is needed to clarify this point.

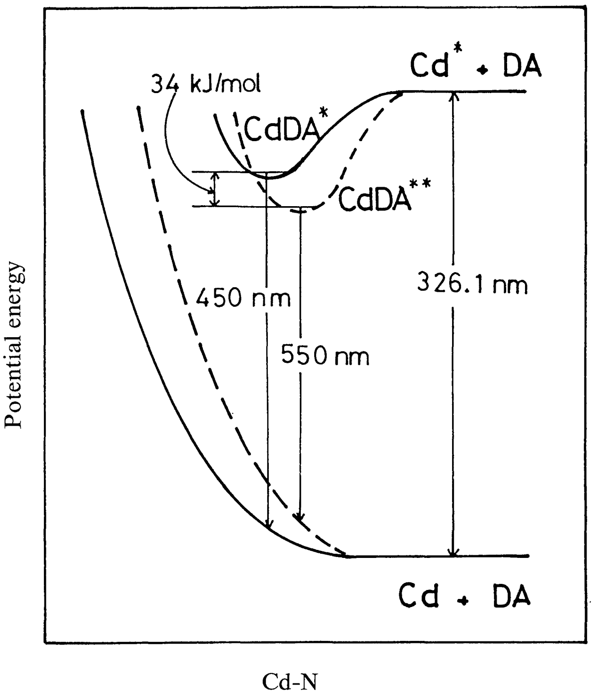


Fig. 5. Schematic potential energy diagram of diamine–Cd($^3P_1$) complexes.

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