The Cadmium-photosensitized Reaction of Water, Alcohols, and Ethers. The Quenching of the Resonance Radiation at 326.1 nm and the Photosensitized Luminescence

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A luminescence similar to the photosensitized luminescence of ammonia was observed in the cadmium-photosensitized reaction of water, alcohols, and ethers. The quantum yields of the luminescence with these compounds were much smaller than that with ammonia. The rate constants for the formation of the excited complexes between the excited cadmium atoms and the substrates generally increased with a decrease in the ionization potentials of the substrates. This shows that the complex has the characteristics of a charge-transfer type. On the other hand, the efficiencies of the quenching of the resonance radiation at 326.1 nm by ethers were smaller than those of alcohols. It is concluded that the quenching through the formation of the complex is a minor process in the quenching of the resonance radiation by water, alcohols, and ethers.

By analogy with the mercury-photosensitization, it can be expected that such electron-donor molecules as ammonia and water react with excited cadmium atoms to form excited complexes, and that such complexes fluoresce.

In previous papers,[1-3] such luminescence was found in the cadmium-photosensitized reactions of ammonia and some aliphatic amines. The quantum yields of the luminescence, the wavelength at the peak, and the rate constants for the formation of excited complexes were measured. From the relationship between these values and the structure of the amines, it was concluded that the complexes are of the charge-transfer type. Further, we discussed a mechanism for the formation and the deactivation of the complexes on the basis of the pressure dependences of the intensities of the resonance line at 326.1 nm and of the luminescence.

It now seems valuable to observe the similar luminescence in the cadmium-photosensitized reactions of water, alcohols, and ether, to measure the rates of the quenching of the resonance radiation and of the formation of the complex, and to determine the effects of the structure of the alcohols and ethers on the quantum yields of the luminescence and the position of the emission band, in order to gain a further understanding of the cadmium-photosensitized luminescence.

Experimental

The apparatus and procedure were the same as those previously described.[1] The reaction cell and the cadmium resonance lamp were kept at 220 ± 1 °C. The vapor pressure of cadmium at this temperature is 1.04×10^{-3} Torr. The lamp was operated by an alternating current (50 Hz). As was described previously,[4] since the lifetimes of $Cd(5^3P_{1,0})$ are very short, the observed intensity of the light from the cell is not affected by the periodic change in the light intensity of the lamp.

The cadmium metal used was high-purity cadmium (99.9999%) manufactured by the Osaka Asahi Metal Co. Distilled water and 99.9% D_2O were freed of dissolved gases by alternate freezing and thawing under a vacuum. Spectro-grade methanol and ethanol were used after having been degassed. The dimethylether and ethylene oxide (G.R. grade) were used after having been degassed at the temperature of liquid nitrogen. The diethylether and tetrahydrofuran were used after having been dried by Na–K and repeated trap-to-trap distillations. In order to minimize the pressure dependence of the absorption intensity at 326.1 nm, the substrates were diluted with argon and the total pressure in the cell was kept constant.

Results

In Fig. 1 the emission bands obtained with water, methanol, and ethanol are shown, together with the analogous band with ammonia. The bands for ethers studied had the same basic shape and so are not given here. We could not detect an emission band with ethylene oxide. The band shapes are very similar to that observed with ammonia (the band widths for water and alcohols are slightly narrower than that for ammonia), but the intensities are much smaller than that for ammonia. The wavelengths at the peaks are listed in Table 1.

The quantum yields of the luminescence with water, alcohols, and ethers were determined by a comparison of the integrated intensity of the emission band for the compound in question that for ammonia under

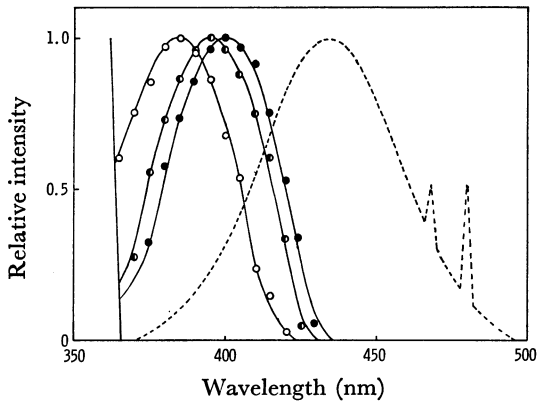

Fig. 1. Emission band contours for H_2O (open circles), methanol (half-filled circles), and ethanol (filled circles). The curve for NH_3, given by the broken line, is derived from Ref. (1).

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Table 1. Wavelength at the peak of the emission band and quantum yield of the luminescence

Compounds	I_p (kcal/mol)	λmax (nm)	Quantum yield
H_2O	291.3	385	1.2×10^{-3}
D_2O		385	5.7×10^{-3}
Methanol	250.6	395	3.1×10^{-3}
Ethanol	242.6	400	1.5×10^{-3}
Dimethylether	230.6	390	4.8×10^{-3}
Diethylether	220.1	398	1.1×10^{-3}
Tetrahydrofuran	217.6	398	8.5×10^{-3}

Table 2. Half-quenching pressure for the quenching of 326.1 nm resonance radiation

Compound	Torr
H_2O	5.38
D_2O	31.5
Methanol	2.95
Ethanol	0.82
Dimethylether	92.6
Diethylether	11.2
Ethylene oxide	0.13
Tetrahydrofuran	26.8

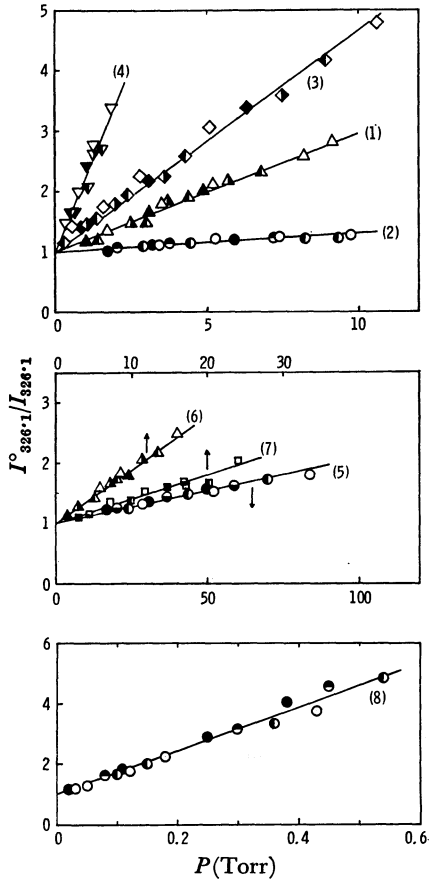

Fig. 2. Stern-Volmer plots for the quenching of the resonance radiation at 326.1 nm by water, alcohols, and ethers diluted with argon.
1) H_2O; Total pressure are 80(△), 67(▲), 56(▲), and 48(▲) in Torr.
2) D_2O; 80(○), 67(◐), 56(◓), and 48(●).
3) methanol; 80(◇), 67(◆), 56(◆), and 48(◆).
4) ethanol; 80(▽), 67(▼), 56(▼), and 48(▼).
5) dimethylether; 210(○), 177(◐), 148(◒), and 126(●).
6) diethylether; 80(△), 67(▲), 56(▲), and 48(▲).
7) tetrahydrofuran; 80(□), 67(◧), 56(◒), and 48(■).
8) ethylene oxide; 80(○), 67(◐), 56(◓), and 48(●).

the same conditions. The results are also listed in Table 1.

In order to estimate the efficiency of the quenching of the 326.1 nm resonance line, the emission intensity at 326.1 nm was measured as a function of the pressure

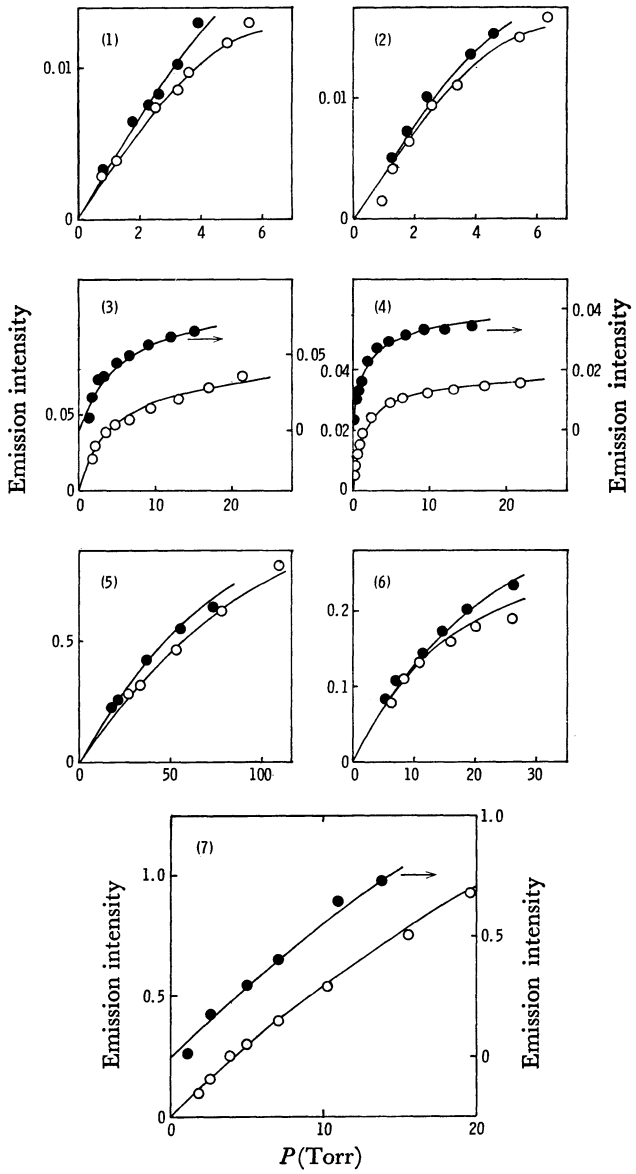

Fig. 3. The intensity at the peak of the emission band from the complex as a function of the partial pressure of substrates. The total pressures are 80(○) and 56(●) in Torr, except for dimethylether, and those for dimethylether are 210(○) and 148(●) in Torr. The plots for 48 Torr in the cases of methanol, ethanol, and tetrahydrofuran are displaced upwards for clearity.
1) H_2O; 2) D_2O; 3) methanol; 4) ethanol; 5) dimethylether; (6) diethylether; 7) tetrahydrofuran.

of the substrates. The Stern-Volmer plots are shown in Fig. 2, where I_0 and I are the intensities of the resonance lines in the absence and in the presence of the substrates respectively. As the intensity decreased with the increase in irradiation time, the I values shown in Fig. 2 were obtained by extrapolation to zero irradiation time. As is shown in Fig. 2, the plots for each substrate at various total pressures lie on one straight line; no total pressure dependence can be seen. The half-quenching pressure obtained from the slopes of the straight lines in Fig. 2 are listed in Table 2. The values for ethers are generally larger than those for alcohols.

The pressure dependence of the intensity at the peak of the emission band is shown in Fig. 3. The intensities were again obtained by extrapolation to zero irradiation time. As was shown in a previous paper,[3] the emission intensities for amines have maximum values, but those for water, alcohols, and ethers increase monotonously with an increase in the pressure.

Discussion

Let us first consider the effect of the structure of the substrates on the position of the emission band. In the mercury-photosensitized luminescence,[5,6] it was previously reported that the band given by the deuterated species is slightly shifted to longer wavelengths. In the present experiment, however, the bands obtained with H_2O and D_2O appeared at the same wavelength. As was described in the previous paper,[3] it would be expected that the decrease in the ionization potential of the substrate would cause the peak of the emission band to shift to a longer wavelength. In fact, as is shown in Table 1, the substitution of alkyl groups for hydrogen atoms in water, which increases the electron-donating ability of the oxygen atom, generally causes a red-shift of the emission band. An inspection of Table 1, however, shows that the peak for methanol is at a longer wavelength than that for dimethylether, while the peak for ethanol is at a longer wavelength than those for diethylether and tetrahydrofuran. It seems that the position of the emission band cannot be explained by the ionization potential alone. Freeman *et al.*[7] found a similar red-shift in Hg–alcohols system. However, they did not detect an emission band with ethers, so the effect of replacing both of the hydrogen atoms in water by alkyl groups remains an open question.

With respect to the quenching of the resonance line, the following reactions may be considered in a manner similar to that described in previous paper:[2,3]

$$Cd^*(^3P_1) \longrightarrow Cd(^1S_0) + h\nu \qquad k_0 \qquad (1)$$

$$Cd^* + M \rightleftarrows Cd^0(^3P_0) + M \qquad k_1, k_{-1} \qquad (2)\ (3)$$

$$Cd^* + A \longrightarrow \text{products} \qquad k_2 \qquad (4)$$

$$Cd^0 + A \longrightarrow \text{products} \qquad k_3 \qquad (5)$$

$$Cd^* + A \rightleftarrows CdA_v^* \qquad k_4, k_{-4} \qquad (6)\ (7)$$

where M stands for Ar or A and where A respesents the substrates. Since Reaction (2) and (3) are very fast in the presence of foreign gases, an equilibrium is established between $Cd(^3P_1)$ and $Cd(^3P_0)$. In the above mechanism, CdA_v^* is an unstabilized complex between the triplet cadmium atoms and the substrates. Reaction (7) was important in the case of ammonia,[2] but in the cases of water, alcohols, and ethers it does not seem to be important, since the Stern-Volmer plots lie on a straight line in the present experiment.[3] The overall rates of the quenching of the resonance line ($k_2+k_1k_3/k_{-1}+k_4$; $k_1/k_{-1}=1.68$ at 220 °C) were evaluated from the values of the half-quenching pressure in Table 2 by the method described in a previous paper;[2] they are listed in Table 3.

Table 3. Overall rate constants of the quenching of the resonance radiation and relative rate for the formation of the complex

Compounds	$k_2+1.68k_3+k_4$ (cm^3 $molecule^{-1}s^{-1}$)	$k_4/_4k^{NH_3}$
H_2O	3.9×10^{-12}	0.035
D_2O	6.7×10^{-13}	0.038
Methanol	7.2×10^{-12}	0.081
Ethanol	2.6×10^{-11}	0.091
Dimethylether	2.3×10^{-13}	0.044
Diethylether	1.9×10^{-12}	0.139
Ethylene oxide	1.6×10^{-10}	—
Tetrahydrofuran	7.8×10^{-13}	0.189

As was described previously,[3] the efficiency of the quenching by amines increases with an increase in the molecular complexity. However, as is shown in Table 3, the quenching by alcohols is generally more efficient than that by ethers.

From the pressure dependence of the intensity at the peak of the emission band, the relative values of k_4 can be estimated by a method described previously.[3] These values are also listed in Table 3. The values of k_4 increase in this order: $H_2O < D_2O <$ dimethylether $<$ methanol $<$ ethanol $<$ diethylether $<$ tetrahydrofuran. This order is in agreement with the order of the decrease in the ionization potential, except for the case of dimethylether. This tendency was also found in the cadmium-photosensitized reaction of amines; this indicates that the complex formed between the excited cadmium atoms and water, alcohols, and ethers is of the charge-transfer type.

The quantum yields of the luminescence for water, alcohols, and ethers given in Table 1 are much smaller than those for amines. As was mentioned in the previous paper,[3] the quenching of the resonance line by amines occurs mainly through the formation of the complex. However, it seems likely that the formation of the complex is not the predominant process in the quenching of the resonance line in the cases of water, alcohols, and ethers. In actuality, the k_4 values for water, alcohols, and ethers are about two or three orders of magnitude smaller than those for amines.

The ratio of the overall rates of the quenching of the resonance line for H_2O and D_2O is 5.9: 1. This value is considerably larger than the value of 1.91: 1 for the quenching of the Hg-253.7 nm resonance line by H_2O and D_2O. On the other hand, the ratio of the k_4 values for H_2O and D_2O is about unity. These findings also show that the quenching through the formation of the complex is not very important, as has been described

above. In the cadmium photosensitization, the available energy is only 87.7 kcal mol^{-1}. It is quite small compared with the O–H bond energy of H_2O (117 kcal mol^{-1}), even if the CdH formation is taken into account. The quenching of the excited cadmium atoms by water seems, then, to occur through the vibrational excitation of water. Therefore, the large isotope effect of H_2O and D_2O on the quenching rates may be due to the difference in the vibrational energies of O–H and O–D.

As was mentioned above, the quenching of the resonance line by alcohols is generally more efficient than that by ethers. Further, contrary to the expectation based on the ionization potential, the k_4 value for dimethylether is quite small. Thus, in the systems of Cd–alcohols and Cd–ethers, these values cannot be explained in terms of the electron-donating ability of the oxygen atom alone. In order to understand the effect of the higher substitution, we examined the effect of the replacement of the hydrogen atoms of ammonia by one, two, and three alkyl groups on the values of k_4 and $k_2+1.68k_3+k_4$. The results are shown in Table 4.

Table 4. The rate constants of the quenching of the resonance radiation and of the formation of the complex for primary-, secondary-, and tertiaryamines

Amines	$k_2+1.68k_3+k_4$ ($cm^3 molecule^{-1} s^{-1}$)	$k_4/k_4^{NH_3}$
Ammonia	2.4×10^{-12}	1.0
Methylamine	2.4×10^{-11}	10.7
Dimethylamine	2.9×10^{-11}	10.0
Trimethylamine	1.9×10^{-11}	5.1
Ethylamine	6.1×10^{-11}	15.8
Diethylamine	1.7×10^{-10}	43.1[a]
Triethylamine	1.1×10^{-10}	15.3[a]

a) These values were evaluated from the intensity at 450 nm (not at the peak) owing to the interference of the scattered light from the lamp, and therefore, they may be somewhat smaller than true values.

In both series of substitutions, methyl and ethyl, k_4 and $k_2+1.68k_3+k_4$ decrease on going from dialkyl amines to trialkyl amines. These tendencies are similar to those between methanol and dimethylether, and between ethanol and diethylether. As has been described in the previous paper,[3] in the series of primary amines a good relationship between k_4 and the ionization potential of amines was found. When secondary and tertiary amines are included, however, k_4 (and the efficiency of the quenching of the resonance line) cannot be explained in terms of the ionization potential (or the electron-donating ability of the nitrogen atom of amine) alone.

The relationship between k_4 and the ionization potential of substrates is shown in Fig. 4. The k_4 values for primary amines are quoted from Ref. (3). In general, k_4 increases with a decrease in the ionization potential. Especially for primary amines and alcohols, there is a good correlation between k_4 and the ionization potential. However, the k_4 values for secondary amines, tertiary amines, and ethers are somewhat smaller than the values predicted from the correlation mentioned above. In this manner, the reactivity of amines, alcohols, and ethers must be mainly governed by the electron-donating ability of the nitrogen and oxygen atoms, but partly by an other factor. This additional factor suppresses the formation of the excited complex in the cases of secondary amines, tertiary amines, and ethers. We tried to identify this factor, but we could not. Moreover, the origin of this factor remains an open question.

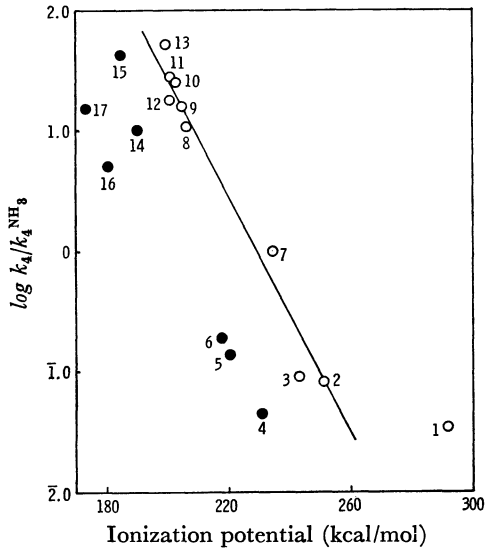

Fig. 4. Relationship between the relative rate constants for the formation of the excited complex and the ionization potential of substrates.
1) H_2O; 2) methanol; 3) ethanol; 4) dimethylether; 5) diethylether; 6) tetrahydrofuran; 7) ammonia; 8) methylamine; 9) ethylamine; 10) *n*-propylamine; 11) *n*-butylamine; 12) *sec*-butylamine; 13) *tert*-butylamine; 14) dimethylamine; 15) diethylamine; 16) trimethylamine; 17) triethylamine.
The plots for *s*- and *t*-amines and ether are shown as filled circles.

References

1) S. Tsunashima, T. Toyono, and S. Sato, This Bulletin, **46**, 2654 (1973).
2) S. Yamamoto, S. Tsunashima, and S. Sato, *ibid.*, **48**, 1172 (1975).
3) S. Yamamoto and S. Sato, *ibid.*, **48**, 1382 (1975).
4) S. Yamamoto, M. Takaoka, S. Tsunashima, and S. Sato, *ibid.*, **48**, 130 (1975).
5) R. H. Newman, C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *Trans. Faraday Soc.*, **66**, 2827 (1970).
6) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *ibid.*, **66**, 2974 (1970).
7) C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, *ibid.*, **67**, 67 (1971).