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Emission Processes in Cadmium Photosensitization

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The possibility of the cadmium-photosensitized luminescence of NH_3, CO_2, CO, and CH_4 was examined at 250 °C. In the case of NH_3, a very strong band emission was observed at 432 nm, with a band width of about 100 nm. The sensitized luminescence of NH_3 was attributed to the emission from an excited complex between triplet cadmium and NH_3. In the case of CH_4, a weak emission was observed at about 420 nm. In the cases of CO_2, CO, and N_2, however, no positive evidence of the sensitized luminescence was obtained. From the pressure dependence of the quenching of the 326.1 nm resonance line, the efficiencies of CO_2, CO, NH_3, and N_2 for quenching the triplet cadmium atoms were estimated to be 0.16, 0.03, 3.3×10^{-4}, and 4.9×10^{-5}, respectively, the efficiencies of *cis*-2-butene being assumed to be unity.

In spite of there having been many investigations of the mercury photosensitization, there have been only a few investigations of the cadmium photosensitization.[1] Since the nature of the $Cd(^3P_1)$ atoms is similar to that of the $Hg(^3P_1)$ atoms except for the amount of available excitation energy, a comparison of the two photosensitized reactions will give further information about the detailed mechanism of photosensitization.

It is known that the triplet mercury atoms cause: (a) an electronic energy transfer to molecules which have low-lying triplet states, such as olefins, aromatics, and ketones; (b) a hydrogen-atom abstraction reaction with paraffins, and (c) the conversion of the electronic energy to a luminescence emission.[1-4] Since Penzes, Strausz, and Gunning reported that CH_4, NH_3, and H_2O give a mercury-photosensitized luminescence in the spectral regions of 240—280, 290—400, and 254—320 nm respectively, many investigations of the mercury-photosensitized luminescence have been made with NH_3, H_2O, amines, alcohols, and rare gases by Gunning *et al.*,[2] Phillips *et al.*,[3] and Callear *et al.*[4] Phillips *et al.* attributed the sensitized luminescence to an excited complex between the $Hg(^3P_0)$ atom and a substrate.[3]

In the cadmium photosensitization, processes similar to (a) and (b) have been shown to occur in the reactions of olefins, acetylene, benzene, ketones, and hydrogen.[5] A process similar to (c) was recently reported to occur in the cadmium-photosensitized reactions of NH_3.[6] By analogy with the Hg–NH_3 system, Phillips *et al.* assigned the observed band emission at 430 nm to the emission from an excited complex between $Cd(^3P_0)$ and NH_3.[6]

The present paper will report the results of an independently-undertaken study of the cadmium-photosensitized luminescence and of the quenching for the 326.1 nm resonance line, using NH_3, CH_4, CO, CO_2, and N_2 as the substrates.

Experimental

Apparatus. A diagram of the experimental arrangement is shown in Fig. 1. The light source used was a home-made, U-shaped cadmium lamp (50 cm long and 8 mm o.d.) made of Pyrex; the emitted light was longer than 300 nm. The cylindrical quartz reaction cell was 20 mm in diameter and 50 cm long, with two flat planes. To minimize the intensity of the reflected light on the cell wall, several black-painted aluminum plates were inserted vertically between the lamp and the cell. The cell, the lamp, and the plates were kept in an electric furnace at 250±1 °C. The light

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[1] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, 1965.

[2] S. Penzes, O. P. Strause, and H. E. Gunning, *J. Chem. Phys.*, **45**, 2322 (1966); H. E. Gunning, S. Penzes, H. S. Sandhu, and O. P. Strausz, *J. Amer. Chem. Soc.*, **91**, 7684 (1969).

[3] C. G. Freeman, M. J. McEvan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **5**, 555 (1970); **6**, 482 (1970); **8**, 226 (1971); **9**, 578 (1971), *Trans. Faraday Soc.*, **66**, 2974 (1970); **67**, 67, 2004, 2565 (1971); R. H. Newman, C. G. Freeman, M. J. McEvan, R. F. C. Claridge, and L. F. Phillips, *ibid.*, **66**, 2827 (1970), **67**, 1360 (1971).

[4] A. B. Callear and J. McGurk, *Chem. Phys. Lett.*, **7**, 491 (1970); J. Koskikallio, A. B. Callear, and J. H. Conner, *ibid.*, **8**, 467 (1971); A. B. Callear and J. H. Conner, *ibid.*, **13**, 245 (1972).

[5] S. Tsunashima and S. Sato, This Bulletin, **40**, 2987 (1967), **41**, 284, 2281 (1968); S. Tsunashima, S. Hirokami, and S. Sato, *Can. J. Chem.*, **46**, 995 (1968); S. Tsunashima, S. Satoh, and S. Sato, This Bulletin, **42**, 329, 1531 (1969); S. Sato, C. Takahashi, and S. Tsunashima, *ibid.*, **43**, 1319 (1970); S. Tsunashima, O. Ohsawa, C. Takahashi, and S. Sato, *ibid.*, **45**, 83 (1973).

[6] P. D. Morten, C. G. Freeman, M. J. McEvan, R. F. C. Claridge, and L. F. Phillips, *Chem. Phys. Lett.*, **16**, 148 (1972).

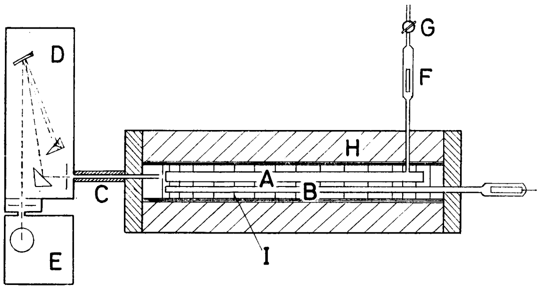

Fig. 1. Experimental system for studying the sensitized emission. A. Quartz Reaction Cell; B. Pyrex Cd Lamp; C. Light Guide; D. Monochromator; E. Photomultiplier; F. Cd Stopper; G. Stop-cock to Vacuum System; H. Furnace; I. Aluminum Plates.

from the cell was detected by means of an 1P28 photomultiplier tube through a light guide and a monochromator. The light guide used was a black-painted porcelain tube 5 mm in i.d. and 30 cm long. The monochromator and the photomultiplier used was a Hitachi Photoelectric Spectrophotometer, model EPU-2A. The emission intensity was measured by means of the photometer of the spectrophotometer and was recorded on a Yokokawa Laboratory Recorder, Type 3043. The reaction cell, containing a few pieces of cadmium metal, was connected to a mercury-free vacuum system through a cadmium stopper, which prevented the cadmium vapor from escaping from the cell. The glass tube between the furnace and the cadmium stopper was heated at about 290 °C by means of an electric heating tape in order to avoid the deposit of cadmium vapor. Some deposits of cadmium were, however, found on the tube at the insulator of the furnace. The pressure of the gas was measured by means of a W & T model 62-075 pressure gauge supplied by the Nagano Keiki Co.

A few experiments on the cadmium-photosensitized decomposition of NH_3 were carried out using a cell 5 cm long and 5 cm in diameter. The experimental details have previously been described.[5]

Materials. The cadmium metal used was high-purity cadmium (99.9999%) manufactured by the Osaka Asahi Metal Co. Pure-grade NH_3, CO_2, and *cis*-2-butene (Takachiho Shoji Co.) were used after degassing at the temperature of liquid nitrogen. Pure-Grade CH_4 and CO (Takachiho Shoji Co.) were used after having been passed through a trap at the temperature of liquid nitrogen. Pure-grade N_2 (Suzuki Shokan Co.) was used after having been passed through a molecular sieve trap at −110 °C.

The light intensity absorbed by cadmium was measured by using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene, assuming the quantum yield of the *trans*-isomer formation to be 0.5.[5] A typical light intensity absorbed in the cell used in the emission study was 6.8 ± 0.4 μEinstein min^{-1}.

Results

Emission Spectrum. When the empty cell only was illuminated by means of the cadmium lamp, line spectra were observed at 326, 340, 347, 361, 468, 480, and 509 nm with the entrance slit of 0.04 mm. These line spectra coincided with the emission spectra of the lamp used. These line spectra may be due to the scattered light on the cell wall. An attempt to minimize the intensity of the scattered light was unsuccessful.

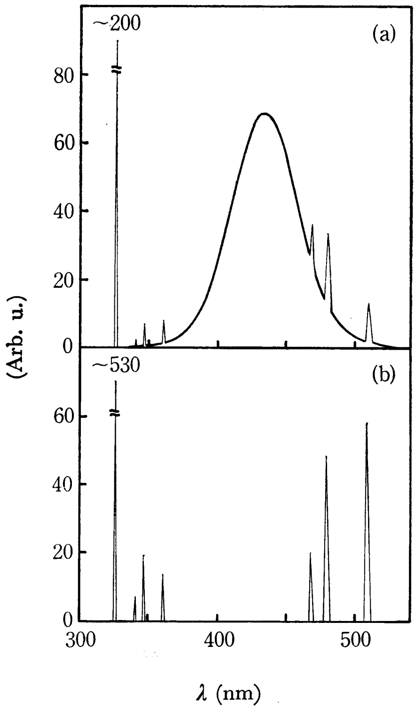

Fig. 2. Observed emission intensity distributions in the presence of 31 Torr of NH_3 (a) and in the absence of NH_3 (b); entrance slit is 0.04 mm and the spectra are not corrected for the sensitivity of the photomultiplier.

In the presence of the cadmium vapor in the cell at 250 °C and *ca.* 4.8×10^{-3} Torr, the intensity of the 326 nm emission increased, but those of the other lines remained almost constant.[7] When 31 Torr of NH_3 was added, as is shown in Fig. 2, the 326 nm line was quenched and a new band emission, with a band width of about 100 nm, was observed at 432 nm. Such a new band emission could not be observed when NH_3 alone was illuminated by the cadmium lamp. When CO_2, CO, or N_2 was the added gas, no emission other than the scattered light was observed in the 300—550 nm region, even when the entrance slit was opened up to 0.8 mm. In the case of CH_4, a very weak emission was observed at about 420 nm. The intensity at 420 nm was about 600 times less than that observed in the case of NH_3. The emission at 420 nm was very faint and decreased with the increase in the irradiation time. A similar tendency was also observed in the intensity at the 326 nm line. Beacuse of the low emission intensity and the large irradiation time dependence, no further study of the case of CH_4 was performed.

Pressure Dependence on the Emission in the NH_3–Cd System. In the case of NH_3, the profile of the band emission at 432 nm was almost the same at 3.0, 31, and 47 Torr, while the intensity at 432 nm increased

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[7] "C. R. C. Handbook of Chemistry and Physics," **50**, D167 (1969—1970).

Table 1. IRRADIATION TIME DEPENDENCE OF THE EMISSIONS AT 326.1 AND 432 nm IN THE PRESENCE OF 63.5 Torr OF NH_3.

Irradiation time (min)	Relative Emission Intensity 326.1 nm	Relative Emission Intensity 432 nm
0	(1.00)	(1.00)
1.0	0.942	0.940
2.0	0.878	0.881
3.0	0.825	0.823
5.0	0.720	0.710
8.0	0.562	0.566
10.0	0.485	0.490
14.0	0.372	0.368

Table 2. PRODUCTS IN THE CADMIUM-PHOTOSENSITIZED DECOMPOSITION OF NH_3 AT 250 °C.

Pressure (Torr)	Absorbed Light Intensity (μEinstein)	Quantum Yield H_2	Quantum Yield N_2
52.5[a]	14.6	0.024	0.007
52.5[a]	40.7	0.032	0.009
76.4[b]	14.6	0.039	0.012
79.6[c]	440	0.212	0.053
92.6[b]	14.6	0.037	0.008
96.6[c]	1100	0.079	0.019

a) cell volume 86 ml, light intensity 0.194 μEinstein min^{-1}.
b) cell volume 95 ml, light intensity 0.194 μEinstein min^{-1}.
c) cell volume 160 ml, light intensity 6.8 μEinstein min^{-1}.

with the increase in pressure. As is shown in Table 1, the intensity at 432 nm decreased with the increase in the irradiation time. The rate of the decrease increased with the increase in pressure. The emission intensities at 432 nm extraporated to zero irradiation time are plotted in Fig. 3. In this case, the entrance slit of the monochromator was kept at 0.05 mm; this corresponds to the band width of about 0.7 nm at 432 nm.

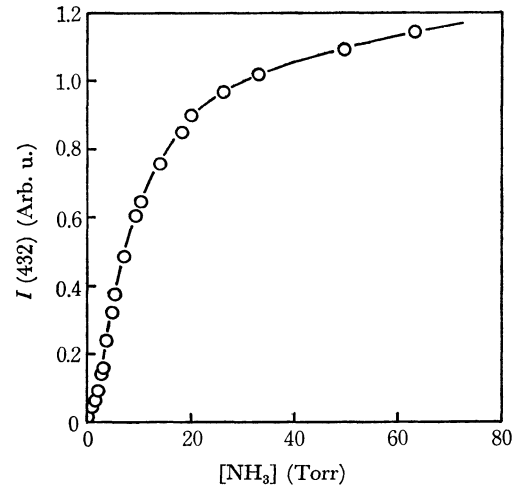

Fig. 3. The emission intensity at 432 nm as a function of NH_3 pressure.

Decomposition of NH_3. After the irradiation of NH_3 in the presence of the cadmium vapor with the cadmium lamp, hydrogen and nitrogen were observed as the decomposition products. We were unsuccessful in trying to detect hydrazine, a possible reaction product, using a gas chromatograph. The relative yield of hydrogen and nitrogen was 3.7±0.8. The apparent quantum yields of the product formation are listed in Table 2.

Quenching of the 326.1 nm Resonance Line. The efficiencies of N_2, NH_3, CO, and CO_2 in quenching the triplet cadmium were studied using the quenching of the 326.1 nm resonance line. The emission intensities at 326.1 nm were measured as a function of the pressure. In order to obtain a good reproducibility, the intensities were measured with a low sensitivity of the photomultiplier and with an entrance slit of 0.5 mm, which corresponds to the band width of 4 nm.

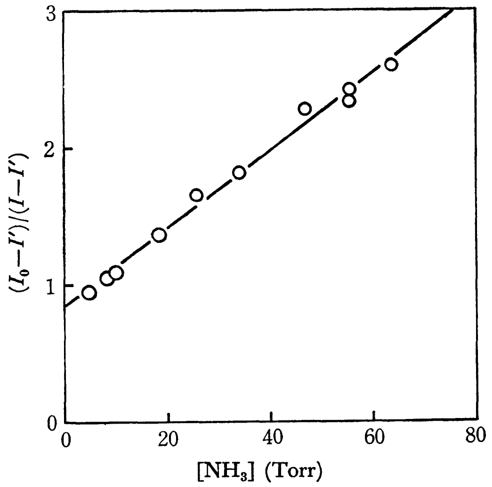

Fig. 4. Stern-Volmer plots of NH_3 for quenching 326.1 nm resonance line.

A typical plot of $(I_0-I')/(I-I')$ against the pressure is shown in Fig. 4, where I_0 and I are the emission intensities at 326.1 nm in the absence and in the presence of a quencher gas respectively. I' is the scattered light intensity at 326.1 nm. On the assumption that 140 Torr of CO quenches the triplet cadmium completely, I' was estimated to be 0.91% of the I_0. In the case of N_2, CO, or CO_2 as the quencher gas, no irradiation time dependence of the emission intensity was observed. In the case of NH_3, however, the intensity decreased with the increase in the irradiation time, as was observed in the case of the 432 nm emission. The irradiation time dependences in both cases agreed well, as is shown in Table 1. In this case, the value of the initial emission intensity was estimated by an extrapolation of the observed intensity to zero irradiation time.

As is shown in Fig. 4, a straight line was obtained. From the intercept and the slope of the straight line, the half-quenching pressure was estimated to be the intercept divided by the slope. The values of the intercept and of the half-quenching pressure are listed in Table 3.

Table 3. Half-quenching pressures and intercepts of Stern-Volmer plots for quenching 326.1 nm resonance line at 250 °C.

Quencher	Intercept	Half-quenching Pressure (Torr)
N_2	0.96±0.01	220 ±3
NH_3	0.85±0.03	29.8 ±1.4
CO	0.84±0.22	0.34 ±0.09
CO_2	0.55±0.27	0.060±0.030

Discussion

Emitting Species in the Cadmium-photosensitized Emission of NH_3. In the case of the vacuum ultraviolet photolysis of NH_3, it has been shown that the NH and NH_2 radicals formed emit their fluorescence at about 324 and 400—600 nm respectively.[8,9] In the case of the cadmium photosensitization, the available energy is only 87.7 kcal mol^{-1}, which is comparable to the N-H bond energy of NH_3 (103 kcal mol^{-1})[10] if the CdH formation is taken into account. The $NH_3 \rightarrow NH+H_2$ (ΔH=89.7 kcal mol^{-1})[9] reaction is energetically impossible in the cadmium photosensitization. When an excited NH_2 radical is assumed to emit the 432 nm band emission, it is necessary to assume the reexcitation of the NH_2 radical by the direct absorption of light and/or the energy transfer from triplet cadmium. A mechanism which includes these processes fails to explain the pressure dependence of the observed emission intensities. The assumption that the emitting species was CdH, which is a possible reaction intermediate in the cadmium-photosensitized reactions of NH_3 and CH_4, was also excluded for the same reason.

In the case of mercury photosensitization, the 350 nm band emission has been attributed to the emission from the complex between the Hg($^3P_0$) atom and the NH_3 molecule.[3] Phillips *et al.*, using a phase-modulation method, found a band emission at 430 nm in the cadmium-photosensitized reactions of NH_3.[6] By analogy with the Hg–NH_3 system, they attributed the emitting species to a complex between Cd($^3P_0$) and NH_3.[6]

Pressure Dependence of the NH_3 Emission. The pressure dependence of the emission intensity at 432 nm, shown in Fig. 3, was not completely explained by the mechanism proposed by Phillips *et al.*[6] In their mechanism, it was assumed that there were bimolecular and termolecular reactions between Cd($^3P_0$) and NH_3 involved in the formation of the complex.[6]

One of the mechanisms which can explain the observed pressure dependence of the emission is shown below:

$$\mathrm{Cd} + h\nu(326.1) \longrightarrow \mathrm{Cd}(^3P_1) \qquad k_a \qquad (1)$$

$$\mathrm{Cd}(^3P_1) \longrightarrow \mathrm{Cd} + h\nu(326.1) \qquad k_0 \qquad (2)$$

$$\mathrm{Cd}(^3P_1) + \mathrm{A} \longrightarrow \mathrm{CdA}^{*\prime} \qquad \alpha k_q \qquad (3)$$

$$\longrightarrow \text{other reactions} \qquad (1-\alpha)k_q \qquad (4)$$

$$\mathrm{CdA}^{*\prime} + \mathrm{A} \longrightarrow \mathrm{CdA}^{*} + \mathrm{A} \qquad k_s \qquad (5)$$

$$\mathrm{CdA}^{*\prime} \longrightarrow \mathrm{Cd} + \mathrm{A} \qquad k_d \qquad (6)$$

$$\mathrm{CdA}^{*} \longrightarrow \mathrm{Cd} + \mathrm{A} + h\nu' \qquad k_f \qquad (7)$$

$$\mathrm{CdA}^{*} + \mathrm{A} \longrightarrow \mathrm{Cd} + 2\mathrm{A} \qquad k_m \qquad (8)$$

Here, CdA*′ and CdA* represent, respectively, an unstabilized and a stabilized complex between the triplet cadmium and NH_3. NH_3 is denoted as A. In this mechanism, it is assumed that the unstabilized complex does not radiate the emission. It is also assumed that the Cd($^3P_1$) atoms are responsible for the formation of the complex, because the participation of Cd($^3P_0$) in the cadmium photosensitization has not been established.[1] If, however, the Cd($^3P_0$) is responsible for the complex formation, Reaction (3) should be replaced by Reactions (9) and (10):

$$\mathrm{Cd}(^3P_1) + \mathrm{A} \longrightarrow \mathrm{Cd}(^3P_0) + \mathrm{A} \qquad \alpha k_q \qquad (9)$$

$$\mathrm{Cd}(^3P_0) + \mathrm{A} \longrightarrow \mathrm{CdA}^{*\prime} \qquad (10)$$

The steady-state treatment of the above mechanism gives the following relation:

$$1/I = (1+k_0/k_q[\mathrm{A}])(1+k_d/k_s[\mathrm{A}])(1+k_m[\mathrm{A}]/k_f)/\alpha I_a. \qquad \mathrm{(I)}$$

Here, I represents the total emission intensity arising from the stabilized complex. Since the emission profile was almost the same at all pressures examined, the observed emission intensity at 432 nm (I(432)) may be proportional to the total emission intensity (I) *i.e.*, $I(432)=cI$. The proportional factor, c, may depend on the geometry of the apparatus and on the sensitivity of the photomultiplier used. At the pressures high enough for $(1+k_d/k_s[\mathrm{A}]) \approx 1$, Eq. (I) can be reduced to this form:

$$1/I(432)(1+k_0/k_q[\mathrm{A}]) = (1+k_m[\mathrm{A}]/k_f)/c\alpha I_a. \qquad \mathrm{(II)}$$

Assuming a value of k_0/k_q equal to the half-quenching pressure of NH_3 (Table 3), the left-hand side of Eq. (II) is plotted against the pressure of NH_3 in Fig. 5. As is shown in Fig. 5, a straight line was obtained in the high-pressure region. At the pressures low enough for $(1+k_m[\mathrm{A}]/k_f) \approx 1$, Eq. (I) can be reduced to this form:

$$1/I(432)(1+k_0/k_q[\mathrm{A}]) = (1+k_d/k_s[\mathrm{A}])/c\alpha I_a. \qquad \mathrm{(III)}$$

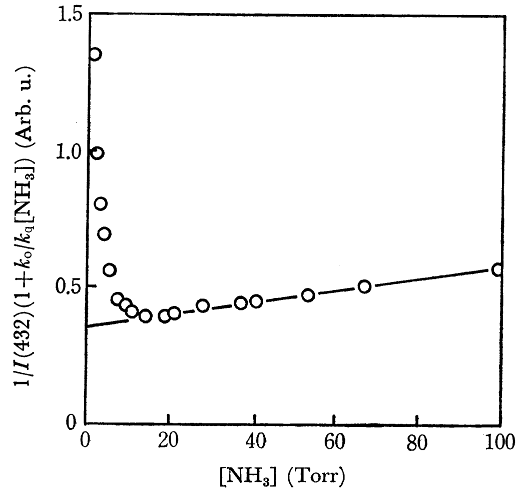

Fig. 5. The plots of $1/I(432)(1+k_0/k_q[\mathrm{A}])$ as a function of NH_3 pressure.

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[8] K. H. Becker and K. H. Werge, *Z. Naturforsch.*, **18a**, 600 (1963).

[9] H. Okabe and M. Lenzi, *J. Chem. Phys.*, **47**, 5241 (1967).

[10] "C. R. C. Handbook of Chemistry and Physics," **50**, F163 (1969—1970).

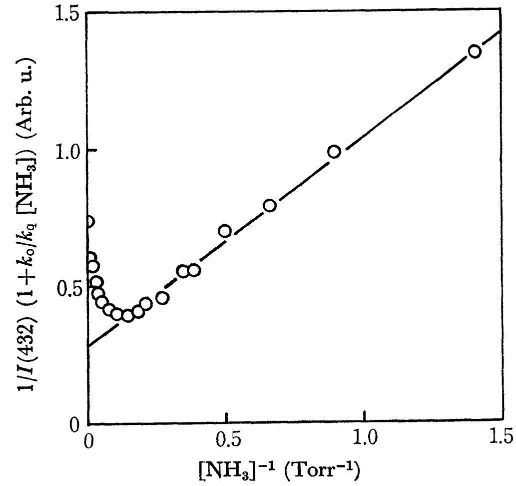

Fig. 6. The plots of $1/I(432)(1+k_o/k_q[\mathrm{A}])$ as a function of reciprocal of $\mathrm{NH_3}$ pressure.

The left-hand side of Eq. (III) is plotted against the reciprocal of the pressures in Fig. 6. As is shown in Fig. 6, the plots show a straight line in the low-pressure region. The intercepts of the straight lines coincided with each other within the limits of experimental error. From the intercepts and the slopes of the straight lines, the values of k_m/k_f and k_d/k_s were calculated to be $(1.2\pm0.2)\times10^{-2}$ Torr^{-1} and 2.8 ± 0.2 Torr respectively.

Assuming the cross section of 9 Å^2 for Reactions (5) and (8),[11] which corresponds to $k_m=k_s=1.4\times10^{11}$ l mol^{-1} s^{-1} at 250 °C, the lifetimes of the unstabilized complex and the stabilized complex were calculated to be 8.2×10^{-8} and 2.9×10^{-9} s respectively. The finding that the lifetime of the unstabilized complex is longer than that of the stabilized complex seems somewhat strange. It may, however, be explained by one of the following chains of reasoning: (a) If the total spin is conserved during Reactions (3) or (10), the unstabilized complex, CdA*′, should be in a triplet state. Because the lifetime of $\sim10^{-9}$ s is a typical value for a fluorescence emission, the stabilized complex, CdA*, may be in an excited singlet state. Generally, an excited singlet state has a shorter lifetime than an excited triplet state. The difference in the spin multiplicity might explain the estimated shorter lifetime of the stabilized complex. (b) If the following reactions are considered to occur in the mechanism:

$$\mathrm{CdA^* + A \longrightarrow Cd + 2A} \qquad k_m' \qquad (8)$$

$$\longrightarrow \mathrm{CdA_2^*} \qquad k_m \qquad (11)$$

$$\mathrm{CdA_2^* \longrightarrow CdA^* + A} \qquad (12)$$

where $\mathrm{CdA_2^*}$ represents a dimer complex between the triplet cadmium atom and two $\mathrm{NH_3}$ molecules, the value of k_m should be smaller than that of k_s. A small value of k_m gives a large value for the lifetime. If k_m'/k_m is larger than 30, the lifetime of the stabilized complex should be longer than 9×10^{-8} s.

Effects of Decomposition Products. The formations of hydrogen and nitrogen in the cadmium-photosensitized reactions of $\mathrm{NH_3}$ may be explained in terms of the following reactions:

$$\mathrm{Cd} + h\nu(326.1) \longrightarrow \mathrm{Cd(^3P_1)} \qquad (1)$$

$$\mathrm{Cd(^3P_1)} \longrightarrow \mathrm{Cd} + h\nu(326.1) \qquad (2)$$

$$\mathrm{Cd(^3P_1) + NH_3 \longrightarrow CdH + NH_2} \qquad (13)$$

$$\mathrm{CdH \longrightarrow Cd + H} \qquad (14)$$

$$\mathrm{H + NH_3 \longrightarrow H_2 + NH_2} \qquad (15)$$

$$\mathrm{2NH_2 \longrightarrow NH + NH_3} \qquad (16)$$

$$\mathrm{2NH \longrightarrow H_2 + N_2} \qquad (17)$$

The CdH formation is assumed because of the small excitation energy of the triplet cadmium. The reactions of NH and $\mathrm{NH_2}$ radicals are still in question, because the reaction of the hydrogen atom and hydrazine, one of the products, is considered to explain the formation of nitrogen and hydrogen in the mercury-photosensitized decomposition of $\mathrm{NH_3}$.[12]

As will be shown later, the efficiency of hydrogen in quenching the triplet cadmium is about 2×10^3 times that of $\mathrm{NH_3}$. One of the products, hydrogen, will compete with $\mathrm{NH_3}$ in quenching the triplet cadmium, even in the presence of 0.05% of $\mathrm{NH_3}$.

$$\mathrm{Cd(^3P_1) + H_2 \longrightarrow CdH + H} \qquad (18)$$

$$\longrightarrow \mathrm{Cd + H_2} \qquad (19)$$

Here, again the CdH formation is assumed.[5] If Reaction (18) is included in the mechanism, the apparent quantum yield of the decomposition should increase with the increase in the irradiation time, while the observed emission intensities at 326.1 and 432 nm should decrease at the same rate. These effects explain well the results shown in Tables 1 and 2.

Using the values of the quantum yield and the half-quenching pressure of $\mathrm{NH_3}$, it was estimated that Reaction (13) accounts for only about 2% of the quenching for the triplet cadmium. This value is about one order of magnitude smaller than that obtained in the mercury photosensitization, in which the available excitation energy is much higher than that in the cadmium photosensitization.[12]

Quenching of the 326.1 nm Resonance Line. In the usual Stern-Volmer plots, the intercept of the straight line is expected to be unity. The intercept obtained here, however, was less than unity for every case examined (Table 3 and Fig. 4). Similar results were obtained by Phillips *et al.* in the mercury-photosensitized luminescence of $\mathrm{NH_3}$.[4] They explained the deviation from unity in terms of the effect of the Lorentz broadening of the resonance line; *i.e.*, the absorbed light intensity increases with the increase in the pressure.[3] To check this possibility in the present study, the Lorentz breadth and the Doppler breadth of the resonance line were compared using the following equations:[13]

$$\Delta\nu_D = 2\nu_0(\sqrt{2R\ln 2}/c)\sqrt{T/M} \qquad (IV)$$

$$\Delta\nu_L = 2\sigma_L{}^2N\sqrt{2RT/\pi\mu} \qquad (V)$$

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[11] "C. R. C. Handbook of Chemistry and Physics," **50**, F151 (1969—1970).

[12] C. C. McDonald and H. E. Gunning, *J. Chem. Phys.*, **23**, 532 (1955); S. Takamuku and R. A. Back, *Can. J. Chem.*, **42**, 1426 (1964); M. Z. Hoffman, M. Goldmaster, and R. L. Damour, *J. Chem. Phys.*, **47**, 2195 (1967).

[13] A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge University Press, London (1934), p. 99, 170.

Here, $\Delta\nu_D$ and $\Delta\nu_L$ are, respectively, the Doppler breadth and the Lorentz breadth for the resonance line. ν_0 and σ_L^2 are, respectively, the frequency of the resonance line and the effective cross-section for the Lorentz broadening. R, T, M, μ, and N are the gas constant, the temperature, the mass, the reduced mass, and the number of foreign gas molecules in 1 cm^3 respectively. The Doppler breadth of the 326.1 nm resonance line was estimated to be $1.4\times10^9\,s^{-1}$ at 250 °C. The Lorentz breadth was $6.4\times10^8\,s^{-1}$ at 250 °C in the presence of 100 Torr of NH_3, assuming the cross-section for the Lorentz broadening to be 40 Å^2. That is, the effect of the Lorentz broadening may be ignored in the present study.

Bender observed in his study of the quenching for the cadmium resonance line, that the absorbed light intensity in the evacuated system was lower than that in the presence of a quencher gas.[14] He explained this in terms of the low vapor pressure of cadmium; *i.e.*, in the evacuated system, the faster distillation of the vapor to the colder part of the apparatus causes a lowering of the vapor pressure.[14] As was mentioned in the Experimental section, the deposit of cadmium was observed in this study. If this effect is operative in the present study, the absorbed light intensity in the evacuated system should be smaller than that expected in the presence of a quencher gas. Even in the presence of 0.1 Torr of a quencher, the mean free path of cadmium is expected to be about two orders of magnitude smaller than that in the evacuated system, in which the pressure may be smaller than the vapor pressure of cadmium (4.8×10^{-3} Torr).[7] This effect may explain the small value of the intercept shown in Table 3.

The relative quenching efficiencies of CO_2 and H_2 have been estimated to be, respectively, 0.16 and 0.8 times that of *cis*-2-butene.[5] Using these values and the values of the half-quenching pressure (Table 3), the efficiencies of H_2, CO_2, CO, NH_3, and N_2 in quenching the triplet cadmium were estimated to be 0.8, 0.16, 0.03, 3.3×10^{-4}, and 4.9×10^{-5} respectively, when the efficiency of *cis*-2-butene was assumed to be unity. The order of the efficiencies obtained is in good agreement with that obtained by Lipson and Mitchell and by Steacie and LeRoy.[15,16] The values of NH_3 and N_2 are, however, much smaller than those obtained by them. This deviation may be mainly due to the presence of a small amount of impurities and/or decomposition products which can quench the triplet cadmium efficiently, such as hydrogen.

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14) P. Bender, *Phys. Rev.*, **36**, 1535 (1930).

15) H. C. Lipson and A. C. G. Mitchell, *ibid.*, **48**, 625 (1935).

16) E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, **11**, 164 (1943).