December, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***54***, *3677—3680 (1981)*

The Cadmium-photosensitized Reaction of Saturated Tertiary Amines

Shunzo Yamamoto,* Masae Yasunobu, and Norio Nishimura
Department of Chemivtry, Faculty of Science, Okayama University, Tsushima, Okayama 700

(Received April 18, 1981)

Rate constants for the quenching of the cadmium resonance line at 326.1 nm by triethylamine (TEA), *N*-ethylpiperidine (NEP), and 1-azabicyclo[2.2.2]octane (ABCO) were obtained. Relative rate constants for the formation of an exciplex between an excited cadmium atom and these amines and quantum yields for the emission from the exciplex were also obtained. Contrary to the case of primary amines, in which the electron-donating ability of the nitrogen atom is operative, the exciplex formation in the present case is mainly governed by the magnitude of the steric effect of ethyl groups on the interaction between the nitrogen atom and an excited cadmium atom. Gaseous products were hydrogen, methane, ethane (and/or ethylene), and butane. The quantum yields of these products indicate that the primary photochemical products are methyl and ethyl radicals for TEA and NEP. The amount of products for ABCO was considerably smaller than those for other amines.

In the cadmium-photosensitized reaction of saturated amines, the quenching of the resonance line at 326.1nm and the exciplex emission have been discussed in previous papers in terms of the following reactions:[1]

$$\mathrm{Cd} + h\nu(326.1) \longrightarrow \mathrm{Cd}(^3\mathrm{P}_1), \qquad (1)$$

$$\mathrm{Cd}(^3\mathrm{P}_1) \longrightarrow \mathrm{Cd} + h\nu(326.1), \qquad (2)$$

$$\mathrm{Cd}(^3\mathrm{P}_1) + \mathrm{M} \rightleftharpoons \mathrm{Cd}(^3\mathrm{P}_0) + \mathrm{M}, \qquad (3), (-3)$$

$$\mathrm{Cd}^* + \mathrm{A} \longrightarrow \text{quenching}, \qquad (4)$$

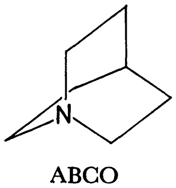
$$\mathrm{Cd}^* + \mathrm{A} \longrightarrow \mathrm{CdA}^*, \qquad (5)$$

$$\mathrm{CdA}^* \longrightarrow \mathrm{Cd} + \mathrm{A} + h\nu_e, \qquad (6)$$

$$\mathrm{CdA}^* + \mathrm{M} \longrightarrow \mathrm{Cd} + \mathrm{A} + \mathrm{M}. \qquad (7)$$

Here, Cd* represents $\mathrm{Cd}(^3\mathrm{P}_1)$ and $\mathrm{Cd}(^3\mathrm{P}_0)$, and CdA* is an exciplex between Cd* and amines. A represents the amine and M stands for a third body. In general, the rate constant for Reaction 5 increases with a decrease in the ionization potential of amines, and for primary amines there is a good correlation between the rate constant and the ionization potential.[2] The rate constants for secondary and tertiary amines are, however, somewhat smaller than the values predicted from the correlation mentioned above. It has been pointed out that the reactivity of amines is mainly governed by the electron-donating ability of the nitrogen atom, but partly by some other factor which supresses the formation of the exciplex in the cases of secondary and tertiary amines. This additional factor was attributed to the steric effect of the alkyl groups.[3] It seems to be necessary to examine decomposition processes which compete with the exciplex formation. In the cadmium-photosensitized reaction of amines, however, products have not been yet reported.

In this study, in order to examine the influence of structural properties on the cadmium-photosensitized reaction of amine, we measured the quenching efficiency and the quantum yields for the exciplex emission and for the products of three saturated tertiary amines (TEA, NEP, and ABCO) which are considered to have different steric hindrances around the nitrogen atom.



ABCO

Experimental

The apparatus and the procedure for measuring the emissions (resonance line at 326.1 nm and exciplex emission) were the same as those described previously.[4] The measurements were done at 220±1 °C.

A Pyrex reaction cell used for measuring the product yields was 20.0 cm long and 2.2 cm in diameter, with a total volume, including access tubing, of about 86 cm^3. It was inserted in an electric furnace kept at 250±1 °C. A hand-made cadmium discharge lamp (filled with *ca.* 2 Torr argon, 1 Torr = 133.32 Pa) made of Pyrex was also placed in the same furnace.

Reaction products were analyzed by means of a gas chromatograph using a column of 5 m VZ-7 (Gasukuro Kogyo Co., Ltd.) at 0 °C. In this column, we could not separate ethane from ethylene. The amounts of gases which are noncondensable at 77 K were determined volumetrically by a Toepler pump. The light intensity absorbed by cadmium atoms was estimated by using the *cis-trans* isomerization of *cis*-2-butene as an actinometer.

Cadmium metal used was high-purity grade (99.9999%) manufactured by the Osaka Asahi Metal Co. Ethylamine (EA), Diethylamine (DEA), TEA, piperidine (P), and NEP (G.R. grade) were used after drying over calcium hydride and repeated trap-to-trap distillation. ABCO·HCl was purchased from Pfaltz and Bauer, Inc. The free base was liberated by combining very concentrated ABCO·HCl and NaOH aqueous solutions. This solid amine was filtered and sublimed *in vacuo* through a layer of anhydrous BaO.

Results

In Fig. 1, the emission bands obtained for the cadmium-photosensitized reaction of TEA, NEP, and ABCO are shown. The band for ammonia is also shown for comparison. The quantum yields of the emission for TEA, NEP, and ABCO were determined by comparing the integrated intensities of the emission band with that for ammonia (whose emission quantum yield is known) under the same conditions. The values of quantum yields were found to be almost independent of amine pressure (0.1—1.2 Torr for TEA and NEP, and 0.1—2.0 Torr for ABCO) and argon pressure (50—200 Torr). The average values are listed in Table 1, together with the wavelengths at the peak of the emission bands.

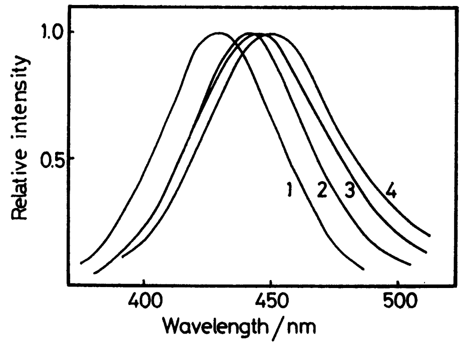


Fig. 1. Emission band contours for NEP (1), TEA (2), and ABCO (3). The curve for NH_3 (4) is derived from Ref. 5.

TABLE 1. WAVELENGTH AT THE PEAK OF THE EMISSION BAND AND QUANTUM YIELD OF THE EMISSION

Compound	$\frac{\lambda_{max}}{nm}$	ϕ_e
TEA	444	0.12±0.01
NEP	448	0.17±0.01
ABCO	442	0.87±0.02

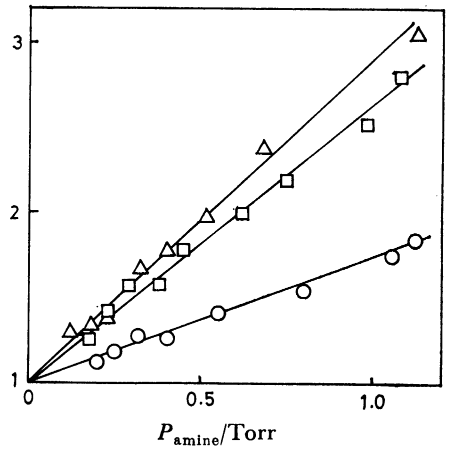


Fig. 2. Stern-Volmer plots for the quenching of the resonance line at 326.1 nm by TEA (□), NEP (△), and ABCO (○).

In order to estimate the efficiency of the quenching of the 326.1 nm resonance line, its emission intensity was measured as a function of the pressure of substrates. The Stern-Volmer plots are shown in Fig. 2, where I_0 and I are the intensities of the resonance line in the absence and in the presence of the substrates, respectively. Half-quenching pressures obtained from the slopes of the straight lines in Fig. 2 are listed in Table 2.

TABLE 2. HALF-QUENCHING PRESSURE FOR THE QUENCHING OF 326.1 NM RESONANCE LINE

Compound	Torr
TEA	0.61±0.02
NEP	0.52±0.02
ABCO	1.33±0.03

TABLE 3. QUANTUM YIELDS OF PRODUCTS IN CADMIUM-PHOTOSENSITIZED REACTION OF SATURATED AMINES[a,b)]

Compound	H_2+CH_4	H_2	CH_4	C_2H_6 (C_2H_4)	C_4H_{10}	ϕ_d[c)]
EA	0.071	0.001	0.070	0.073	0.013	0.169
DEA	0.162	0.001	0.161	0.143	0.022	0.348
P	0.027	0.001	0.026	0.023	0.033	0.115
TEA	0.147	0.002	0.145	0.289	0.044	0.522
NEP	0.049	0.002	0.047	0.050	0.022	0.141
ABCO	0.013	0.004	0.009	0.021	0	0.030

a) Uncertainties in quantum yields, except for hydrogen, are within 5%. b) Pressure of amines was 30 Torr. c) $\phi_d=\phi_{CH_4}+\phi_{C_2H_6}+2\phi_{C_4H_{10}}$.

The pressure dependence of the intensity at the peak of the emission band (which was expressed on the basis of that at 430 nm for Cd*-NH_3 system) is shown in Fig. 3. The emission intensities were independent of argon pressure.

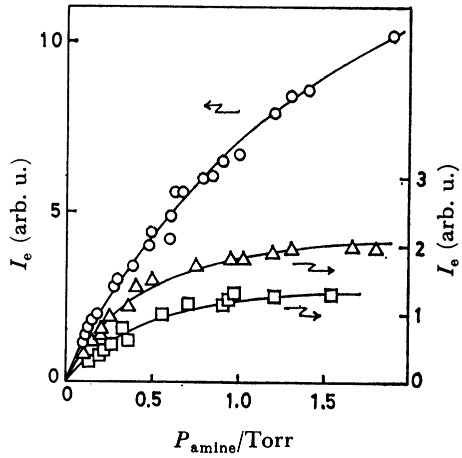


Fig. 3. The intensity at the peak of the emission band from the exciplex as a function of the pressures of TEA (□), NEP (△), and ABCO (○).

Quantum yields of products in the cadmium-photosensitized reaction of saturated amines are summarized in Table 3. In order to check the thermal reaction and the direct photolysis, 30 Torr of the amine was kept in the cell at 250 °C for a few hours in the absence of cadmium under irradiation of the 326.1 nm cadmium resonance line. No decomposition was detected for any amine. The light intensity absorbed by cadmium atoms was estimated to be 0.26×10^{-6} Einstein min^{-1}.

Discussion

In previous papers,[1)] the quenching of the resonance line and the exciplex emission were explained according to Reactions 1—7. Because the equilibrium between $Cd(^3P_0)$ and $Cd(^3P_1)$ is easily established under the present experimental conditions,[6)] we cannot discriminate the reactions of these two states.

A steady-state treatment leads to the following equation:

$$I_0/I = 1 + k_q[A]/k_2. \quad (8)$$

Here, I_0 and I represent the intensities of the resonance line (defined as $k_2[\mathrm{Cd}(^3\mathrm{P}_1)]$) in the absence and in the presence of amines respectively; k_q is the composite quenching rate constant: $k_\mathrm{q}=k_4+(k_3/k_{-3})k_4'+k_5+(k_3/k_{-3})k_5'$ (k_4 and k_5 are rate constants for Reaction 4 and 5 in the case of $\mathrm{Cd}^*=\mathrm{Cd}(^3\mathrm{P}_1)$ and k_4' and k_5' are those in the case of $\mathrm{Cd}^*=\mathrm{Cd}(^3\mathrm{P}_0)$); ($k_3/k_{-3}=1.68$ at 220 °C). The Stern-Volmer plots in Fig. 1 are expressed by this equation. As was mentioned in previous papers,[1,6] the effective lifetime is almost independent of the pressure of foreign gases in the range we were studying. Therefore, k_2 may be set equal to $1/\tau_0$ (τ_0 is the natural lifetime of $\mathrm{Cd}(^3\mathrm{P}_1)$ and has been reported to be 2.39×10^{-6} s[7])). From the half-quenching pressure, the values of k_q can be estimated; they are listed in Table 4, together with those for some primary and secondary amines. As is shown in Table 4, the values of k_q for tertiary amines are smaller than those for primary and secondary amines. This tendency has been explained in terms of the steric hindrance of the alkyl groups.[4]

TABLE 4. THE RATE CONSTANTS FOR THE QUENCHING OF THE RESONANCE LINE AND FOR THE EXCIPLEX FORMATION

Compound	$\frac{k_\mathrm{q}\times10^{11}}{\mathrm{cm^3\ molecule^{-1}\ s^{-1}}}$	$\frac{k_5}{k_5^{\mathrm{NH_3}}}$	$\frac{I_\mathrm{p}{}^{\mathrm{b)}}}{\mathrm{kJ\ mol^{-1}}}$
EA[a]	6.1±0.1	15.3	913.8
DEA[a]	17.0	43.1	832.6
P[a]	7.0±0.18	14.0	835.5
TEA	3.6±0.1	4.40	779.4
NEP	4.2±0.2	6.89	812.5[c]
ABCO	1.6±0.1	13.8	776.6

a) Ref. 4. b) Ref. 8. c) Value for *N*-methylpiperidine.

The steady-state treatment leads to the following equation for the intensity of the exciplex emission:

$$I[\mathrm{A}]/I_\mathrm{e}=\alpha(k_2/k_5)(1+k_7[\mathrm{M}]/k_6), \tag{9}$$

where I_e is the emission intensity at the peak of the band and I is the intensity of the resonance line at the same pressure of amines; α is the proportional factor between I_e and the total emission intensity. From the pressure dependence of the intensity at the peak of the emission band, relative values of k_5 have been estimated by the method described previously,[3,4] and are listed in Table 4.

In general, the rate constant for the exciplex formation increases with a decrease in I_p values of amines.[2] In the present case, the values of k_5 increase in the order: TEA<NEP<ABCO. This order is not in agreement with the order of the decrease in I_p. TEA is "flexible" in the sense that its ethyl groups hinder the access of the excited cadmium atom to the nitrogen atom. Meanwhile, ABCO is a rigid, bicyclic amine having bridgehead nitrogen atom and is little sterically hindered. Among these amines, if the steric effects overwhelm other factors affecting k_5, the smallest value of k_5 for TEA and the largest value for ABCO could be ascribed to the steric effects.

As mentioned above, the quantum yields of the emission for three tertiary amines are almost independent of amine and argon pressures, indicating that the exciplexes are little quenched by amine and argon. As ABCO has the largest quantum yield of the emission, we assumed that $\phi_\mathrm{e}=k_5/k_\mathrm{q}$ for ABCO. This indicates that the quantum yield of the emission is determined by the ratio of the rate constant (k_5) for the exciplex formation to the overall quenching rate constant (k_q). We obtained the value of k_5 (1.40×10^{-11} cm^3 molecule^{-1} s^{-1}) for ABCO by the observed values of ϕ_e and k_q. Further, we obtained the values of k_5 for other amines by using the relative values of k_5 shown in Table 4; these values are shown in Table 5. In Table 5, the values of k_5/k_q are also shown. These values are in fair agreement with the experimental values of ϕ_e. This indicates that the above assumption is valid for all these amines. Practically all of the exciplexes formed decay out through the emission process, that is, neither unimolecular decomposition nor a bimolecular quenching of the exciplex occurs.

TABLE 5. THE VALUES OF k_5, k_5/k_q, AND ϕ_r

Compound	$\frac{k_5\times10^{11}}{\mathrm{cm^3\ molecule^{-1}\ s^{-1}}}$	$\frac{k_5}{k_\mathrm{q}}$	ϕ_e	ϕ_r
EA	1.55	0.25	0.26[a]	0.57
DEA	4.37	0.26	—	0.39
P	1.42	0.20	0.20[a]	0.68
TEA	0.45	0.13	0.12	0.36
NEP	0.70	0.17	0.17	0.69
ABCO	1.40	0.87	0.87	0.10

a) Ref. 4.

As is shown in Table 3, gaseous products in the cadmium-photosensitized reaction of the saturated amines studied are hydrogen, methane, ethane (and/or ethylene), and butane. It has been reported that in the direct photolysis of TEA,[9] the primary products were hydrogen molecule and methyl and ethyl radicals produced from an excited TEA molecule and that from these radicals methane, ethane, ethylene, propane, and butane were formed. It is reasonable that, in the cadmium-photosensitized reaction of TEA, methyl and ethyl radicals are also precursors of products: methane, ethane, ethylene, and butane are produced *via* processes of hydrogen atom abstraction from amines, disproportionation, and recombination.

In the case of quenching of $\mathrm{Cd}(^3\mathrm{P}_{0,1})$ by alkane hydrocarbons, it has been pointed out that direct abstraction of a hydrogen atom to form CdH is a major quenching pathway. The quenching cross sections have been explained by assuming an additive cross section for each C–H bond of 1×10^{-5} nm^2, irrespective of type of C–H bond.[10] From the quenching cross section (4×10^{-3} nm^2) and the quantum yield of hydrogen (0.014) in the cadmium-photosensitized reaction of ammonia, the cross section corresponding to an abstraction of hydrogen atom for each N–H bond is similarly calculated to be about 1×10^{-5} nm^2. The quenching cross sections for the abstraction of hydrogen atom from saturated amines can be calculated by using these values. For example, the values for TEA, NEP, and ABCO are about 1.5×10^{-4}, 1.5×10^{-4}, and 1.3×10^{-4}

nm^2, since TEA, NEP, and ABCO have 15, 15, and 13 C–H bonds respectively. From these values and the overall quenching rate constants, the quantum yields of hydrogen (ϕ_{H_2}) for TEA, NEP, and ABCO are estimated to be 0.002, 0.002, and 0.004 respectively. These values are listed in Table 3, together with the values for other amines. The values of ϕ_{H_2} estimated for all amines investigated here are very small. The quantum yield of methane (ϕ_{CH_4}) are calculated by subtracting ϕ_{H_2} from $\phi_{H_2+CH_4}$. For P and ABCO, ϕ_{CH_4} is very small, as expected from molecular structure.

In the cadmium-photosensitized reaction of amines, the primary processes are expressed by the following reactions;

$$\begin{aligned} \mathrm{Cd^*} + \mathrm{A} &\longrightarrow \mathrm{CdA^*}, && (5)\\ &\longrightarrow \mathrm{CdH} + \mathrm{R}, && (10)\\ &\longrightarrow \mathrm{Cd} + \mathrm{CH_3} + \mathrm{A'}, && (11)\\ &\longrightarrow \mathrm{Cd} + \mathrm{C_2H_5} + \mathrm{A''}, && (12)\\ &\longrightarrow \mathrm{Cd} + \text{biradical}, && (13)\\ &\longrightarrow \mathrm{Cd} + \mathrm{A}. && (14) \end{aligned}$$

Reaction 10 indicates a hydrogen atom abstraction by excited cadmium atom from C–H or N–H bond of amines and Reaction 14 indicates a physical quenching process. A′ and A″ in Reactions 11 and 12 indicate the moieties of methyl and ethyl radicals respectively. In the cases of cyclic amines, the formation of biradical must be taken into account (Reaction 13). Reactions 10—14 are included in Reaction 4. In the cases of P and ABCO, Reactions 11 and 12 rarely occur.

The relative values of ϕ_d (defined as $\phi_d = \phi_{CH_4} + \phi_{C_2H_4,C_2H_6} + 2\phi_{C_4H_{10}}$; it can be regarded as equal to the sum of initial quantum yields of methyl and ethyl radicals) are 1.00, 2.06, 3.09, and 0.83 for EA, DEA, TEA, and NEP. This ratio is almost the same that of the number of ethyl groups. This suggests that the reasoning that methane, ethane (and/or ethylene) and butane are primarily produced from methyl and ethyl radicals is valid. The values of ϕ_d for tertiary amines decrease in the order; TEA>NEP>ABCO. This decreasing order is in agreement with the increasing order of the emission quantum yield. It is difficult to explain the way by which methyl and ethyl radicals are produced for P and ABCO. In these cases the origin of products remains an open question.

The ratio of recombination to disproportionation of ethyl radicals has been reported to be about 7.4.[11] As is shown in Table 3, however, the ratios of the yields of butane to those of ethane (ethylene) are about 0.15—0.18 for EA, DEA, and TEA. This indicates that ethane is formed exclusively by the abstraction of a hydrogen atom from amines.

The contribution (ϕ_r) of Reactions 14 and/or 13 to the overall quenching processes is estimated by $\phi_r = 1 - (\phi_e + \phi_d + \phi_{H_2})$. The values of ϕ_r are listed in Table 5. For TEA, as Reaction 13 does not occur, the value of ϕ_r indicates the contribution of the physical quenching process; it is about one-third of the total quenching. On the other hand, in the case of NEP, both Reactions 13 and 14 contribute to the overall quenching processes. If the physical quenching process is almost the same for NEP and TEA, the difference in ϕ_r between NEP and TEA indicates the quantum yield for Reaction 13; it is 0.33. This value is about twice as much as ϕ_d for NEP; the difference is attributed to the number of bonds to be broken. Reaction 13 seems to be responsible for the large difference in ϕ_d between TEA and NEP. The same thing seems to hold between DEA and P. For ABCO, however, the quantum yields for processes other than the exciplex formation are very small. On the other hand, it has a large quantum yield for the emission (the largest value of those reported to date). That is, the quenching by ABCO can be concluded to occur overwhelmingly through the exciplex formation.

References

1) S. Yamamoto and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 1382 (1975); S. Tsunashima, K. Morita, and S. Sato, *ibid.*, **50**, 2283 (1977); S. Yamamoto, M. Yasunobu, N. Nishimura, and S. Hasegawa, *Mol. Photochem.*, **9**, 277 (1979).

2) S. Yamamoto and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 1381 (1975).

3) S. Yamamoto, K. Tanaka, and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 2172 (1975).

4) S. Yamamoto, M. Yasunobu, N. Nishimura, and S. Hasegawa, *Mol. Photochem.*, **9**, 277 (1979).

5) S. Tsunashima, T. Toyono, and S. Sato, *Bull. Chem. Soc. Jpn.*, **46**, 2654 (1973).

6) S. Yamamoto, M. Takaoka, S. Tsunashima, and S. Sato, *Bull. Chem. Soc. Jpn.*, **48**, 130 (1975).

7) F. W. Byron, Jr., M. N. McDermott, and R. Novick, *Phys. Rev. A*, **134**, 615 (1964).

8) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 311 (1976).

9) P. J. Kozak and H. Gesser, *J. Chem. Soc.*, **1960**, 448.

10) W. H. Breckenridge and A. M. Renlund, *J. Phys. Chem.*, **83**, 303 (1979).

11) J. A. Kerr and A. F. Trotman-Dickenson, "Progress in Reaction Kinetics," ed by G. Porteir, Pergamon Press, Oxford (1961), Vol. 1, p. 105.