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The Quenching of the Cadmium Resonance Radiation at 326.1 nm by Some Aliphatic Amines and the Cadmium-sensitized Luminescence of These Amines

Shunzo YAMAMOTO and Shin SATO*

Department of Chemistry, Faculty of Sciences, Okayama University, Tsushima, Okayama 700
* *Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*

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From the pressure dependence of the intensity of the 326.1 nm resonance line, the efficiencies of the quenching of the resonance line by methylamine, ethylamine, *n*-propylamine, *n*-butylamine, *sec*-butylamine, *tert*-butylamine, diethylamine, and triethylamine were estimated to be 14.2, 36.0, 58.6, 71.2, 116.7, 434.5, 69.6, and 66.0 respectively, the efficiency of ammonia being assumed to be unity. The relative values of rate constants for the formation of excited complexes between the excited cadmium atoms and the amines, and the wavelengths at the peaks of the emission bands from the complexes, were measured. The quantum yields of luminescence were also measured by comparing the integrated intensities of the emission bands with the decrease in the intensities of the resonance line at 326.1 nm upon the addition of amines. From the relationship between these values and the structure of the amines, it is concluded that the complexes are of the charge-transfer type.

In a previous study[1] of the cadmium-sensitized reaction of rare gases and nitrogen, we indicated that the Cd($^3P_0$) state is produced by collisions between Cd($^3P_1$) atoms and rare gases or nitrogen, and that, at pressures higher than a few Torr of foreign gases, an equilibrium is established between the 5 $^3P_1$ and 5 $^3P_0$ states. Therefore, in spite of the fact that Morten *et al.*[2] described the emitting species in the cadmium-sensitized luminescence of ammonia as being produced by the reaction between Cd($^3P_0$) atoms and ammonia, it is impossible to distinguish between Cd($^3P_1$) and Cd($^3P_0$) atoms as precursors of the emitting species.

In an earlier study of the quenching of the resonance radiation at 326.1 nm by ammonia,[3] we proposed a mechanism by which an unstabilized complex, produced from the excited cadmium atoms (Cd($^3P_1$) or Cd($^3P_0$)) and ammonia, is partly decomposed to the original excited cadmium atoms and ammonia and is partly stabilized by collisions with third bodies. Since a back reaction exists, the Stern-Volmer plots for the quenching of the 326.1 nm resonance line deviate from a straight line in the low-pressure region. If other molecules more complex than ammonia can form the emitting species, and if the back reaction is not so important, we shall not be able to observe the second-order pressure dependence of the Stern-Volmer plots in the low-pressure region, as in the case of ammonia. The present paper will report the results of a study of the cadmium-sensitized luminescence of some aliphatic amines and their quenching for the 326.1 nm resonance line.

Experimental

The apparatus and procedure were the same as those previously described.[3–5] The reaction cell and the cadmium resonance lamp were kept in an electric furnace at 220±1 °C. The vapor pressure of cadmium at 220 °C is 1.04×10^{-3} Torr. The lamp was operated by an alternating current (50 Hz).[1]

The cadmium metal used was high-purity cadmium (99.9999%) manufactured by the Osaka Asahi Metal Co. Pure-grade methylamine and ethylamine were used after degassing at the temperature of liquid nitrogen. Other amines (G.R. grade) were used after drying by calcium hydride and repeated trap-to-trap distillation. Pure-grade argon was used after repeated adsorption and desorption on a molecular sieve at the temperature of liquid nitrogen. In order to minimize the pressure dependence of the absorption intensity, the amines were diluted with argon, and the total pressure in the reaction cell was kept constant.

In order to estimate the quantum yields of the luminescence, the dependence of the sensitivity on the wavelength for the monochromator/photomultiplier combination was determined by using a tungsten lamp operated at 2307 K, using the emissivity data of tungsten presented by de Vos.[6]

Results

In order to estimate the efficiency of the quenching of the 326.1 nm resonance line by amines, the emission intensity at 326.1 nm was measured as a function of the pressure of amines. The Stern-Volmer plots are shown in Fig. 1, where $I_{326.1}{}^0$ and $I_{326.1}$ are the emission intensities at 326.1 nm in the absence and in the presence of amines respectively. On the assumption that 100 Torr carbon dioxide quenches the 326.1 nm resonance line completely,[1] the scattered-light intensity at 326.1 nm was estimated to be less than 0.2% of the $I_{326.1}{}^0$ and thereafter it was neglected. As the intensity, $I_{326.1}$, decreased with the increase in the irradiation time because of the influence of reaction products (one of them may be hydrogen[4]), the intensities shown in Fig. 1 were obtained by extrapolation to zero irradiation time. As has been described previously,[3] the plots obtained with ammonia do not lie on a straight line. However, the plots for the other amines from typical Stern-Volmer plots (straight lines, the intercepts of which

TABLE 1. HALF-QUENCHING PRESSURE FOR THE QUENCHING OF 326.1 nm RESONANCE LINE

Amine	Torr	Amine	Torr
Ammonia	12.6	*sec*-Butylamine	0.108
Methylamine	0.885	*tert*-Butylamine	0.029
Ethylamine	0.350	Diethylamine	0.181
n-Propylamine	0.215	Triethylamine	0.191
n-Butylamine	0.177		

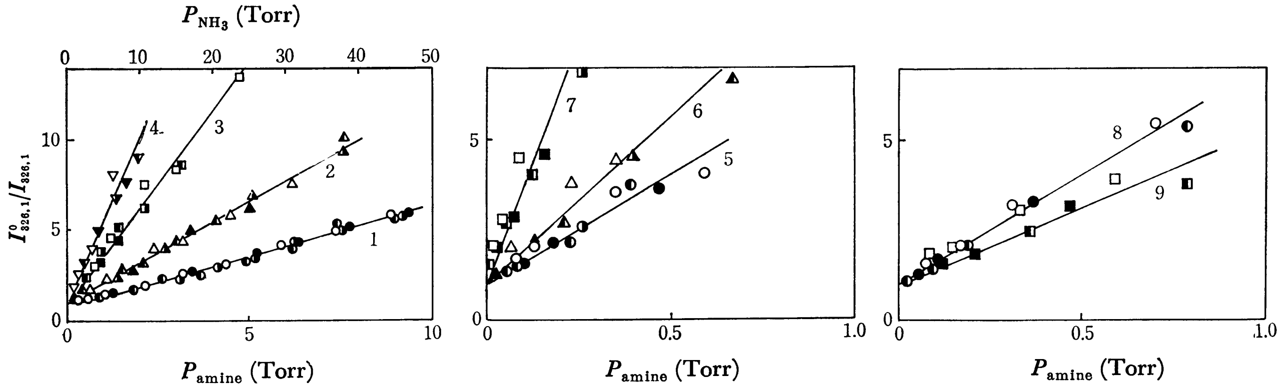

Fig. 1. Stern-Volmer plots for the quenching of the resonance radiation at 326.1 nm by amines diluted with argon. 1) ammonia; Total pressures are 208 (○), 175 (◐), 147 (◑), and 123 (●) in Torr. 2) methylamine; 106 (△), 70 (◭), 48 (◮), and 32 (▲). 3) ethylamine; 106 (□), 70 (◧), 48 (◨), and 32 (■). 4) *n*-propylamine; 106 (▽), 70 (⧨), 48 (⧩), and 32 (▼). 5) *n*-butylamine; 106 (○), 70 (◐), 48 (◑), and 32 (●). 6) *sec*-butyl-amine; 106 (△), 70 (◭), 48 (◮), and 32 (▲). 7) *tert*-butylamine; 106 (□), 70 (◧), 48 (◨), and 32 (■). 8) diethylamine; 80 (○), 48 (◑), and 28 (●). 9) tri-ethylamine; 80 (□), 48 (◧), and 28 (■).

are equal to unity). As is shown in Fig. 1, the plots for each amine at various total pressures all lie on one straight line, and no total pressure dependence can be seen. The half-quenching pressures obtained from Fig. 1 are listed in Table 1. The efficiency of the quenching by primary amines increases with an increase in the molecular complexity.

Table 2. Wavelength at the peak of the emission band and quantum yield of the luminescence

Amine	λ (nm)	Quantum yield
Ammonia	432±2	0.67±0.10
Methylamine	449±5	0.58±0.10
Ethylamine	452±5	0.26±0.09
n-Propylamine	452±5	0.20±0.09
n-Butylamine	453±5	0.18±0.05
sec-Butylamine	453±5	0.12±0.05
tert-Butylamine	454±5	0.04±0.02
Diethylamine	longer than 460 nm	
Triethylamine	longer than 460 nm	

The emission band for ammonia was shown previously.[4] The band for the primary amines studied had the same basic shape and so will not be given here. The wavelengths at the peak of the emission band are listed in Table 2. Since the emission intensity changes with the irradiation time, the position of the peak is somewhat obscure. The wavelength at the peak for diethylamine and triethylamine could not be measured because of the interference of the scattered light of the line at 468 nm from the lamp.

According to the method of Newman *et al.*,[7] the quantum yield of the luminescence for ammonia was calculated. The ratios of the intensity of the luminescence at 432 nm to the decrease in the fluorescence intensity of the 326.1 nm line were measured at various ammonia pressures (5—50 Torr), the total pressure being kept constant. The intensity of the 326.1 nm line should be corrected for the absorption of the line on its way out of the cell. The transmission was calculated for the pure Doppler-broadening case,[8] using the known dimensions of the cell. Some typical data for ammonia are as follows:

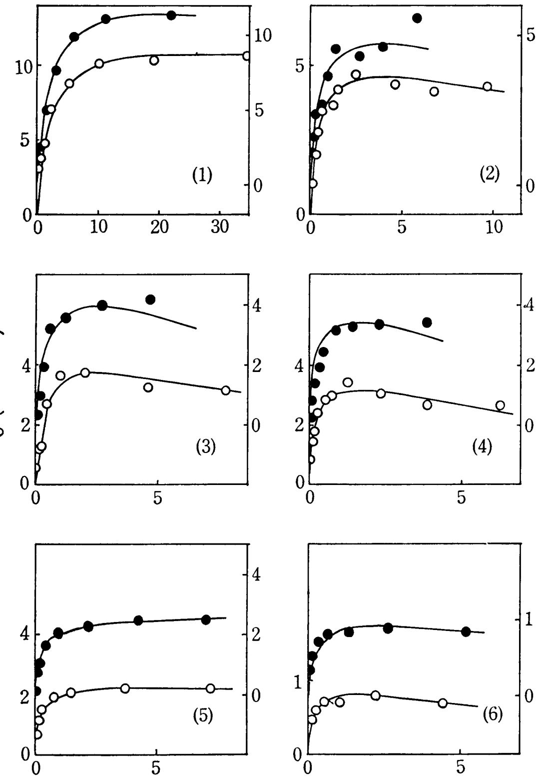

Fig. 2. The intensity at the peak of the emission band from the complex as a function of the partial pressure of amines. The total pressures are 80 (○) and 48 (●) in Torr. The plots for 48 Torr are displaced upwards for clarity. 1) methylamine; 2) ethylamine; 3) *n*-propylamine; 4) *n*-butylamine; 5) *sec*-butylamine; 6) *tert*-butylamine.

$$\frac{I_{432}}{\Delta I_{326.1}} = \frac{2.15}{19.31}$$

$$\frac{\text{sensitivity at 326.1 nm}}{\text{sensitivity at 432 nm}} = 0.42$$

$$\frac{\text{area under emission band}}{\text{instrumental bandwidth}} = \frac{53.4}{2.74}$$

$$\text{cell transmission at 326.1 nm} = 0.685$$

$$\text{quantum yield} = \frac{2.15\times 0.42\times 53.5\times 0.685}{19.31\times 2.74} = 0.63$$

The mean of 25 determinations was 0.67±0.10. The quantum yields for the other amines were determined by a comparison of the integrated intensity of the emission band for the amine in question with that for ammonia under the same conditions. The results are listed in Table 2.

The pressure dependence of the intensity at the peak of the emission band is shown in Fig. 2. The intensities were obtained by extrapolation to zero irradiation time. The maximum intensity is reached at a lower pressure in this order: *tert*-butylamine, *n*-butylamine, *n*-propylamine, ethylamine, *sec*-butylamine, methylamine, and ammonia. This order (except for *sec*-butylamine) is in agreement with the order of molecular complexity.

Discussion

As was described in the previous paper,[5] in the presence of foreign gases—for example, 5 Torr of Ar or 0.1 Torr of ammonia, the equilibrium between the 5 $^3P_1$ and 5 $^3P_0$ states of cadmium is readily established. Consequently, we cannot specify which state is the precursor of the emitting species. In the following treatment, therefore, we will use the symbol Cd* to express either Cd($^3P_1$) or Cd($^3P_0$).

In a manner similar to that described in a previous paper,[3] the following reaction mechanism was considered:

$$\begin{array}{ll}
\mathrm{Cd} + h\nu \longrightarrow \mathrm{Cd}(^3\mathrm{P}_1) & I_a \\
\mathrm{Cd}(^3\mathrm{P}_1) \longrightarrow \mathrm{Cd} + h\nu & k_0 \\
\mathrm{Cd}(^3\mathrm{P}_1) + \mathrm{M} \rightleftharpoons \mathrm{Cd}(^3\mathrm{P}_0) + \mathrm{M} & k_1, k_{-1} \\
\mathrm{Cd}(^3\mathrm{P}_1) + \mathrm{A} \longrightarrow \text{products} & k_2 \\
\mathrm{Cd}(^3\mathrm{P}_0) + \mathrm{A} \longrightarrow \text{products} & k_3 \\
\mathrm{Cd}^* + \mathrm{A} \rightleftharpoons \mathrm{CdA_v}^* & k_4, k_{-4} \\
\mathrm{CdA_v}^* + \mathrm{A} \longrightarrow \mathrm{CdA}^* + \mathrm{A} & k_5 \\
\mathrm{CdA_v}^* + \mathrm{Ar} \longrightarrow \mathrm{CdA}^* + \mathrm{Ar} & k_5' \\
\mathrm{CdA}^* \longrightarrow \mathrm{Cd} + \mathrm{A} + h\nu' & k_6 \\
\mathrm{CdA}^* + \mathrm{A} \longrightarrow \mathrm{Cd} + 2\mathrm{A} & k_7 \\
\mathrm{CdA}^* + \mathrm{Ar} \longrightarrow \mathrm{Cd} + \mathrm{A} + \mathrm{Ar} & k_7'
\end{array}$$

Here, M stands for Ar or amine, while A represents amine. CdA_v* and CdA* represent, respectively, an unstabilized and a stabilized complex between the triplet cadmium atoms and amines. In this mechanism, it is assumed that the unstabilized complex does not fluoresce.

The steady-state treatment on the assumption that the equilibration reaction between $^3P_1$ and $^3P_0$ states is very fast gives the following relation with respect to the quenching of the resonance radiation:

$$\frac{I_{326.1}}{I^0_{326.1}} = 1 + a[\mathrm{A}] + \frac{b[\mathrm{A}]}{1+\dfrac{1}{c[\mathrm{M}]+d[\mathrm{A}]}} \tag{1}$$

Here, $I_{326.1}{}^0$ and $I_{326.1}$ are the emission intensities at 326.1 nm in the absence and in the presence of amines respectively. a, b, c, and d are constants; they are expressed as follows: when Cd* = Cd($^3P_1$),

$$a = \frac{1}{k_0}\left(k_2+\frac{k_1}{k_{-1}}k_3\right),\ b = \frac{k_4}{k_0},\ c = \frac{k_5'}{k_{-4}},$$

and $$d = \frac{k_5-k_5'}{k_{-4}}.$$

In the case of Cd* = Cd($^3P_0$), k_4 should be replaced by $(k_1/k_{-1})k_4$. If c and/or d are sufficiently large, Eq. (1) can be approximated to:

$$\frac{I^0_{326.1}}{I_{326.1}} = 1 + (a+b)[\mathrm{A}] \tag{2}$$

The Stern-Volmer plots for amines other than ammonia in Fig. 1 are expressed by Eq. (2). The constants, $(a+b)$, were evaluated by the least-squares method; they are listed in Table 3.

The steady-state treatment of the above mechanism gives the following relation for the intensity of the emission from the complex:

$$\frac{I_{326.1}[\mathrm{A}]}{I_c} = \alpha(e+f[\mathrm{A}])\left(1+\frac{g}{h+[\mathrm{A}]}\right) \tag{3}$$

TABLE 3. CONSTANTS INVOLVED IN EQS. (2) AND (3)

Amine	[M] (Torr)	$a+b$ (Torr^{-1})	αe(Torr)	αf	g (Torr)	h/[M]
Ammonia	208	0.113±0.04	2.17	0	3.20	0.0072
	175	0.113±0.04	1.99	0	3.23	0.0072
	147	0.113±0.04	1.87	0	2.78	0.0072
	123	0.113±0.04	1.74	0	2.52	0.0072
Methylamine	80	1.13 ±0.02	0.155	0.0005	1.23	0.0073
	48	1.13 ±0.02	0.135	0.0005	1.23	0.0073
Ethylamine	80	2.86 ±0.06	0.126	0.0048	0.239	0.0073
	48	2.86 ±0.06	0.104	0.0048	0.287	0.0073
n-Propylamine	80	4.65 ±0.09	0.090	0.0065	0.287	0.0073
	48	4.65 ±0.09	0.072	0.0065	0.287	0.0073
n-Butylamine	80	5.65 ±0.20	0.090	0.0097	0.112	0.0073
	48	5.65 ±0.20	0.070	0.0097	0.112	0.0073
sec-Butylamine	80	9.30 ±0.38	0.098	0	0.128	0.0025
	48	9.30 ±0.38	0.084	0	0.128	0.0025
tert-Butylamine	80	34.7 ±2.1	0.049	0.0073	0.434	0.0025
	48	34.7 ±2.1	0.038	0.0073	0.434	0.0025

Here, I_c represents the observed emission intensity from the complex at the peak. α is a proportional factor between the total emission intensity and the observed one; it depends on the geometry of the apparatus, the slit width, and the sensitivity of the photomultiplier used. e, f, g, and h are constants depending only on the total pressure:

when Cd*=Cd($^3P_1$),

$$e=\frac{k_0}{k_4}+\frac{k_0k_7'}{k_4k_6}[\mathrm{M}],\quad f=\frac{k_0(k_7-k_7')}{k_4k_6},$$

$$g=\frac{k_{-4}}{k_5-k_5'},\ \text{and}\ h=\frac{k_5'}{k_5-k_5'}[\mathrm{M}].$$

In the case of Cd*=Cd($^3P_1$), k_4 should be replaced by $(k_1/k_{-1})k_4$. These constants have been evaluated by the method described in the previous paper[3] and are listed in Table 3. The solid lines in Fig. 2 were drawn by substituting the values in Table 3 into Eq. (3).

From the relationships between the constants, $(a+b)$, αe, αf, g, and h and [M], several ratios of the rate constants can be evaluated. The results are summarized in Table 4. The lifetime (τ_0) of Cd($^3P_1$) has been reported to be 2.39×10^{-6} s.[9] As was mentioned in the previous paper,[1] the effective lifetime is independent of the pressure of foreign gases. Therefore, k_0 may be set equal to $1/\tau_0$ ($4.19\times10^5\,\mathrm{s}^{-1}$). By using this value, some rate constants can be calculated. The relative values of k_4 can also be calculated by assuming that α does not depend on the kind of amine. This assumption seems reasonable, because the profile of the emission band is almost independent of the amines. These values are also listed in Table 4.

The rate constants, k_4, for the primary amines increase in this order: ammonia<methylamine<ethylamine<*sec*-butylamine<*n*-propylamine<*n*-butylamine<*tert*-butylamine. This order is in agreement with the order of the decrease in the ionization potential of amines, except for *sec*-butylamine. Figure 3 shows the correlation between the relative values of k_4 and the ionization potential of amines. Relationship of this type have also been reported in the cases of the quenching of I($5^2P_{1/2}$)[10] and P(3^2D_j) and P(3^2P_j).[11] This relationship indicates that the complex has the characteristics of a charge-transfer type. The tendency of the efficiency of the quenching of the resonance radiation by amines shown in Table 1 is almost the same as that of k_4. This suggests that the quenching occurs mainly through the formation of the complex (Reaction (k_4)).

The k_5/k_{-4} and k_5'/k_{-4} ratios increase generally with an increase in the molecular complexity. Thus, it can be said that, for the complex amines, the back reaction (Reaction (k_{-4})) is not important (c and d in Eq. (1) are large); therefore, the Stern-Volmer plots lie on a straight line.

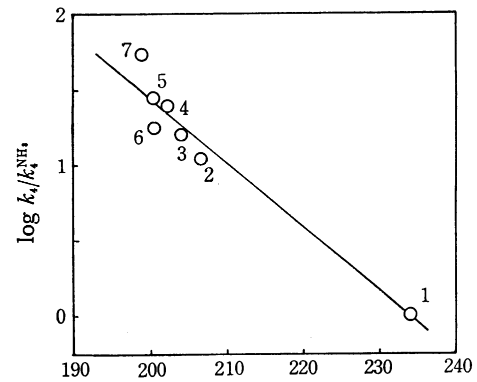

Fig. 3. Relationship between the relative values of the rate constant for the formation of complex and the ionization potential of amines.
1) ammonia; 2) methylamine; 3) ethylamine; 4) *n*-propylamine; 5) *n*-butylamine; 6) *sec*-butylamine; 7) *tert*-butylamine.

As is shown in Table 2, the peak wavelength shifts to longer wavelengths as the ionization potentials of the amines decrease. Most of the wavelength shift occurs upon methyl substitution. These tendencies agree with the observations in the mercury-sensitized luminescence of alcohols[12] and amines.[13] These findings indicate that the complex formed between the excited cadmium atoms and amines is of the charge-transfer type, by analogy with the mercury-amines and mercury-alcohols systems. This explains why the emission band has no fine structure.

The quantum yield of the luminescence for ammonia given in Table 2 is approximately equal to that of the mercury-sensitized luminescence of ammonia. As is shown in Table 2, the quantum yield for amines decrease steadily with the increase in the molecular complexity. This tendency differs from that observed in the mercury-amines system.[13]

In the mercury-sensitized reaction, it was shown that the quenching process of Hg($^3P_1$) with all alcohols and amines except methylamine yields mainly Hg ($^3P_0$).[12,13] However, in the cadmium-sensitized reaction an equilibrium between the $^3P_1$ and $^3P_0$ states is established; the quenching of the resonance radiation by amines occurs mainly through the formation of

TABLE 4. RATE CONSTANTS AND RATIOS BETWEEN RATE CONSTANTS

Amine	$k_2+1.68k_3+k_4$ (or $k_2+1.68(k_3+k_4)$) (cm^3 molecule^{-1} s^{-1})	$k_4/k_4^{\mathrm{NH_3}}$	k_5'/k_{-4} (Torr^{-1})	k_5/k_{-4} (Torr^{-1})	$10^3k_7/k_6$ (Torr^{-1})	k_7/k_7'
Ammonia	$(2.4\pm0.4)\times10^{-12}$	1.0	0.0024	0.336	4.9	1.0
Methylamine	$(2.4\pm0.2)\times10^{-11}$	10.7	0.0059	0.813	10.8	1.8
Ethylamine	$(6.1\pm0.1)\times10^{-11}$	15.8	0.0275	3.80	77.6	8.0
n-Propylamine	$(9.9\pm0.2)\times10^{-11}$	24.9	0.0253	3.48	153.7	12.2
n-Butylamine	$(1.2\pm0.1)\times10^{-10}$	28.0	0.0649	8.93	259.0	16.4
sec-Butylamine	$(2.0\pm0.1)\times10^{-10}$	17.8	0.0195	7.81	7.0	1.0
tert-butylamine	$(7.4\pm0.4)\times10^{-10}$	53.3	0.0058	2.30	347.9	20.8

the complex, as has been mentioned above. It has been reported that, in the mercury-sensitized reaction of methylamine, the abstraction of an α-hydrogen by $Hg(^3P_1)$ atoms is important; this reaction competes with the luminescence. Therefore, in spite of the large efficiency of the quenching of $Hg(^3P_1)$ by methylamine, the quantum yield of the luminescence is very small. This explanation is supported by the fact that the quantum yield with *tert*-butylamine, which has no α-hydrogen, is large.[12] On the other hand, in the cadmium-sensitized reaction of amines the relative values of k_4 vary steadily with the decrease in the ionization potential of amines; this was taken as an indication that the relative efficiency of the formation of complex did not change markedly on going from one amine to the next. That is to say, the efficiency of the quenching can be interpreted in terms of the electron-donating ability of the nitrogen atom of amines alone.

As is seen in Table 4, the k_7/k_6 ratio increases with an increase in the molecular complexity of the amines with the exception of the case of *sec*-butylamine. If it is assumed that $1/k_6$, or the lifetime of the complex, dose not depend appreciably on the kind of amines, the above order indicates the order of the efficiency of the quenching of the complex luminescence by amines. As is shown in Table 2, therefore, the quantum yields of the luminescence decrease in this order, though the rate constants of the complex formation increase in the same order. The efficiency of the quenching of the luminescence by ammonia is very small. On the other hand, the efficiency by *tert*-butylamine is about two orders of magnitude larger than that by ammonia. This large efficiency of the quenching by *tert*-butylamine cannot be explained by the increase in the cross section of collision alone. Morten *et al.*[2] described how, at high pressures of ammonia, complexes with two or more ammonia molecules may be formed, and how the possibility of the formation of the higher complexes, which radiate at almost the same wavelength, probably provides a good explanation of the small efficiency of the quenching of the complex luminescence by ammonia. Such complexes were indeed found in the mercury–ammonia system.[14] If this explanation is correct, it can be said that the increase in the efficiency of the quenching by amines with an increase in the molecular complexity results from the difficulty in the formation of the higher complexes because of the steric hindrance of alkyl group.

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