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Enhancement of Hg($^3P_1$)-Photosensitized Luminescence of Amines on Addition of Ethanol

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The Hg($^3P_1$)-photosensitized luminescence of amine(AM)-ethanol(AL) mixtures was studied under the condition of steady illumination. The intensity of luminescence from an HgAL* complex decreased with increasing amine pressure, while the emission intensity from an HgAM* complex increased on addition of AL. We propose that the ligand exchange reaction, HgAL* + AM ⇀ HgAM* + AL, is involved in this system.

It is well known that mixtures of mercury vapor and substrates containig N or O atom (NH_3, H_2O, aliphatic amines and alcohols) give sensitized luminescence when subjected to irradiation with the 253.7 nm mercury resonance radiation.[1,2] In spite of many investigations of the mercury-photosensitized luminescence of aliphatic amines and alcohols, no investigation has been made for amine-alcohol mixtures.

We have studied the mercury-photosensitized emission of amine-alcohol mixtures to obtain a more comprehensive understanding for molecular attachment to the excited mercury atom. We have observed the significant decrease in the intensity of the sensitized luminescence of ethanol by adding a small amount of propylamine and the increase in the emission intensity for the amine on addition of ethanol. In the present letter, we report briefly the mercury-photosensitized luminescence of propylamine-ethanol and triethylamine-ethanol mixtures.

The emission spectra were obtained with a Hitachi 203 fluorescence spectrophotometer equipped with a Hamamatsu R-446 photomultiplier. The reaction cell was a 10 mm quartz cuvette with four transparent planes. The cell, containing a mercury droplet was connected to a vacuum system. A low pressure mercury lamp (Toshiba Electric Co., gemicidal lamp) was used. The 253.7 nm resonance radiation isolated with a monochromator excites

$Hg(^3P_1)$ atoms from mercury vapor. Alcohol-amine mixtures of various proportions were prepared by circulating gas mixtures of known amounts of alcohol and amine with a magnetically operated fan around closed loop. Sample gases were introduced to the cell and permitted to stand for a few minutes before the measurement of the luminescence. All experiments were conducted at room temperature. Ethanol, propylamine, and triethylamine were obtained from commercial sources (G.R. grade). These reagents were used after drying and repeated trap-to-trap distillation.

Figure 1 shows the emission spectra obtained in the mercury-photosensitized reactions of ethanol and propylamine. The positions and shapes of the bands are in good agreement with those reported previously.[3,4] In Fig. 2, the effect of the addition of amine on the emission intensity of the mercury-photosensitized luminescence of ethanol is shown. As Fig. 2 shows, the intensity at 300 nm increases with increasing ethanol pressure for pure ethanol. In the case of ethanol-propylamine mixtures, however, the intensity decreases drastically with increasing amine pressure.

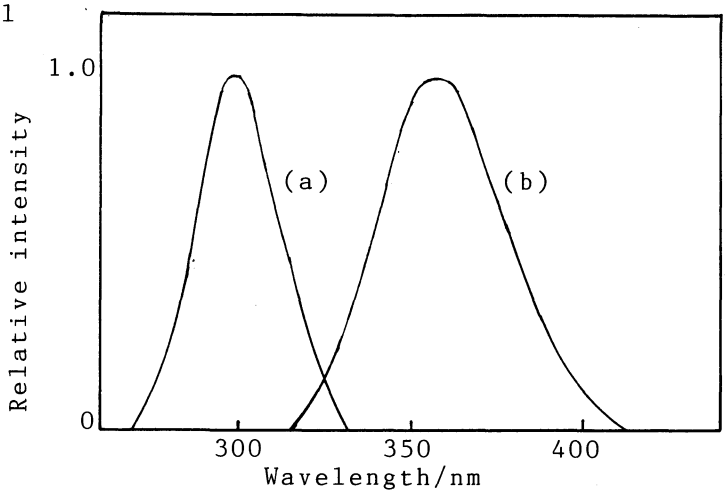

Fig. 1. Emission bands obtained in the $Hg(^3P_1)$-sensitized reactions of (a) ethanol and (b) propylamine. The bands are adjusted to unit intensity at the peak wavelength.

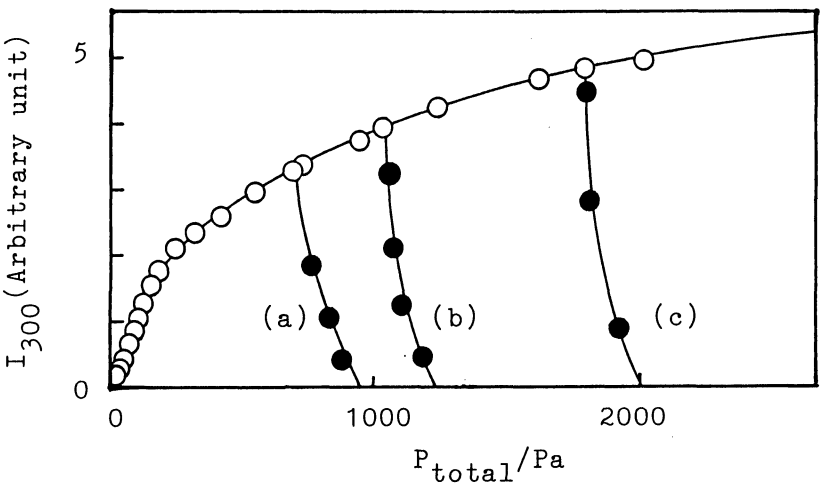

Fig. 2. Effect of propylamine on the emission intensity for ethanol at 300 nm.
○ : pure ethanol
● : ethanol-propylamine mixtures;
(a) $P_{ethanol}$ = 690, (b) 1030, (c) 1790 Pa.

In Fig. 3, the effect of ethanol on the emission intensity of the mercury-photosensitized luminescence of propylamine is shown. In the absence of ethanol, the intensity at 360 nm increases with increasing amine pressure in the low pressure region and then reaches to a constant value. When ethanol was added to constant amounts of the amine, the intensity at 360 nm increased with increasing ethanol pressure. The effect of the addition of ethanol is more remarkable in the case of smaller amount of amine.

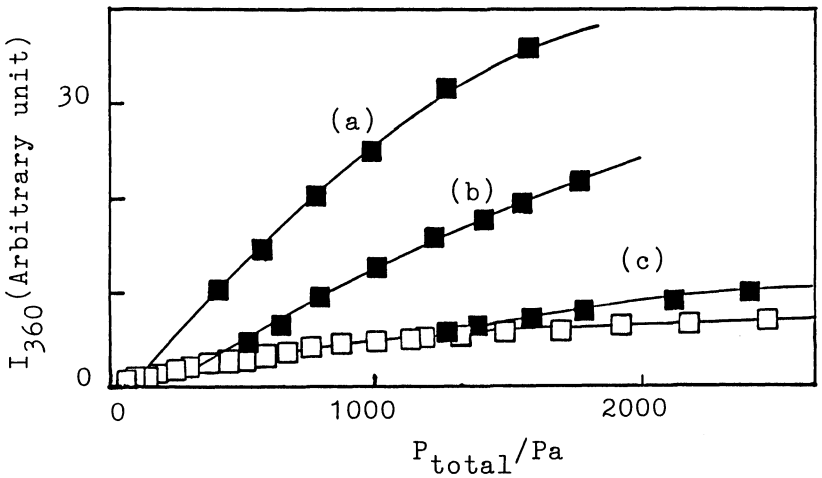

Fig. 3. Effect of ethanol on the emission intensity for propylamine at 360 nm.
□ : pure propylamine
■ : propylamine-ethanol mixtures;
(a) $P_{propylamine}$ = 90, (b) 285, (c) 1320 Pa.

From the variation of luminescent efficiency with the structure of amine, Newman et al. concluded that the main process competing with luminescence is the abstraction of an -hydrogen atom.[4] They also pointed out that for secondary and tertiary amines the absence of sensitized luminescence is due to the abundance of α-hydrogen or steric effect during collision with excited mercury atoms. Indeed, we could not observe any emission band in the wavelength region around 360 nm for pure triethylamine (weak emission was observed at 290 nm, which was attributed to the directly-excited

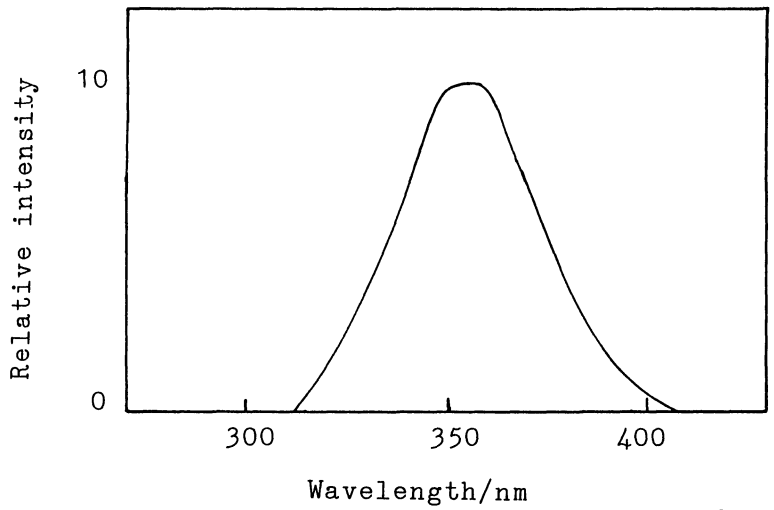

Fig. 4. Emission band obtained in the $Hg(^3P_1)$-sensitized reaction of triethylamine-ethanol (1:1) mixture.

fluorescence of the amine[4]). However, when ethanol was added to the amine, we observed that the emission band appeared at around 360 nm (Fig. 4), and its intensity increased with increasing ethanol pressure. The shape and position of this emission band are very similar to those observed for some primary amines.

The above findings can not be explained by the superposition of the mechanisms provided for amines and alcohols. The additional process which produces effectively the excited complex between an excited mercury atom and an amine molecule becomes possible on addition of ethanol. We propose the ligand exchange reaction; $HgAL^* + AM \longrightarrow HgAM^* + AL$. Since the excitation energy of the complex ($HgAL^*$) is smaller than that of an excited mercury atom, the decomposition of amine seems to be supressed. This type of ligand exchange reaction was proposed in the $Hg-NH_3$-diethylamine system.[5]

Further study to elucidate the feature of the ligand exchange reaction in some alcohol-amine mixtures is in progress.

References

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