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THE ISOTOPE EFFECT IN THE Cd-PHOTOSENSITIZED REACTION OF METHANOL

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The isotope effect in the Cd-photosensitized reaction of methanol has been investigated using CH_3OH, CH_3OD, and CD_3OD. The quenching efficiencies for the 326.1 nm resonance line were 1 : 0.31 : 0.31 in the order of CH_3OH, CH_3OD, and CD_3OD. The intensity of the emission from the intermediate complex between an excited cadmium atom and methanol was also measured. The intensity ratio was 1 : 3.1 : 3.1 in the order of CH_3OH, CD_3OD, and CD_3OD. The band-shape of the emission was not affected by the substitution of D atoms. These results are compared with the isotope effect recently reported in the study of the Hg-photosensitized reaction of methanol.

In the study of the Hg-photosensitized reaction of methanol, Luther et al. recently found a large isotope effect and suggested that the cleavage of the C-H bond in methanol is an important process as well as the cleavage of the O-H bond in methanol.1) This suggestion is different from the reaction mechanism widely believed, in which almost all the cleavage occurs at the O-H bond.2)

Last several years, we have studied the Cd-photosensitized reaction and have found many similarities between the Hg- and Cd-photosensitizations.3) In a previous paper, we showed that methanol formed a radiative complex with an excited cadmium atom in the process of quenching of the cadmium resonance line at 326.1 nm, although the quantum yield was very small (3.1×10^{-3}).4) If hydrogen atoms in methanol are replaced by deuterium atoms, the isotope effect may be observed in the quenching efficiency and in the emission from the complex.

Using the apparatus described in the previous paper,4) we have measured the quenching efficiencies of CH_3OH, CH_3OD, and CD_3OD for the 326.1 nm resonance line and also the emission intensities from the intermediate complex. Since methanol is known to be reactive to Pyrex glass,5) all vacuum lines which contact methanol vapor were constructed with molybdenum glass. In order to prevent the change of the light absorption due to the pressure broadening, argon was used as a diluent. The temperature of the reaction cell was kept at 220±1°C. The isotopic methanols, CH_3OD and CD_3OD, were purchased from Merck Sharp and Dohme of Canada.

Figure 1 shows the reciprocal of the light intensity of the 326.1 nm resonance line from the reaction cell as a function of the pressure of three methanols. The slope of the straight line corresponds to the quenching efficiency, k_q.

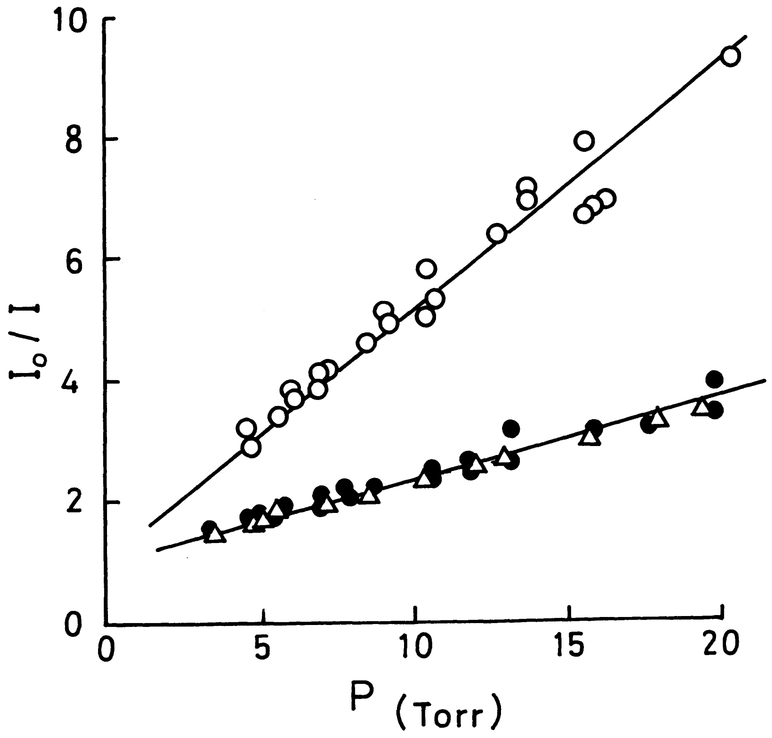


Fig. 1. Stern-Volmer Plots for the Quenching of the 326.1 nm Resonance Line by CH_3OH(○), CH_3OD(●), and CD_3OD(△).

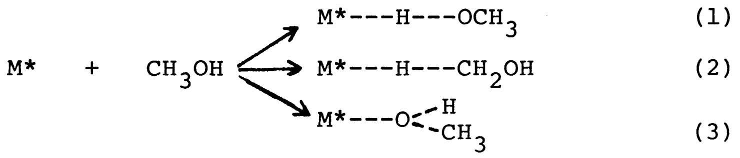
The relative k_q values thus obtained are summarized in Table 1, together with the relative quantum yield of the emission from the intermediate complex at 395 nm. The band-shape of the emission was not affected by the substitution of D atoms. Table 1 also contains the quenching efficiency ratio of four isotopic methanols for the excited mercury(Hg $^3P_0$) which were recently reported by Luther et al.$^{1)}$ Obviously, the isotope effect observed in the Cd-photosensitization is different from that obtained in the Hg-photosensitization.

Table 1. The Isotope Effects on the Quantum Yield of the Emission(Φ_{em}) and on the Quenching Efficiency(k_q)[a]

	Φ_{em}	k_q	
		Cd	Hg[b]
CH_3OH	1	1	1
CH_3OD	3.1 ± 0.3	0.31 ± 0.04	0.31
CD_3OH	——	——	0.093
CD_3OD	3.1 ± 0.3	0.31 ± 0.04	0.088

[a] relative to the values obtained with CH_3OH.
[b] from Ref. 1.

In order to explain the isotope effect, we assume the following three quenching processes.



$$M^* + CH_3OH \rightarrow M^*\text{---}H\text{---}OCH_3 \qquad (1)$$

$$M^* + CH_3OH \rightarrow M^*\text{---}H\text{---}CH_2OH \qquad (2)$$

$$M^* + CH_3OH \rightarrow M^*\text{---}O{<}^{H}_{CH_3} \qquad (3)$$

Here, M* stands for the excited cadmium or mercury atom. When the energy of the excited atom is large as that in the case of the Hg-photosensitization, the processes (1) and (2) will lead to the formation of radicals. The process (3) corresponds to the formation of the radiative intermediate complex. Then, the total quenching rate, k_q, may be set equal to the sum of the rates of the three processes.

$$k_q = k_1 + k_2 + k_3$$

The quantum yield of the emission from the intermediate complex [the process (3)] may be expressed as follows,

$$\Phi_{em} = \alpha\, k_3 / k_q$$

The α value depends on the collisional deactivation of the radiative intermediate complex. If the processes proposed above are operative, the D/H isotope effect may be important in the processes (1) and (2), and not in the process (3).

Assuming the same emission processes from the intermediate complex as those reported previously,[4] the α value was estimated to be between 0.6 and 0.9 in the present experimental conditions from the pressure dependence of the emission intensity at 395 nm. The α value depends on the pressures of methanol and argon but not on the isotopic methanols. Since k_3 is expected to be independent of the isotopic alcohols, the isotope effect on Φ_{em} should be reversely proportional to the isotope effect of k_q. This is consistent with the experimental results as was shown in Table 1. The smallness of the quantum yield of the emission from the intermediate complex suggests that the process (3) cannot be a main process ($k_1 \gg k_3$). As was shown in Table 1, we could not find the difference between CH_3OD and CD_3OD in Φ_{em} and k_q. This suggests that the process (2) is not important ($k_1 \gg k_2$). The observed isotope effect on Φ_{em} and k_q may be due to the isotope effect on k_1 in the case of the Cd-photosensitization.

We tried to apply a similar explanation of the isotope effect to the quenching efficiencies obtained for the Hg-photosensitization by Luther et al.1); however, a self-consistent explanation could not be obtained. In order to explain the data of Luther et al., it is very likely that we have to consider a different type of the quenching process.

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