September, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (9), 2283—2287 (1977) 2283

The Isotope Effect on the Quenching of the Cadmium Triplet State by Methanol

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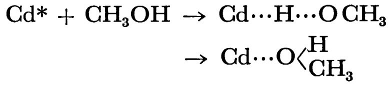
(Received November 15, 1976)

The isotope effect on the Cd-photosensitized emission of methanol has been investigated using CH_3OH, CH_3OD, CD_3OH, and CD_3OD. The relative quenching efficiencies for the 326.1 nm resonance line were 1 : 0.3 : 0.9 : 0.3 in the order of CH_3OH, CH_3OD, CD_3OH, and CD_3OD. The emission intensities from the intermediate complex between an excited cadmium and methanol were also measured. The band-shape was not affected by the substitution of D atoms. The intensity ratio was 1 : 3.1 : 1.1 : 3.1 in the order of CH_3OH, CH_3OD, CD_3OH, and CD_3OD, when the incomplete quenching was corrected. These results were explained by the following quenching processes:



$$\begin{aligned} \mathrm{Cd^* + CH_3OH} &\rightarrow \mathrm{Cd\cdots H\cdots OCH_3} \\ &\rightarrow \mathrm{Cd\cdots O}\langle^{\mathrm{H}}_{\mathrm{CH_3}} \end{aligned}$$

where Cd* represents $Cd(^3P_1)$ and/or $Cd(^3P_0)$. The D/H kinetic isotope effect on the former process was estimated to be 0.3

Recently, Luther *et al.* found a large isotope effect on the quenching of $Hg(^3P_0)$ atoms by methanol using CH_3OH, CH_3OD, CD_3OH, and CD_3OD; for example, the quenching efficiency of CH_3OH is about ten times that of CD_3OD.[1] They also found a HgH formation from CH_3OD, suggesting that the cleavage of the C–H bond in methanol is an important process, as is the cleavage of the O–H bond.[1] This observation, however, contradicts the reaction mechanism widely belived in which almost all the cleavage occurs at the O–H bond in the reaction of methanol photosensitized by triplet mercury, although the bond strength of the C–H is smaller than that of the O–H in methanol.[2]

In the case of the Cd-photosensitized reaction, the isotope effect was also found, as was briefly reported in a previous short communication; for example, the quenching efficiency of CH_3OH for the 326.1 nm resonance line was three times that of CD_3OD and CH_3OD.[3] Based on several assumptions, a reaction mechanism was proposed which explains the observed isotope effect on the quenching of the 326.1 nm resonance line and on the band emission at 395 nm.[3] This mechanism, however, was not consistent with the mechanism proposed by Luther *et al.* for the mercury photosensitization.

The present paper will report the details of the previous short communication, together with new results obtained with CD_3OH. The use of CD_3OH was expected to confirm some of the assumptions made previously.

Experimental

The apparatus and the procedure were essentially the same as those previously described.[4,5] The reaction cell and the cadmium lamp were kept in a furnace at 220±1 °C. Since Pyrex glass is known to be reactive to methanol vapor,[6] the use of Pyrex glass was avoided in constructing the vacuum lines which come in contact with methanol vapor. In order to minimize the effect of the possible D/H exchange reaction on the wall, the reaction system was treated with the same isotopic methanol before every run. All the experiments were carried out in the presence of an excess amount of argon. In order to minimize the pressure dependence of the absorption of the 326.1 nm resonance line, the total pressure in the reaction cell was kept constant.[4,5] The pressure of methanol was changed between 4 and 15% of the total pressure.

The isotopic methanols, CH_3OD, CD_3OH, and CD_3OD, were purchased from Merck Sharp and Dohme of Canada, Ltd. The nominal isotopic purities were more than 99%. All of the methanols were used after being degassed at −80 °C. High purity argon (Jonan Kyodo Sanso) was used after having been passed through a trap containing a molecular sieve, 4A, kept at −120 °C and a reduced copper furnace at 300 °C.

Results

In order to estimate the quenching efficiency for the $5^3P_1 \rightarrow 5^1S_0$ resonance line, the emission intensities at 326.1 nm were measured as a function of the pressure of methanol. The Stern-Volmer plots are shown in Fig. 1, where $I^\circ_{326.1}$ and $I_{326.1}$ are the emission intensities at 326.1 nm in the absence and in the presence of methanol respectively. Since the emission intensities were dependent on the irradiation time because of the accumulation of the reaction products, the $I_{326.1}$ values were obtained by extrapolation to zero irradiation time.

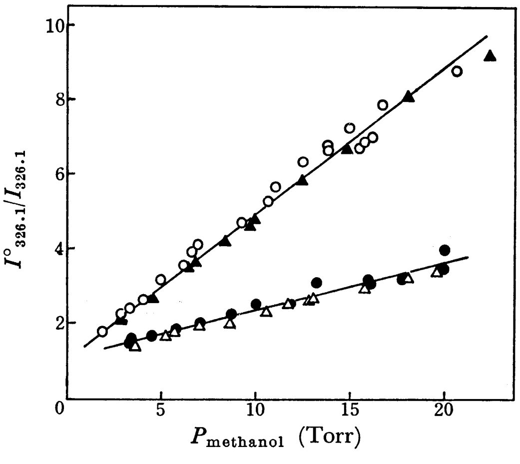


Fig. 1. Stern-Volmer plots for the quenching of the 326.1 nm resonance line by CH_3OH(○), CH_3OD(●), CD_3OH(▲), and CD_3OD(△).

TABLE 1. OBSERVED ISOTOPE EFFECT IN THE QUENCHING OF THE 326.1 nm RESONANCE LINE AND THE EMISSION INTENSITY AT 395 nm

	CH_3OH	CH_3OD	CD_3OH	CD_3OD
H. Q. P. (Torr)[a]	2.4±0.2	7.6±0.7	2.7±0.1	8.0±0.3
Intercept (Torr)[b]	7.4±0.4	8.0±0.4	8.1±0.5	8.1±0.4
Slope (×100)[b]	3.9±0.4	4.3±0.5	4.6±0.4	4.5±0.4
Intensity[c]	1	3.1±0.3	1.1±0.1	3.1±0.3

a) Half-quenching pressure. b) Intercepts and slopes of the straight lines in Fig. 3. c) Total emission intensity at 395 nm, corrected for the incomplete quenching; see Text.

The effect of the argon pressure on the value of $I^\circ_{326.1}/I_{326.1}$ was negligibly small. The plots for the $I^\circ_{326.1}/I_{326.1}$ ratios *vs.* the methanol pressure lie on a straight line for each methanol. The half-quenching pressures were obtained from the slopes of the straight lines in Fig. 1 and are listed in Table 1.

As was stated in a previous paper,[5] a new band emission at 395 nm was obtained when the Cd–methanol mixture was irradiated with the 326.1 nm resonance line. The emission profile was not affected by the substitution of D atoms. The emission intensities, however, depended on the total pressure and the pressure of methanol. Figure 2 shows the results obtained with CD_3OD. Similar plots were also obtained with CH_3OH, CH_3OD, and CD_3OH. The values of $I_{326.1}[\mathrm{Me}]/I_{395}$ were nearly independent of the methanol pressure, but depended on the total pressure, as is shown in Fig. 3. Here, I_{395} is the emission intensity at 395 nm and [Me] is the pressure of methanol. The values of the intercepts and the slopes of the straight lines in Fig. 3 are listed in Table 1.

The areas of the emission band at 395 nm were compared with that obtained with CH_3OH at the same total pressure and the pressure of methanol. When the incomplete quenching of the resonance line was corrected, the ratios of the total emission intensity at 395 nm were nearly independent of the total pressures (35—120 Torr) and also of the pressures of methanol (5—20 Torr). The ratios thus obtained are listed in Table 1.

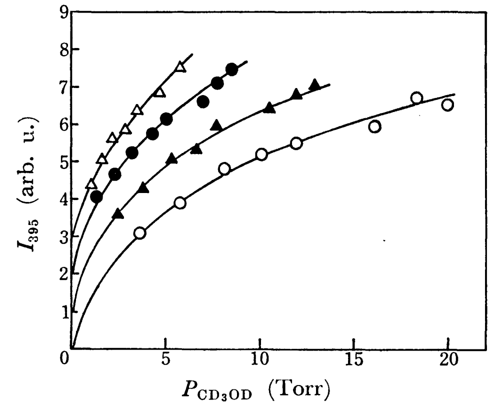


Fig. 2. The intensity of emission at 395 nm from the Cd-CD_3OD system as a function of the pressure of CD_3OD. The total pressures are 121(○), 80(▲), 53(●), and 35(△) in Torr. The plots are displaced upwards by one unit of I_{395} for clarity in the above order of the total pressure.

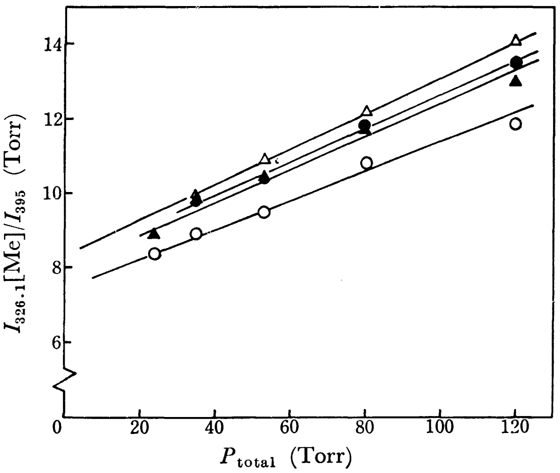


Fig. 3. Plots of $I_{326.1}$ $[\mathrm{Me}]/I_{395}$ as a function of the total pressure for CH_3OH(○), CH_3OD(●), CD_3OH(▲), and CD_3OD(△).

Discussion

Reaction Mechanism. As was shown in a previous paper,[4] the Stern-Volmer plots for the quenching of the Cd resonance line at 326.1 nm by ammonia were not linear at a low pressure of ammonia. In the cases of methanol, however, the Stern-Volmer plots give straight lines, as is shown in Fig. 1. This suggests that the reaction mechanism for the 326.1 nm and the 395 nm emissions is simpler than that considered in the case of ammonia.[4] Consequently, the following simplified reaction mechanism may be considered to explain the results obtained here:

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

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

$$\mathrm{Cd}(^3P_1) + \mathrm{M} \rightleftharpoons \mathrm{Cd}(^3P_0) + \mathrm{M}, \qquad 3$$

$$\mathrm{Cd}^* + \mathrm{Me} \longrightarrow \mathrm{Products}, \qquad 4$$

$$\mathrm{Cd}^* + \mathrm{Me} \longrightarrow \mathrm{CdMe}^*, \qquad 5$$

$$\mathrm{CdMe}^* \longrightarrow \mathrm{Cd} + \mathrm{Me} + h\nu(395), \qquad 6$$

$$\mathrm{CdMe}^* + \mathrm{Me} \longrightarrow \mathrm{Cd} + 2\mathrm{Me}, \qquad 7$$

$$\mathrm{CdMe}^* + \mathrm{Ar} \longrightarrow \mathrm{Cd} + \mathrm{Me} + \mathrm{Ar}. \qquad 8$$

Here, Cd* represents $\mathrm{Cd}(^3P_1)$ or $\mathrm{Cd}(^3P_0)$. Because the equilibrium between $\mathrm{Cd}(^3P_1)$ and $\mathrm{Cd}(^3P_0)$ is easily established under the present experimental conditions,[7] we cannot discriminate the reactions of these two states. The stationary concentration of $\mathrm{Cd}(^3P_0)$ may be approximated as $(k_3/k_{-3})[\mathrm{Cd}(^3P_1)]$.[4] CdMe* is a complex between Cd* and methanol(Me), which can emit the band emission at 395 nm. In the case of ammonia, the formation of an "unstabilized" complex has been assumed; this complex dissociates into the triplet cadmium and methanol or is deactivated to an emissible complex through collision.[4] In the case of methanol, however, it is not necessary to assume the formation of the "unstabilized" complex, since the Stern-Volmer plots give a straight line. If the "unstabilized" complex is formed even in the case of methanol, the lifetime of the "unstabilized" complex must be long enough to be stabilized through collision under the present experimental conditions.

The steady-state treatment of the above mechanism gives the following relation for the quenching of the 326.1 nm resonance line:

$$I^{\circ}_{326.1}/I_{326.1} = 1 + k_q[\mathrm{Me}]/k_2. \qquad (1)$$

Here, $I^{\circ}_{326.1}$ and $I_{326.1}$ represent the emission intensities observed at 326.1 nm in the absence and in the presence of methanol respectively. k_q is the sum of the quenching rate constants and is k_4+k_5 in the case of $\mathrm{Cd}^*=\mathrm{Cd}(^3\mathrm{P}_1)$. When Cd* represents a mixture of $\mathrm{Cd}(^3\mathrm{P}_1)$ and $\mathrm{Cd}(^3\mathrm{P}_0)$, k_4 and k_5 should be replaced by $k_4{}^1+(k_3/k_{-3})k_4{}^0$ and $k_5{}^1+(k_3/k_{-3})k_5{}^0$ respectively. Here, the superscripts 1 and 0 stand for the reactions of $\mathrm{Cd}(^3\mathrm{P}_1)$ and $\mathrm{Cd}(^3\mathrm{P}_0)$ respectively.

From the values of the half-quenching pressure listed in Table 1, the relative values of k_q can be estimated; they are listed in Table 2. The isotope effect on the efficiency of methanol has been observed for the quenching of $\mathrm{Hg}(^3\mathrm{P}_0)$ by Luther *et al.*[1] The relative values obtained by them are compared in Table 2 with those obtained in this study. In contrast with the case of $\mathrm{Hg}(^3\mathrm{P}_0)$-photosensitization, the quenching efficiency of CD_3OD is 0.3 times that of CH_3OH and is close to that of CH_3OD.

TABLE 2. ISOTOPE EFFECTS IN THE REACTION OF METHANOL[a)]

	CH_3OH	CH_3OD	CD_3OH	CD_3OD
k_q(Cd)	1	0.31±0.04	0.88±0.10	0.30±0.03
k_q(Hg)[b)]	1	0.31	0.093	0.088
k_5	1	0.93±0.09	0.91±0.09	0.91±0.09
k_8/k_6	1	1.0 ±0.1	1.1 ±0.1	1.1 ±0.1

a) Relative to the values obtained with CH_3OH. b) From Ref. 1.

The imprisonment lifetime of $\mathrm{Cd}(^3\mathrm{P}_1)$ is not known under the present experimental conditions. Breckenridge *et al.* have estimated the ratio of the imprisonment lifetime to the natural lifetime of $\mathrm{Cd}(^3\mathrm{P}_1)$ in the presence of argon.[8] According to their estimation, the ratio is 1.09 at 260 °C and increases with an increase in the vapor pressure of cadmium. In the present experiment, a smaller imprisonment lifetime may be expected, since the vapor pressure of cadmium in this study is lower than that in their studies.[8] When the lifetime of $\mathrm{Cd}(^3\mathrm{P}_1)$ in the present study is assumed to be equal to the natural lifetime, *i.e.*, 2.3×10^{-6} s, the quenching efficiency of CH_3OH can be estimated to be 0.4 Å^2. Because of the rough estimation, this value should be accepted as un upper limit. The cross section of methanol for quenching triplet cadmium is about twenty times smaller than that for quenching triplet mercury.[9]

For the intensity of the emission at 395 nm, I_{395}, the following equation can be derived from the above reaction mechanism:

$$I_{326.1}[\mathrm{Me}]/I_{395} = \alpha(k_2/k_5)(1+k_8[\mathrm{Ar}]/k_6+k_7[\mathrm{Me}]/k_6). \qquad (2)$$

The factor, α, depends on the experimental conditions; the geometry of the apparatus, the slitwidth, the efficiency of the monochromator, and the sensitivity of the photomultiplier used. Substituting $[\mathrm{Ar}]=[\mathrm{M}]-[\mathrm{Me}]$ into Eq. 2, where [M] represents the total pressure, we can obtain Eq. 2′:

$$I_{326.1}[\mathrm{Me}]/I_{395} = \alpha(k_2/k_5)(1+k_8[\mathrm{M}]/k_6+(k_7-k_8)[\mathrm{Me}]/k_6). \qquad (2')$$

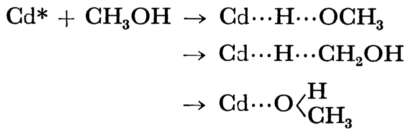
As was stated in the Results section, the observed values of $I_{326.1}[\mathrm{Me}]/I_{395}$ are independent of the change in the pressure of methanol under the same total pressure. Therefore, the third term in the right-hand side of Eq. 2′ may be ignored. From the intercepts and the slopes of the straight lines in Fig. 3, the relative values of k_5 and k_8/k_6 can be estimated; they are listed in Table 2. As is shown in Table 2, the isotope effects on k_5 and k_8/k_6 are negligibly small.

Let us define quantum efficiency of the band emission at 395 nm as the number of photons emitted from the intermediate complex, CdMe*, per quenched $\mathrm{Cd}(^3\mathrm{P}_1)$ atom. Then this efficiency, Φ_{em}, may be expressed as follows:

$$\Phi_{\mathrm{em}} = (k_5/k_q)/(1+k_8[\mathrm{M}]/k_6). \qquad (3)$$

The quantum efficiency of the emission thus defined should be proportional to the emission intensity at 395 nm. Since the isotope effects on k_5 and k_8/k_6 were negligibly small, as is shown in Table 2, the total emission intensity should be inversely proportional to the quenching efficiency. This is indeed the case, as is shown in Tables 1 and 2. Thus, it may be said that the isotope effects observed in the Cd-photosensitized reaction of methanol are mainly due to the isotope effect on the quenching process.

Isotope Effect on the Quenching Process. In a previous short communication, the following three quenching processes were considered in an attempt to explain the results obtained with CH_3OH, CH_3OD, and CD_3OD:[3]



$$\begin{aligned} \mathrm{Cd}^* + CH_3OH &\rightarrow \mathrm{Cd}\cdots\mathrm{H}\cdots OCH_3 && \text{(a)}\\ &\rightarrow \mathrm{Cd}\cdots\mathrm{H}\cdots CH_2OH && \text{(b)}\\ &\rightarrow \mathrm{Cd}\cdots\mathrm{O}\langle^{\mathrm{H}}_{CH_3} && \text{(c)} \end{aligned}$$

The D/H kinetic isotope effects on the (a) and (b) processes are expected to be large. On the other hand, the effect on the (c) process is expected to be small because of the secondary effect. The band emissions have been observed at about 390 nm in the Cd-photosensitized reactions of water and ethers.[5] This fact suggests that the (c) process corresponds to Reaction 5, *i.e.*, the formation of a radiative intermediate complex. In fact, a very small isotope effect on k_5 was observed, as is shown in Table 2.

The observed quenching efficiency, k_q, may be set as equal to the sum of k_a, k_b, and k_c. If the secondary isotope effect can be neglected, we should obtain the following relation between the quenching efficiencies for the isotopic methanol:

$$k_{q,CH_3OH} + k_{q,CD_3OD} = k_{q,CH_3OD} + k_{q,CD_3OH}. \qquad (4)$$

As is shown in Table 2, Eq. 4 is satisfied within the limits of experimental error. Since $k_{q,CH_3OH} \simeq k_{q,CD_3OH}$ and $k_{q,CH_3OD} \simeq k_{q,CD_3OD}$, the (b) process may not be important compared with the (a) and (c) processes. Moreover, the quantum yield of the emission at 395 nm has been estimated to be 0.0032.[5] The smallness of the quantum yield of the emission suggests that the (c) process cannot be the main process. Consequently, it may be said that the observed isotope effect on k_q is mainly due to the isotope effect on k_a. The D/H kinetic isotope effect on k_a can be estimated to be about 0.3.

Theoretical Estimation of D/H Kinetic Isotope Effect. The D/H kinetic isotope effect on the (a) process can be estimated by the use of the theory of the kinetic isotope effect:[10]

$$k_D/k_H = \exp\left[-(hc/2kT)\left\{\sum^{3n^\dagger-7}(\nu_i^\dagger(D)-\nu_i^\dagger(H)) - \sum^{3n-6}(\nu_i(D)-\nu_i(H))\right\}\right]. \qquad (5)$$

Here, $\nu_i(D)$ and $\nu_i(H)$ are vibrational frequencies in cm^{-1}. The superscript † indicates the transition state. The *h*, *c*, *k*, and *T* symbols have their conventional significance. Equation 5 has been derived under a heavy-molecule approximation; *i.e.*, the changes in the molecular mass and moment of inertia have no significant influence upon the isotopic rate ratio.[10] The term of the symmetry-number ratio can be set as equal to unity in this reaction system, and so it is omitted in Eq. 5. An approximation, $1-\exp(-hc\nu/kT)\simeq 1$, has already been applied in Eq. 5. When the vibrational frequency is less than 1000 cm^{-1}, however, it is necessary to include the factor of $1-\exp(-hc\nu/kT)$. When the secondary isotope effect can be neglected, the contribution of all the vibrations except for the O–H stretching and two bending frequencies disappear in the reactant part of Eq. 5. Similarly, only a Cd–H–R stretching and two bending frequencies can contribute in the transition state. Here, R denotes the CH_3O radical.

In order to estimate the vibrational frequencies in the transition state, the following three models are considered:

Model a: The Cd atom is located apart from the methanol molecule and has no effect on the vibrational frequencies in the transition state. The reacting hydrogen atom is located in the neighborhood of the R radical. Thus, the two bending frequencies in the transition state may be set as equal to those in the reactant.

Model b: Much as in Model a, the Cd atom is located far from the methanol molecule, but the R–H bond is stretched so that the two bending frequencies in the transition state can be approximated as zero.

Model c: The R–H bond is stretched further, and the reacting hydrogen atom is located in the neighborhood of the Cd atom. The stretching frequency in the transition state is approximated by the Cd–H stretching. The two bending frequencies are also approximated as zero. In Models b and c the term which contains the two bending frequencies in the transition state may be approximated by m_D/m_H.[10] Here, m_D and m_H are the masses of the D and H atoms respectively.

TABLE 3. FREQUENCIES USED IN THE CALCULATION OF Eq. 5[a]

Atom transferred		H	D
O–H	Stretching	3682	2720
	Bending	1340	869
	Twisting	270[b]	191[c]
C–H	Stretching	2977	2227
	Bending	1430	1055
Cd–H	Stretching	1430[d]	1011[c]

a) In cm^{-1} unit. From H. D. Noether, *J. Chem. Phys.*, **10**, 693 (1942) unless otherwise cited. b) G. Herzberg, "Molecular Spectra and Molecular Structure II, Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Princeton (1945). c) Calculated using $\nu(D)=(1/\sqrt{2})\nu(H)$. d) G. Herzberg, "Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules," D. Van Nostrand Co., Princeton (1950).

TABLE 4. CALCULATED D/H KINETIC ISOTOPE EFFECT

	Process (a)	Process (b)
Model a	0.25	0.33
Model b	0.16	0.22
Model c	0.29	0.41
Observed	0.31±0.04	

On the base of the above assumptions, the D/H kinetic isotope effect on the (a) process was calculated using the frequency assignments shown in Table 3. The results are listed in Table 4. For comparison, Table 4 also contains the results of a similar calculation of the (b) process. As is shown in Table 4, the observed D/H isotope effect on the (a) process is close to the case of Model c; *i. e.*, the reacting hydrogen atom is located in the neighborhood of the Cd atom in the transition state.

The present study suggested that the (a) process is the predominant process compared with the (b) and (c) processes in the Cd-photosensitized reaction of methanol. This coincides with the results obtained by Knight *et al.* and Pottie *et al.* in the case of mercury photosensitization.[2] However, it is different from the results obtained by Luther *et al.*[1]

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