Dependence of Quenching Cross-section of 326.1 nm Cadmium Resonance Line by Alkane Hydrocarbons on C-H Bond Strength

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The intensity of the 326.1 nm resonance line of cadmium were measured at 485 °C and various pressures of the quenchers (methane, ethane, propane, butane, and isobutane). The quenching rate constants were determined on the basis of the Stern-Volmer plots. A dependence of the quenching cross-section on C-H bond strength was observed.

Although remarkable dependences of the quenching cross-sections of the 307.6 nm zinc[1] and 253.7 nm mercury[2] resonance lines by alkanes on C-H bond strength were observed, virtually no dependence of the quenching rate of the 326.1 nm cadmium resonance line was observed at 280 °C.[3] A mechanism was tentatively sugested in which a loose complex is formed between $Cd(^3P_J)$ and alkane molecules, followed by a low-probability potencial surface crossing which has little dependence on C-H bond strength. It was also sugested that differences between $Cd(^3P_J)$ and $Hg(^3P_J)$ quenching by the alkanes can be understood if the mechanistic pathways which account for the $Hg(^3P_J)$ results are merely energetically inaccessible to the lower-energy $Cd(^3P_J)$ state at moderate temperatures. In order to examine whether the quenching cross-section depends on C-H bond strength at high temperatures or not, the quenching rates of $Cd(^3P_J)$ by alkanes were measured at 485 °C.

The intensity of the resonance line at 326.1 nm was measured. When argon was introduced in the cell , an increase in the intensity of the resonance line was observed. This increase has been attributed to the pressure broadening of the absorption line of cadmium atoms.[4] In order to minimize this effect, the quenchers were diluted with argon, and the total pressure in the cell was kept constant. The vapor pressure of cadmium was kept constant by maintaining the temperature of the cadmium storage at 280 ± 1 °C.

The cadmium metal used was high-purity cadmium(99.9999%) manufactured by Osaka Asahi Metal Co. Pure-grade argon(Daido Sanso Co., 99.999%) was used without further purification. Methane(Takachiho-Trading Co., Ltd., Research-grade 99.99%) was used after passing it several times through a 1m column kept at -196 °C. Ethane(Tokyo Kasei Kogyo Co., Ltd. Research-grade 99.9%), propane(Takachiho-Trading Co., Research-grade 99.9%), butane(Tokyo Kasei Kogyo Co., Ltd., Research-grade 99.9%), and isobutane(Tokyo Kasei Kogyo Co., Ltd., Researcg-grade 99.9%) were

purified by bubbling them through a 60 cm column of H_3PO_4 in H_2SO_4, then through 120 cm column of saturated basic $KMnO_4$ and finally a drierite-ascarite drying column, with subsequent low temperature distillation.[5] This procedure effecttively eliminate traces of unsaturated compounds from the alkanes (below 10^{-3}%).

In order to estimate the quenching rate of $Cd(^3P_J)$, the emission intensity at 326.1 nm was measured as a function of the pressure of the quenchers. The Stern-Volmer plots are shown in Fig. 1, where I_0 and I are the emission intensities in the absence and in the presence of quenchers respectively. All of the plots for methane, ethane, propane, and isobutane give straight lines, the intercepts of which are equal to unity.
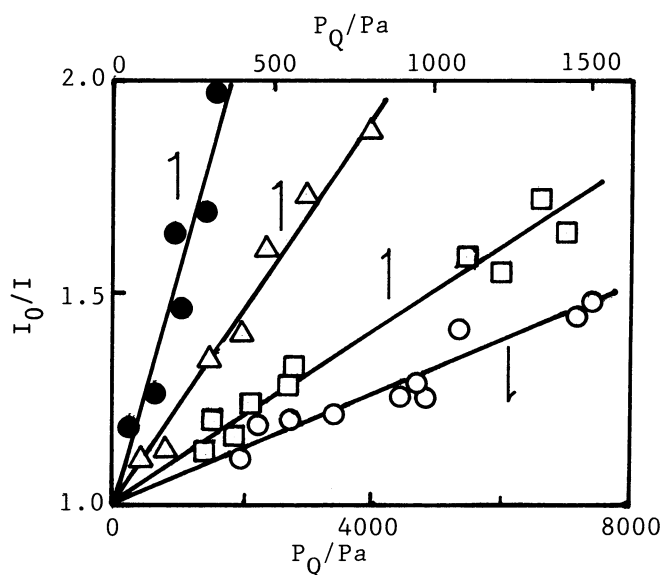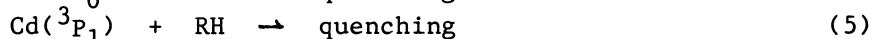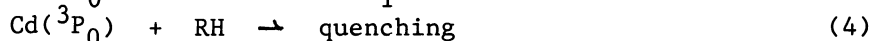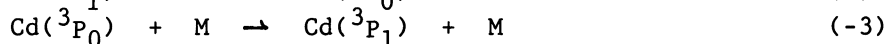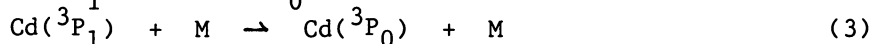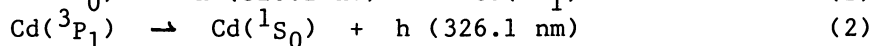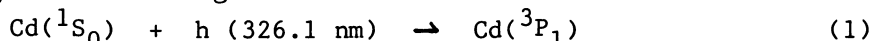

Fig. 1. Stern-Volmer plots for quenching of resonance
line at 326.1 nm by alkanes.
methane (O), ethane (□), propane (△),
and isobutane (●).

According to Breckengidge and Renlund,[4] the quenching of $Cd(^3P_{0,1})$ can be discribed by the following set of reactions:

$$Cd(^1S_0) + h \ (326.1 \ nm) \rightarrow Cd(^3P_1) \qquad\qquad (1)$$
$$Cd(^3P_1) \rightarrow Cd(^1S_0) + h \ (326.1 \ nm) \qquad\qquad (2)$$
$$Cd(^3P_1) + M \rightarrow Cd(^3P_0) + M \qquad\qquad (3)$$
$$Cd(^3P_0) + M \rightarrow Cd(^3P_1) + M \qquad\qquad (-3)$$
$$Cd(^3P_0) + RH \rightarrow \text{quenching} \qquad\qquad (4)$$
$$Cd(^3P_1) + RH \rightarrow \text{quenching} \qquad\qquad (5)$$

where M denotes Ar and/or the quenchers and RH is any alkane molecule. A steady-state analysis results in the following equation

$$\frac{\left[Cd(^3P_1)\right]_0}{\left[Cd(^3P_1)\right]} = 1 + \frac{1}{k_2}(\frac{k_3}{k_{-3}} k_4 + k_5)[Q]. \qquad\qquad (6)$$

As $I_0 = k_2[Cd(^3P_1)]_0$ and $I = k_2[Cd(^3P_1)]$, the above equation becomes to

$$\frac{I_0}{I} = 1 + \frac{1}{k_2}\left(\frac{k_3}{k_{-3}}k_4 + k_5\right)[Q].\qquad(7)$$

The Stern-Volmer plots in Fig. 1 are expressed by Eq. 7. As k_3/k_{-3} = $(1/3)\exp(6700/8.314T)$, $(k_3/k_{-3})k_4 + k_5 = k_Q = (0.96k_4 + k_5)$ at 485 °C. For simplicity, the composite quenching constant, $(0.96k_4 + k_5)$, will hereafter be designated k_Q.

Table 1. Rate constant and cross-section for quenching
of $Cd(^3P_J)$ by alkanes

Alkanes	$\dfrac{10^4 k_Q/k_2}{Pa^{-1}}$	$k_Q(rel)$	$\sigma_Q(rel)$	$\dfrac{10^{16}\sigma_Q{}^{a)}}{cm^2}$
methane	0.64	1.00	1.00	0.0041
ethane	4.79	7.44	9.63	$\langle$0.016
propane	13.5	21.0	31.4	0.0082
butane	20.6	32.0	52.7	—
isobutane	28.8	44.7	73.7	0.011

a) Ref. 3.

From the slopes of the straight lines in Fig. 1, the values of k_Q/k_2 are estimated and are listed in Table 1. As has been discussed by Breckenridge et al. previously,[4] at the vapor pressure of cadmium at 280 C the effective lifetime of $Cd(^3P_1)$($\tau = 1/k_2$) is slightly greater than the natural radiation lifetime because "imprisonment" of resonance radiation cannot be totally ignored. Since k_2 is not equal to the reciprocal of the natural lifetime of $Cd(^3P_1)$, it is difficult to estimate the absolute k_Q values. Since the quenchers are diluted with a large amount of argon, it can be assumed that k_2 is independent of the kind of the quenchers and of the pressures of the quenchers. The relative values of k_Q and relative quenching cross-sections are listed in Table 1. Table 1 also contains the quenching cross-sections obtained at 280 °C by Breckenridge and Renlund.[4] They pointed out that there is virtually no dependence of the $Cd(^3P_J)$ quenching rate per C-H bond on C-H bond strength, and explained it by a mechanism in which a loose complex is formed between $Cd(^3P_J)$ and alkane molecules, followed by a low-probability potential surface crossing which has little dependence on C-H bond strength (the abstraction of hydrogen atom from alkane molecule by excited atoms, which accounts for $Hg(^3P_J)$ and $Zn(^3P_J)$ quenchings, is energetically inaccessible to the lower-energy $Cd(^3P_J)$ state at 280 °C).

$$Cd(^3P_J) + H-R \longrightarrow (Cd-H-R)^3 \qquad (8)\ (-8)$$
$$(Cd-H-R)^3 \longrightarrow (Cd-H-R)^1 \qquad (9)$$
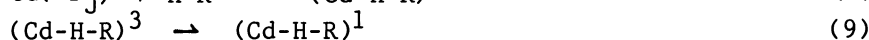
A steady-state analysis leads to $k_Q = k_8k_9/(k_{-8} + k_9)$. If $k_{-8} \gg k_9$ (this explains that the cross-section for the quenching of $Cd(^3P_J)$ are remakably small), $k_Q = k_9(k_8/k_{-8})$. As Table 1 shows, however, the quenching cross-sections change largely from methane to isobutane at 485 °C. The quenching cross-section, σ_i, for each C-H

bond(CH_3-H, primary, secondary, and tertiary) is obtained by assuming that the quenching cross-section, σ_Q, of a certain molecule is defined as the sum of σ_i:[1,2]

$$\sigma_Q = \sum n_i \sigma_i \qquad\qquad\qquad (10)$$

where n_i is the number of C-H bond of type i. The relative values of σ_i for CH_3-H, primary, secondary-, and tertiary C-H bonds are 1.00, 6.42, 43.3, and 237. These values show that at 485 °C the cross-sections depend on C-H bond strength. At this temperature, the following reaction should be taken into account.

$$(Cd-H-R)^3 \longrightarrow CdH + R \qquad\qquad\qquad (11)$$

If Reaction 11 is taken into account, $k_Q = (k_9 + k_{11})(k_8/k_{-8})$, and k_Q is expected to show a dependence on C-H bond strength, because k_{11} is expected to depend on C-H bond strength, as pointed out for the quenchings of $Zn(^3P_J)$ and $Hg(^3P_J)$.[1,2] Thus, the findings that the quenching cross-section of $Cd(^3P_J)$ observed at 485 °C depends on C-H bond strength can be explained by considering that the abstraction of hydrogen atom by excited atoms in the triplet state is possible at this temperature. In order to make sure of this point, further investigation including the isotope effect and the temperature dependence of the quenching rate is in progress.

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