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Mercury(6^3P_1)- and Cadmium(5^3P_1)-Photosensitized Decompositions of Tetramethyltin

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The mercury(6^3P_1)-photosensitized decomposition of tetramethyltin (TMT) has been studied at 120 and 250 °C and at pressures from 10 to 20000 Pa. The gaseous products detected were ethane, methane, and hydrogen. The yields of these products increased linearly with increasing reaction time and light intensity. From the effects of O_2, NO, and H_2 on the yield of ethane, the major primary reactions of the mercury-photosensitized decomposition of TMT were concluded to be processes with an Sn–C bond cleavage. The quantum yields of these products were independent of the TMT pressure at higher pressures than 200 Pa at 120 °C. The quantum yield of ethane was also independent of the TMT pressure, while that of methane increased upon increasing the pressure at 250 °C. The cadmium (5^3P_1)-photosensitized decomposition of TMT has been studied at 280 °C. The detected products were the same as those from the mercury-photosensitized decomposition, although the yield of hydrogen was very small. The pressure dependence of the yields of ethane and methane in the cadmium-photosensitized decomposition was very similar to those in the mercury-photosensitized decomposition of TMT at 250 °C.

Organometallic compounds have been widely used for the development of microelectronic devices. There have been many quantitative studies of the thermal and photochemical decompositions of organometallic compounds in the gas phase. The major primary products of the thermal[1,2] and photochemical[3,4] decompositions of tetramethyltin (TMT) have been reported to be methane and ethane, indicating that the primary process in these decompositions is an Sn–C bond cleavage.

The mercury-photosensitized decomposition of TMT, which apparently has not been studied before, is interesting for a comparison with the mercury-photosensitized decompositions of tetramethyl compounds of other group-14 elements(neopentane (NP),[5,6] tetramethylsilane (TMS),[7,8] and tetramethylgermane (TMG)[9]) which have been quantitatively studied, and also for a comparison with the thermal decomposition and the direct photolysis of TMT. The primary processes in the mercury-photosensitized decompositions of NP, TMS, and TMG have been reported to be C–H bond cleavage; this is clearly different from that in the thermal decomposition and the direct photolysis of TMT.

The present study was undertaken in order to investigate the mercury- and cadmium-photosensitized decompositions of TMT.

Experimental

The mercury-photosensitized reaction of TMT was carried out at 120 and 250 °C in a conventional cylindrical quartz vessel (5 cm long and 4 cm in diameter) fitted with plane quartz windows at each end. Mercury vapor of constant pressure (vapor pressure at room temperature) and volume was admitted into the reaction vessel with various amounts of TMT. In this way the concentration of mercury in the vessel was kept constant irrespective of the TMT pressure and the reaction temperature ([Hg]=9.3×10^{-7} mol dm^{-3}). A low-pressure mercury lamp (Toshiba Electric Co., germicidal lamp) made of a quartz tube was used. The 184.9 nm resonance line was filtered out by a Vicor filter. The light intensity absorbed by mercury atoms at 253.7 nm was determined by means of *cis*-2-butene actinometry[10] ($I_{abs}=4.5\times10^{-9}$ mol s^{-1}).

The cadmium-photosensitized reaction of TMT was carried out at 280 °C in the cylindrical quartz vessel mentioned above. A few small piecies of cadmium metal were placed within the vessel before various amounts of TMT were admitted. A home-made spiral cadmium discharge lamp (filled with about 2700 Pa Ar) made of Pyrex was used. This lamp emits only the resonance line at 326.1 nm. The absorbed light intensity at 326.1 nm was determined by *cis*-2-butene actinometry[11] ($I_{abs}=1.23\times10^{-8}$ mol s^{-1}).

Product analysis was carried out by fractionation at −196 and −89 °C, and measurements by gas buret and gas chromatography. The first portion, noncondensable at −196 °C was collected using a Toepler pump. This portion consisted of hydrogen and methane, and was analyzed by combustion over copper (II) oxide at 280 °C. Noncondensable products at −196 °C from a TMT–O_2 system were analyzed by means of gas chromatography, using a 2 m column of molecular sieve (5A) at 25 °C. The second portion, which was not condensable at −89 °C, was analyzed by means of gas chromatography, using a 6-m column of VZ-7 (Gasukuro Kogyo Co., Ltd.) at 0 °C and a 2-m column of Gasukuro-pack 55 (Gasukuro Kogyo Co., Ltd.) at 180 °C. The third portion, which was condensable at −89 °C contained a large amount of TMT; it was not analyzed.

TMT (Kanto Chemical Co., Ltd.) was dried over a molecular sieve 4A and purified by trap-to-trap distillation. *cis*-2-Butene (Nihon Tokushu Gasu K. K., pure grade), O_2, NO, N_2O, and H_2 (these inorganic gases are comercially available and all pure grade) were used as supplied.

Results

The Hg($^3P_1$)-Photosensitized Decomposition. The thermal decomposition and direct photolysis were found to be negligible under the conditions for the mercury-photosensitized reaction. The gaseous products detected in the mercury-photosensitized reaction were ethane, methane, and hydrogen. The yields of these

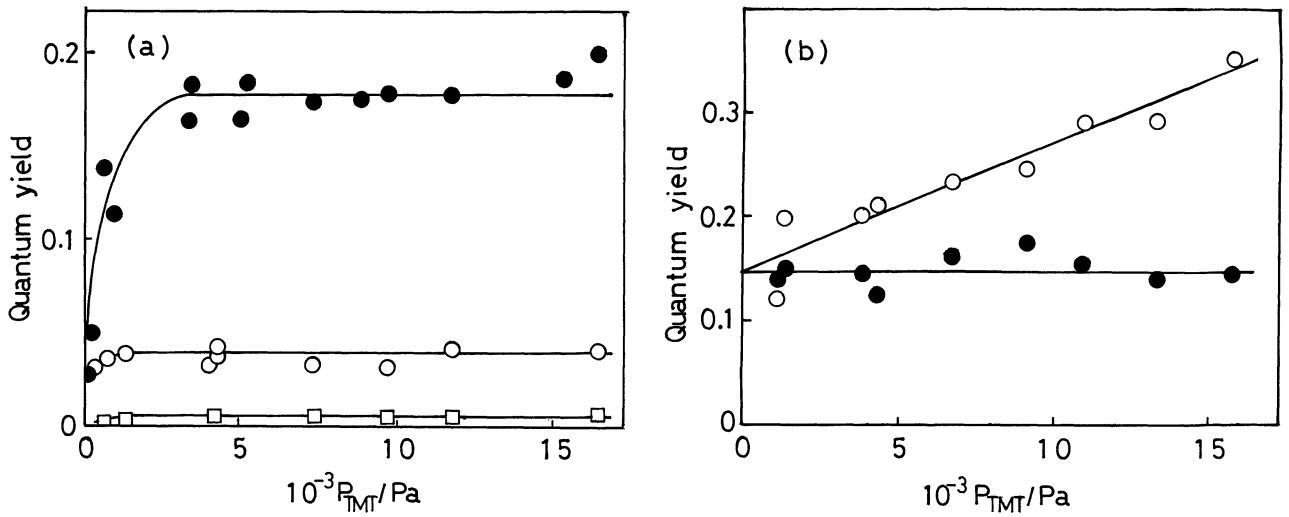

Fig. 1. Pressure dependence of the quamtum yields of ethane (●), methane (○), and hydrogen (□) in the mercury-photosensitized reaction of TMT at 120 °C (a) and 250 °C (b).

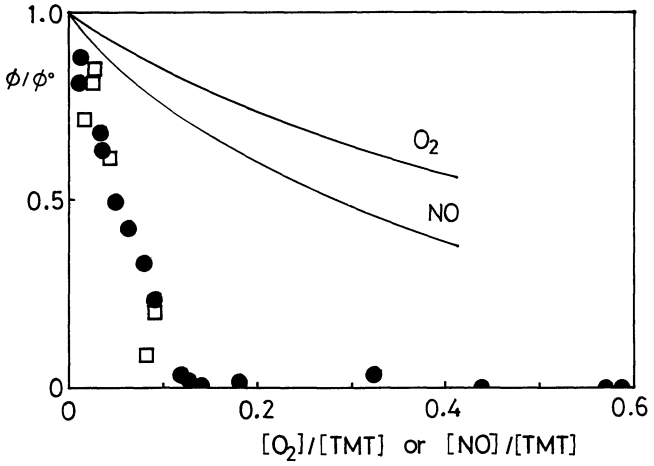

Fig. 2. Quantum yield of ethane in the mercury-photosensitized reaction of TMT at 120 °C in the presence of O_2 (●) and NO (□).

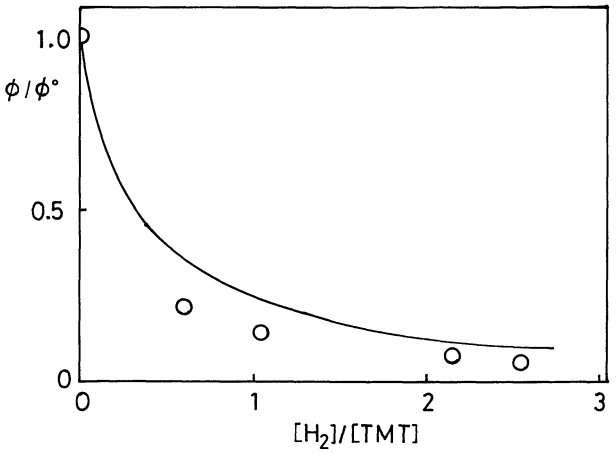

Fig. 3. Quantum yield of ethane in the mercury-photosensitized reaction of TMT at 120 °C in the presence of H_2.

products increased linearly with increasing reaction time and light intensity, showing they were primary products.

The quantum yields of these products are shown in Fig. 1 as a function of the TMT pressure (since the yield of hydrogen was very small at 250 °C, that is not shown in Fig. 1(b)). The quantum yields of all products are constant at higher pressures than 2000 Pa and decrease with decreasing TMT pressure in the low-pressure region at 120 °C (Fig. 1(a)). The quantum yield of ethane is also constant, while that of methane increases with increasing TMT pressure at 250 °C (Fig. 1(b)).

Figure 2 shows the effect of added O_2 and NO on the yield of ethane, while Fig. 3 shows the effect of added H_2 on the yield of ethane. The yield of ethane decreases with increasing the ratios of O_2/TMT, NO/TMT, and H_2/TMT.

The quenching cross section for TMT was obtained

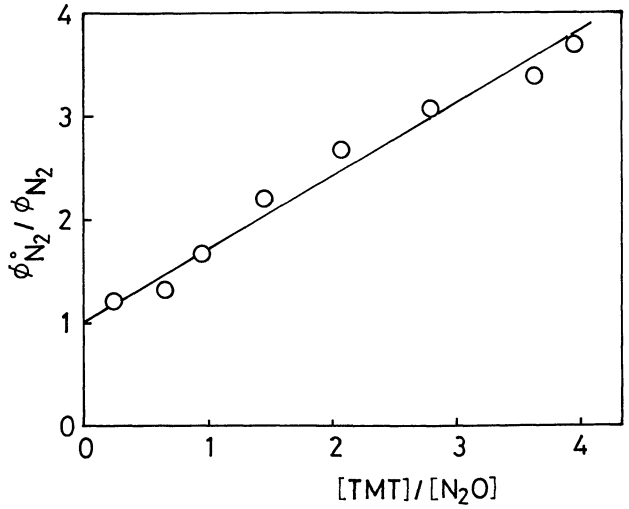

Fig. 4. Competitive quenching plot for TMT and N_2O.

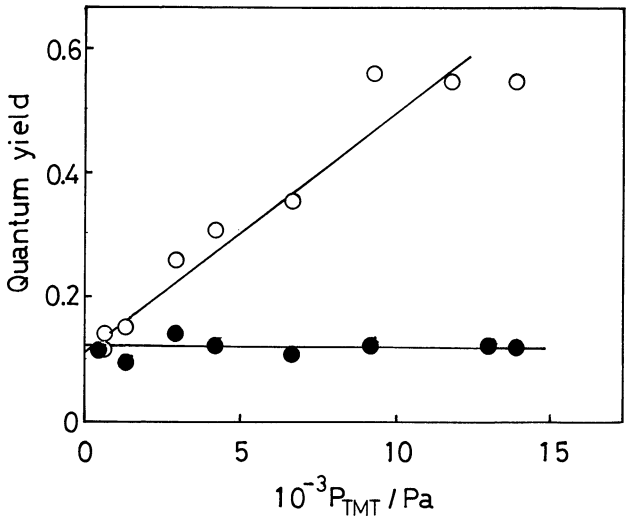

Fig. 5. Pressure dependence of the quantum yields of ethane (●) and methane (○) in the cadmium-photosensitized reaction of TMT at 280 °C.

from the competitive rates of the mercury-photosensitized reactions of TMT and N_2O. The yields of nitrogen from N_2O are expressed by

$$\frac{\phi^{\circ}_{N_2}}{\phi_{N_2}} = 1 + \beta\frac{[TMT]}{[N_2O]}, \quad (1)$$

where $\phi^{\circ}_{N_2}$ and ϕ_{N_2} are the yields of nitrogen in both the absence and presence of TMT. A β-value of 0.70 was obtained from the straight line in Fig. 4 by a least-squares method. The quenching cross section ($\sigma_Q = k_Q(8RT/\pi\mu)^{-1/2}$; k_Q is the quenching rate constant and μ is the reduced mass) for TMT can be calculated using

$$\frac{\sigma_Q(TMT)}{\sigma_Q(N_2O)} = \beta\left(\frac{1+M_{Hg}/M_{N_2O}}{1+M_{Hg}/M_{TMT}}\right)^{1/2}, \quad (2)$$

where $\sigma_Q(N_2O)$ is the cross section for N_2O; we used the value of 56.5×10^{-16} cm^2.[12] A value of 63.7×10^{-16} cm^2 for TMT was obtained. This value is considerably larger than those for NP (4.4×10^{-16} cm^2) and TMS (15.7×10^{-16} cm^2).[7]

The Cd($^3P_1$)-Photosensitized Decomposition. Primary products were the same as those from the mercury-photosensitized decomposition, with the production of ethane and methane again being linear with the reaction time. Hydrogen was a very minor product. The methane/ethane ratio of the cadmium-photosensitized decomposition was appreciably larger than that of the mercury-photosensitized decomposition at 120 °C and comparable to that at 250 °C. As Fig. 5 shows, the yield of ethane was constant and that of methane increased with increasing the TMT pressure. The effect of added H_2 on the yield of ethane was very similar to that observed in mercury-photosensitized decomposition.

Discussion

From the facts that the major products in the mercury-photosensitized reaction of TMT were ethane and methane (while hydrogen was the minor product), and that O_2 and NO in quantities of about 15% completely suppressed ethane formation (Fig. 2), the following simple sequence is indicated as being the major initial reactions:

$$Hg^* + TMT \rightarrow Hg + CH_3 + (CH_3)_3Sn, \quad (3)$$

$$CH_3 + CH_3 \rightarrow C_2H_6, \quad (4)$$

$$CH_3 + TMT \rightarrow CH_4 + CH_2Sn(CH_3)_3. \quad (5)$$

Contrary to the effect of O_2 on ethane formation,methane formation was not completely suppressed by the addition of O_2 in quantities of about 2 of O_2/TMT. The following molecular formation of methane may contribute:

$$Hg^* + TMT \rightarrow CH_4 + CH_2{=}Sn(CH_3)_2. \quad (6)$$

The primary molecular formation of methane was proposed in the direct photolysis of TMT at 185 nm.[3] Minor reactions for hydrogen formation are

$$Hg^* + TMT \rightarrow Hg + H + CH_2Sn(CH_3)_3, \quad (7)$$

and

$$H + TMT \rightarrow H_2 + CH_2Sn(CH_3)_3. \quad (8)$$

In the mercury-photosensitized rections of NP, TMS, and TMG,reactions corresponding to Reactions (7) and (8) are the major initial reactions; C–M bond cleavage (M is a central atom) as Reaction (3) was not observed.

As described above, the addition of O_2 and NO to the photosensitization system suppressed the formation of ethane (Fig. 2). As Fig. 2 shows, the yield of ethane decreases with increasing the ratios of O_2/TMT and NO/TMT. The solid lines show the relative yields calculated using the following relative quenching efficiencies for TMT, O_2, and NO:

$$k_Q(TMT)/k_Q(O_2) = 0.56$$

and

$$k_Q(TMT)/k_Q(NO) = 0.30.$$

These were obtained from the following cross sections for TMT, O_2, and NO: $\sigma_Q(TMT)=63.7\times10^{-16}$ cm^2, $\sigma_Q(O_2)=62.5\times10^{-16}$ cm^2,[12] and $\sigma_Q(NO)=111\times^{-16}$ cm^2.[12] The decreases in the yields of ethane observed in the presence of O_2 and NO are steeper than those expected by the competitive quenching of the triplet mercury atoms by TMT and O_2 or NO. This shows that O_2 and NO have an additional effect (as radical scavengers) on the formation of ethane.

The primary process in the mercury-photosensitized decompositions of NP and TMG is known to be C–H bond cleavage. It has been pointed out, however, that at high light intensities and low substrate pressures, methane is found as one of the major products, and that

atom crackings occur under these conditions.[7,9] To examine the possibility of atom cracking in the present reaction, we examined the effect of hydrogen addition to the system. If atom cracking (shown by Reactions (9) and (10)) contributes to the formation of the methyl radical, one would expect that the yield of ethane continuously increases with increasing ratio of H_2/TMT, because of the large efficiency of the formation of hydrogen atoms for H_2-triplet mercury atom system:[12]

$$H + CH_2Sn(CH_3)_3 \rightarrow TMT^* \quad (9)$$

and

$$TMT^* \rightarrow CH_3 + Sn(CH_3)_3. \quad (10)$$

As shown in Fig. 3, however, the yield of ethane decreases with increasing the ratio of H_2/ TMT. The solid line shows the relative quantum yield calculated using the following relative quenching efficiencies for H_2 and TMT ($k_Q(H_2)/k_Q(TMT)=2.90$; obtained from $\sigma_Q(H_2)=27\times10^{-16}$ cm^2 [12] and $\sigma_Q(TMT)=63.7\times10^{-16}$ cm^2). The decrease in the quantum yield can be roughly explained by a competitive quenching of the triplet mercuty by H_2 and TMT. Therefore, atom cracking can be ruled out.

The following reactions are considered to explain the pressure dependence of the yields of ethane and methane:

$$Hg^* \longrightarrow Hg + h\nu \qquad k_0 \quad (11)$$

$$Hg^* + TMT \xrightarrow{\alpha_1} Hg + CH_3 + (CH_3)_3Sn \quad (3)$$

$$Hg^* + TMT \xrightarrow{\alpha_2} Hg + CH_4 + CH_2{=}Sn(CH_3)_2 \qquad k_Q \quad (6)$$

$$Hg^* + TMT \xrightarrow{1-\alpha_1-\alpha_2} Hg + TMT \quad (12)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad k_1 \quad (4)$$

$$CH_3 + TMT \longrightarrow CH_4 + CH_2Sn(CH_3)_3 \qquad k_2 \quad (5)$$

$$CH_2Sn(CH_3)_3 \longrightarrow CH_3 + CH_2{=}Sn(CH_3)_2 \qquad k_3 \quad (13)$$

$$\text{Radicals} \rightarrow \text{recombination reactions.} \quad (14)$$

From the above mechanism, the following relationship can be derived by neglecting the contribution of CH_3 and $CH_2Sn(CH_3)_3$ radicals to Reactions (14):

$$\phi(C_2H_6)=\frac{1}{2}\alpha_1 \quad (15)$$

$$\phi(CH_4)=\alpha_2+\alpha_1\frac{k_2[TMT]}{k_1[CH_3]_{ss}} \quad (16)$$

$$\frac{\phi(CH_4)}{\phi(C_2H_6)}=\frac{2\alpha_2}{\alpha_1}+\frac{2k_2}{k_1[CH_3]_{ss}}[TMT]. \quad (17)$$

Since Reaction (5) requires an activation energy, as shown by Borrell and Platt,[3] the contribution of this reaction increases with increasing temperature. If this reaction can be neglected at 120 °C, $\phi(CH_4)$ equals to α_2. Therefore, at this temperature the quantum yields of ethane and methane are independent of the pressure of TMT. This is in agreement with the experimental results shown in Fig. 1(a) (decrease in yields with decreasing TMT pressure at low pressures seem to be due to incomplete quenchlng of excited mercury atoms). At higher temperature (250 °C), however, Reaction (5) can not be neglected, and the yield of methane may depend on TMT pressure. The steady-state concentration of methyl radical can be expressed as

$$[CH_3]_{ss}=\left(\frac{\alpha_1 I_0}{2k_1}\right)^{1/2}; \quad (18)$$

this can be regarded as being independent of TMT pressure. Figure 6 shows the ratio of the yield of methane to that of ethane obtained at 120 °C and 250 °C as a function of the pressure of TMT. The ratio increases at 250 °C linearly with increasing the pressure of TMT; this is in agreement with the expectaion from Eq. 17. The slopes and intercepts of the lines in Fig. 6 are listed in Table 1.

The main products from the cadmium-photosensitized reaction of TMT were ethane and methane. The pressure dependences of the yields of these products are similar to those in the mercury-photosensitized reaction at 250 °C. The effect of H_2 on the yield of ethane is also very similar to that in the mercury-photosensitized reaction. These findings show that the reaction mechanism for the cadmium-photosensitized reaction of TMT is similar to that for the mercury-photosensitized reaction. The ratio of the yield of methane to that of ethane is shown as a function of the TMT pressure in Fig. 6. The ratio again increases linearly with increasing TMT pressure. The slope and intercept of the line for the cadmium-photosensitization are also listed in Table 1.

The values of α_2/α_1 obtained from the intercepts are listed in Table 1. The value of α_2/α_1 for the mercury-photosensitized reaction at 250 °C is very similar to that for the cadmium-photosensitized reaction. It is sensitive to temperature, and is large at high temperatures.

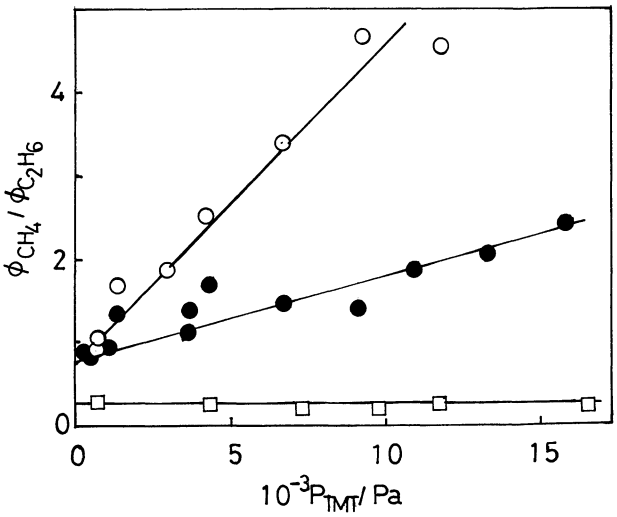

Fig. 6. Plots of $\Phi_{CH_4}/\Phi_{C_2H_6}$ against the TMT pressure for the mercury-photosensitized reaction at 120 °C (□) and 250 °C (●) and the cadmium-photosensitized reaction at 280 °C (○).

Table 1. Comparison of Various Constants for Mercury- and Cadmium-Photosensitized Reactions

	Hg		Cd
	120 °C	250 °C	280 °C
Intercept	0.12	0.89	0.80
10^5 slope/Pa^{-1}	0	9.0	43
α_2/α_1	0.10	0.45	0.40
10^{-10} k_1/l mol^{-1} s^{-1}	2.5	2.5	2.5
10^{-4} k_2/l mol^{-1} s^{-1}	0.34	4.6	7.0
10^9 $[CH_3]_{ss}$/mol l^{-1}		9.5	2.8

This shows that the ratio of the molecular formation of methane (Reaction (6)) to the formation of methyl radical (Reaction (3)) increases with increasing temperature. This molecular process for the formation of methane is known to occur in a direct photolysis of TMT vapor at 185 nm.[3] Since we have no information, however, on the temperature dependence of this process, further discussion of the temperature dependence of the α_2/α_1 seems not to be justified.

The value of the slope seems to depend on the temperature and kind of sensitizer. The k_1- and k_2-values included in the slope can be obtained from the literatures:

$$k_1/\text{l mol}^{-1}\text{ s}^{-1} = (2.5 \pm 0.2) \times 10^{10}$$ [13]

and

$$k_2/\text{l mol}^{-1}\text{ s}^{-1} = 1.2 \times 10^8 \exp(-4100/T).$$ [3]

These values are also listed in Table 1. The steady-state concentrations of CH_3 can be estimated from the values of the slope and those of k_1 and k_2 and are listed in Table 1. The value of $[CH_3]_{ss}$ obtained for the mercury-photosensitized reaction at 250 °C is larger than that for the cadmium-photosensitized reaction. This tendency is not apparently in agreement with the fact that the rate of the ethane formation in the mercury-photosensitized reaction of TMT is smaller than that in the cadmium-photosensitized reaction of TMT (the values of 6.7×10^{-10} and 15.7×10^{-10} mol s^{-1} for the mercury- and cadmium photosensitized reactions were obtained from the time dependences of the yield of ethane). This discrepancy may result from the difference in the volume of reaction zone, based on the differences in the cross sections of the beams of exciting light and the absorption coefficients of mercury and cadmium: that is, the mercury-photosensitized reaction occurs locally near the front window of the cell because of the large absorption coefficient of mercury (the ratio of the volumes of reaction zone ($V_{Hg}/V_{Cd}=1/26$) is consistent with the values of $[CH_3]_{ss}$ and the apparent rate of ethane formation in the mercury- and cadmium-photosensitized reactions).

Contrary to the mercury-photosensitized decompositions of NP, TMS, and TMG, the main initial reactions of the mercury- and cadmium-photosensitized decomposition of TMT are processes with a cleavage of an Sn–C bond (the formation of CH_3 and the molecular formation of methane). In this respect, the present reactions are very similar to the direct photolysis of TMT as well as the cadmium-photosensitized reaction of acetaldehyde, which was reported to proceed through the formation of an excited complex between the Cd* and an aldehyde molecule, or after an energy transfer from Cd* to an aldehyde molecule.[14] The triplet energy of TMT is not yet known, but is probably lower than those of NP and TMS, because the absorption band of TMT shifts to a longer wavelength than do those of NP and TMS.[15] Since the quenching cross section of triplet mercury atom for TMT is larger than those for NP and TMS, as described above, the triplet energy transfer from Hg ($^3P_1$)(and Cd($^3P_1$)) to TMT to produce a triplet state of the TMT molecules seems to occur. This is the reasoning used to explain that the mechanism for TMT is different from those for NP, TMS, and TMG, and that it is rather similar to those of the cadmium-photosensitized reactions of aldehydes.

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