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Mercury- and Cadmium-photosensitized Reactions of γ-Butyrolactone

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The mercury- and cadmium-photosensitized reactions of γ-butyrolactone have been compared. The products obtained in the two photosensitizations were quite different. The gaseous products from the mercury-photosensitized reaction were carbon dioxide, cyclopropane, and propylene, while the products obtained in the cadmium-photosensitized reaction were carbon monoxide and ethylene. This difference suggests that the decomposition of γ-butyrolactone takes place through different intermediates in the two reactions. Possible mechanisms are discussed.

Numerous studies of chemical reactions induced by excited atoms have been published. Cadmium-photosensitized reactions have often been compared with mercury-photosensitized reactions to obtain information about the detailed mechanism of the reaction. It is generally accepted that these reactions are the same by nature, and that a difference in quantum yields of products can be explained by the difference in their excitation energies.

We studied the mercury- and cadmiun-photosensitized reactions of γ-butyrolactone and found quite different products in these reactions. In a previous short communication,[1] we reported briefly the results of these studies. The present paper will report the details of the reactions.

Experimental

The mercury-photosensitized reaction was studied at 125 °C in a cylindrical quartz cell, 4cm in diameter and 10 cm long, fitted with plane quartz windows. A spiral quartz mercury discharge lamp filled with 670 Pa Ar was used. The 184.9 nm resonance line was filtered out by a Vycor filter. Light intensity absorbed by mercury atoms at 253.7 nm was determined by ethylene actinometry.[2]

The cadmium-photosensitized reaction was studied at 300 °C in a cylindrical Pyrex cell, 2 cm in diameter and 20 cm long. A U-shaped cadmium discharge lamp made of Pyrex, filled with 670 Pa Ar, was used. Absorbed light intensity at 326.1 nm was determined by *cis*-2-butene actinometry.[3]

Product analysis was done by fractionation at −196 and −60 °C, and measurement with gas burette and gas chromatography, using a 12 m column of VZ-7 (Gasukuro Kogyo Co., LTD) at 0 °C.

γ-butyrolactone (Tokyo Kasei Ind., E.P. grade) was purified by trap-to-trap distillation. Liquid butyrolactone was injected into the cell by a microsyringe, and was fully degassed by many careful freeze-pump cycles. *cis*-2-Butene (Nihon Tokushu Gasu K. K., pure-grade) and N_2O (Nihon Sanso K. K., pure-grade) were used as supplied.

Results and Discussion

The Mercury-photosensitized Reaction. Since the vapor pressure of butyrolactone is low at room temperature, it is necessary to elevate the reaction temperature in order to obtain sufficient vapor pressure. The thermal decomposition of butyrolactone at 125 °C was found to be negligible.

The major products were carbon dioxide, cyclopropane, and propylene, while carbon monoxide and hydrogen were minor products. These major products were also observed by Simonatis and Pitts[4] and Krull and Arnold,[5] in mercury-photosensitized reaction of γ-butyrolactone. These products are also those which originate from the triplet manifold of lactone in the direct photolysis.[4] This is reasonable, because sensitization by $Hg(^3P_1)$ is expected to give triplet lactone due to spin conservation.

Yields of Carbon dioxide, cyclopropane, and propylene increased linearly with reaction time and light intensity. This shows that carbon dioxide, cyclopropane, and propylene are primary products. Quantum yields of product formation are shown in Fig. 1 as a function of lactone pressure; the quantum yield of carbon dioxide is independent of lactone pressure, while that of cyclopropane increases and that of propylene decreases with increasing lactone pressure. The quantum yield of carbon dioxide was only 0.25, even at the lowest pressure examined. This suggests that most of the triplet lactone formed undergoes the other reactions. As no products volatile at −60 °C were obtained except for carbon dioxide, cyclopropane, and propylene, the isomerization to succinaldehyde which was obtained in the direct photolysis of γ-butyrolactone[4] and the process that the triplet lactone loses its excitation energy without forming any products seem to be important.

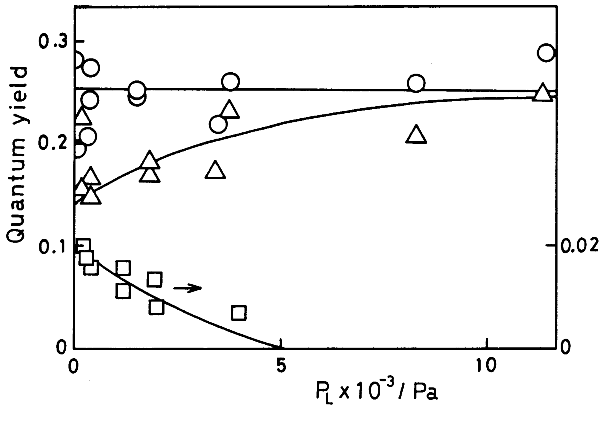

Fig. 1. Pressure dependence of quantum yields of CO_2 (○), cyclopropane (△), and propylene (□) in the mercury-photosensitized reaction of γ-butyrolactone.

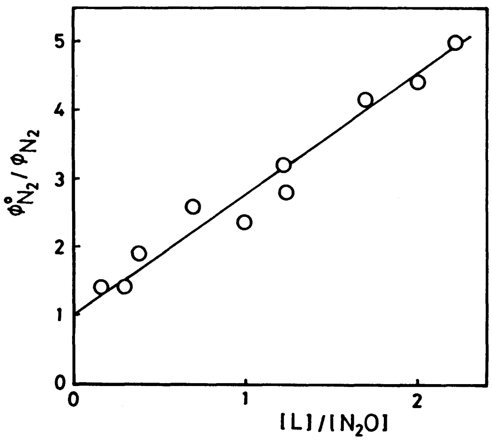

Fig. 2. Competitive quenching plots for lactone.

The quenching cross-section for lactone was obtained from competitive rates of the mercury-photosensitized reactions of lactone and N_2O. Figure 2 shows the competitive quenching plots for lactone. Yields of nitrogen from N_2O are expressed by the expression;

$$\frac{\phi^\circ_{N_2}}{\phi_{N_2}} = 1 + \beta\frac{[L]}{[N_2O]}, \tag{1}$$

where $\phi^\circ_{N_2}$ and ϕ_{N_2} are quantum yields in the absence and in the presence of lactone. The best straight line was obtained by the method of least squares. The quenching cross-section for lactone can be calculated by the following equation;[6]

$$\frac{\sigma^2_L}{\sigma^2_{N_2O}} = \beta\left(\frac{1+M_{Hg}/M_{N_2O}}{1+M_{Hg}/M_L}\right)^{-1/2}, \tag{2}$$

where $\sigma^2_{N_2O}$ is the cross-section for N_2O and we used the value of 18.0 Å^2. The value of 41 Å^2 for lactone was obtained and it can be compared with that for acetone (53 Å^2) and for acetoaldehyde (41 Å^2). In the presence of N_2O, the observed decrease in the quantum yield of cyclopropane agreeds with that expected from competitive quenching within the limits of experimental error.

The following set of reactions is proposed to explain our results:

$$\mathrm{Hg} + h\nu\ (253.7\ \mathrm{nm}) \longrightarrow \mathrm{Hg}(^3P_1), \tag{3}$$

$$\mathrm{Hg}(^3P_1) + L \longrightarrow \mathrm{Hg} + {}^3L, \tag{4}$$

$${}^3L \longrightarrow CO_2 + C_3H_6^*, \tag{5}$$

$${}^3L \longrightarrow \text{other reactions}, \tag{6}$$

$$C_3H_6^* \longrightarrow CH_3CH{=}CH_2, \tag{7}$$

$$C_3H_6^* + L \longrightarrow \text{cyclo-}C_3H_6 + L. \tag{8}$$

Here, ^3L denotes triplet lactone and $C_3H_6^*$ is a "hot" cyclopropane intermediate. From this mechanism the quantum yields of products should be given by

$$\phi_{CO_2} = \frac{k_5}{k_5+k_6}, \tag{9}$$

$$\phi_{CH_3CH=CH_2} = \frac{k_5}{k_5+k_6}\,\frac{k_7}{k_7+k_8[L]}, \tag{10}$$

$$\phi_{\text{cyclo-}C_3H_6} = \frac{k_5}{k_5+k_6}\,\frac{k_8[L]}{k_7+k_8[L]}. \tag{11}$$

These equations explain the observed pressure dependence of the quantum yields.

The Reaction, L→cyclo-C_3H_6+CO_2, is endothermic by about 29 kJ mol^{-1}.[4] Since the excitation energy of Hg($^3P_1$) is 469 kJ mol^{-1}, the energy to be distributed among the products is greater than 440 kJ mol^{-1}. This value is almost the same as that estimated for the average energy transferred to the cyclobutanone molecule from the Hg($^3P_1$) atom.[7] Photosensitized reaction of cyclobutanone has been reported to yield vibrationally excited cyclopropane and carbon monoxide, and the former is known to isomerize to propylene. In this case a propylene/cyclopropane ratio of 0.58 at about 1330 Pa was obtained. As is shown in Fig. 1, however, propylene was only about one-fifteenth of the cyclopropane at the same pressure. In order to explain this difference, it is suggested that if triplet carbon dioxide (with an energy of about 356 kJ mol^{-1} [18]) is formed in Reaction 5, the energ content of cyclopropane would be greatly reduced, making the isomerization impossible. If the reaction, $^3L \rightarrow {}^3CO_2$+cyclo-C_3H_6 (5′), is added to the mechanism, the following relation can be derived.

$$\frac{\phi_{\text{cyclo-}C_3H_6}}{\phi_{CH_3CH=CH_2}} = \frac{k_{5'}}{k_5} + \left(1+\frac{k_{5'}}{k_5}\right)\frac{k_8}{k_7}[L] \tag{12}$$

From the intercept of the straight line shown in Fig. 3, a value of $k_{5'}/k_5$ of about 12 is obtained. Thus the reaction which produces excited carbon dioxide, is the main process. Simonaitis and Pitts also pointed out the possibility of the formation of triplet carbon dioxide in the direct photolysis of γ-butyrolactone at 210 to 260 nm.[4] A value of 3.45×10^{-4} Pa^{-1} for k_8/k_7 ratio is also obtaine from the intercept and the slope of the straight line. This gives the value of k_7 as 2.75×10^8 s^{-1} by adopting 9.5×10^4 s^{-1} as the kinetic collision frequency at 1 Pa and by assuming unit collisional deactivation efficiency for lactone. The excess energy of energized cyclopropane can be estimated by the equation given by Rabinovitch and Diesen:[9]

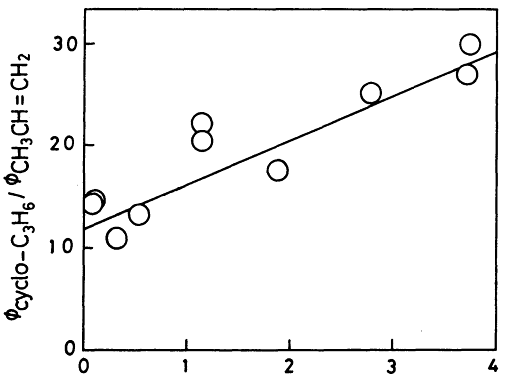

Fig. 3. Plots of $\phi_{\text{cyclo-}C_3H_6}/\phi_{CH_3CH=CH_2}$ against lactone pressure.

TABLE 1. COMPARISON OF EXCESS ENERGY OF CYCLOPROPANE

Compounds	Reactions	E / kJ mol^{-1}
γ-butyrolactone	Hg($^3P_1$)photosensitization	339
cyclobutanone	Hg($^3P_1$)photosensitization$^{a)}$	314±21
1-pyrazoline	direct photolysis(312.6 nm)$^{b)}$	314
tetrahydrofuran	direct photolysis(197.3 and 194.2 nm)$^{c)}$	331

a) Ref. 7. b) P. Cadman, H. M. Meunier, and A. P. Trotman-Dickenson, *J. Am. Chem. Soc.*, **91**, 7640 (1969). c) B. C. Roquitte, *J. Am. Chem. Soc,*. **91**, 7664 (1969).

$$k_7 = A'\left[\frac{E-E_0+a^+E_z{}^+}{E+aE_z}\right]^{s-1}. \tag{13}$$

Using experimental value of k_7 and substituting $A'=10^{15.80}\,s^{-1}$, $E_0=262.4$ kJ mol^{-1}, $E_z=205.2$ kJ mol^{-1}, $E_z{}^+=179.1$ kJ mol^{-1}, s=21, and a and a' which were obtained by being extrapolated from those given in Ref. (10), the value of E was found to be 339 kJ mol^{-1}. This corresponds to about 83% of the total energy (440 kJ mol^{-1}) to be distributed among the products. A comparison of the excess energy of cyclopropane in different systems is given in Table 1. As is shown in Table 1, the value of E in the present system is in fair agreement with those in other system, showing our result is reasonable.

The Cadmium-photosensitized Reaction. In the cadmium-photosensitized reaction, it is necessary to raise the reaction temperature to get a sufficient vapor pressure of cadmium. The thermal decomposition at 300 °C was found to give a small amount of carbon dioxide and cyclopropane, but not to give carbon monoxide and ethylene. The main products in the cadmium-photosensitized reaction were carbon monoxide and ethylene, quite different from those in the mercury-photosensitized reaction. To make sure that the difference between the two reactions is not owing to the difference in temperature, we examined the two reactions at the same temperature (235 °C), and obtained the same results as those obtained under the conditions mentioned above. If the triplet state of lactone lies at about 439 kJ/mol above the ground state, as Simonatitis and Pitts estimated,[11] it can not be formed by reaction of Cd($^3P_1$) which has energy of only 367 kJ mol^{-1}. This probably accounts for the difference between the mercury- and cadmium-photosensitized reactions of lactone. In the presence of a large pressure of nitrogen, oxetane was also observed.

Yields of carbon monoxide and ethylene increased linearly with reaction time, showing that those are primary products. The quantum yields of carbon monoxide and ethylene are shown in Fig. 4 as a function of lactone pressure. The yield of ethylene decreases a little more rapidly than that of carbon monoxide with increasing pressure.

When *cis*-2-butene was added to lactone, the quantum yields of the decomposition products decreased as the quantum yield of *trans*-2-butene formation increases. From the slope of the reciprocal plot of the quantum yield of *trans*-2-butene *vs.* the lactone/*cis*-2-butene ratio (Fig. 5), the quenching efficiency of lactone relative to that of *cis*-2-butene was estimated to be 0.92±0.10. This value is close to those for ethylene (1.03±0.09[12]), propylene (1.18±0.04[12]), and cyclopentanone (0.8±0.2[13]). Figure 6 shows the effect of *cis*-2-butene on the yields of carbon monoxide and ethylene. Solid line shows the relative quantum yields calculated using the relative quenching efficiency of lactone obtained above. As Fig. 6 shows, the decrease in the quantum yields of carbon monoxide and ethylene observed in the presence of *cis*-2-butene can be explained by competitive quenching of triplet lactone alone; *i.e.* the nature of the decomposition was not affected.

In order to explain the experimental results, the following set of reactions is proposed:

$$\mathrm{Cd(^1S_0)} + h\nu\ (326.1\ \mathrm{nm}) \longrightarrow \mathrm{Cd(^3P_1)}, \tag{14}$$

$$\mathrm{Cd(^3P_1)} + \mathrm{L} \longrightarrow \mathrm{CdL^*}, \tag{15}$$

$$\mathrm{CdL^*} \longrightarrow \cdot\mathrm{COCH_2CH_2CH_2O\text{-}Cd}\cdot, \tag{16}$$

$$\mathrm{CdL^*} \longrightarrow \text{other reactions}, \tag{17}$$

$$\mathrm{CdL^*} + \mathrm{L} \longrightarrow \mathrm{Cd} + 2\mathrm{L}, \tag{18}$$

$$\cdot\mathrm{COCH_2CH_2CH_2O\text{-}Cd}\cdot \longrightarrow \mathrm{CO} + \cdot\mathrm{CH_2CH_2CH_2O\text{-}Cd}\cdot, \tag{19}$$

$$\cdot\mathrm{CH_2CH_2CH_2O\text{-}Cd}\cdot \longrightarrow \mathrm{CH_2{=}CH_2} + \mathrm{CH_2O} + \mathrm{Cd}, \tag{20}$$

$$\cdot\mathrm{CH_2CH_2CH_2O\text{-}Cd}\cdot + \mathrm{M} \longrightarrow \underbrace{\mathrm{CH_2CH_2CH_2O}} + \mathrm{Cd} + \mathrm{M}. \tag{21}$$

Here, CdL* stands for a transient complex between the excited cadmium atom and a lactone molecule, which is tentatively proposed to explain the difference between the mercury- and cadmium-photosensitized reactions of lactone. Formation of a similar complex between excited cadmium and saturated alcohols and ethers was suggested previously.[14] Formation of an O–Cd bond in Reactions 17 and 20 was assumed, because the excitation energy of Cd($^3P_1$) alone is not enough to produce biradicals $\cdot COCH_2CH_2CH_2O\cdot$ and $\cdot CH_2CH_2CH_2O\cdot$, as is shown in Table 2.

From this mechanism the following relation can be derived:

$$\frac{\phi_{\mathrm{CO}}}{\phi_{\mathrm{C_2H_4}}} = 1 + \frac{k_{21}}{k_{20}}[\mathrm{M}]. \tag{23}$$

A plot of $\phi_{CO}/\phi_{C_2H_4}$ *vs.* lactone pressure is presented in Fig. 7, from which $k_{21}/k_{20}=1.3\times10^{-5}$ Pa^{-1}. The low value implies a relativly short lifetime for the biradical, $\cdot CH_2CH_2CH_2O\text{-}Cd\cdot$.

From the proposed mechanism, it is expected that the yield of oxetane should increases with increasing lactone pressure. We obtained only small amounts of oxetane in the pure lactone, and found that the yield was independent of lactone pressure. In the presence of a large pressure of nitrogen, however, we obtained

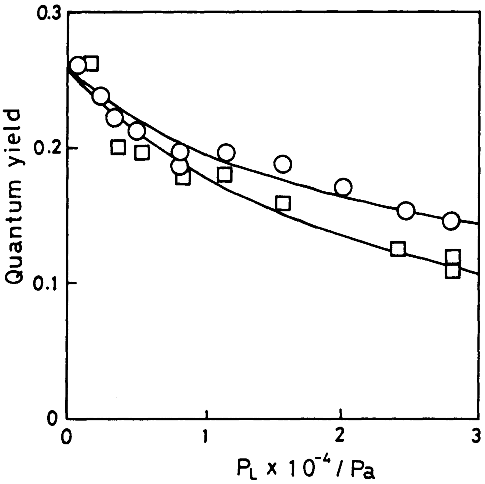

Fig. 4. Pressure dependence of quantum yields of CO (○) and ethylene (□) in the cadmium-photosensitized reaction of γ-butyrolactone.

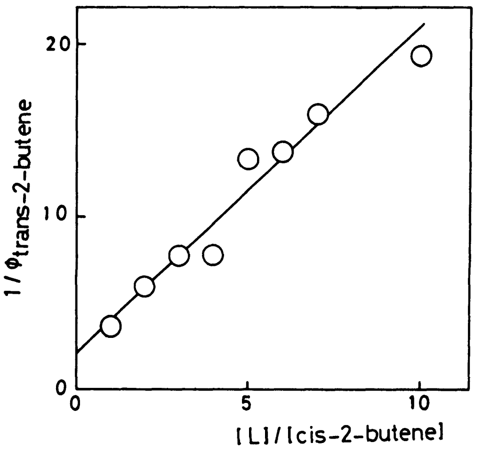

Fig. 5. Plots of the reciplocal of the quantum yield of *tran*-2-butene against the lactone/*cis*-2-butene pressure ratio.

a considerably more oxetane and found that the yield increased with increasing nitrogen pressure. These findings suggest that the biradical produced in Reaction 20 may react with lactone, limiting the yields of oxetane in the pure lactone.

In general, excitation of an ester molecule can be followed by any of three possible bond cleavages (processes I, II, and III); I and II would be indistinguishable for the usual experimental conditions, since radical decomposition (RCO_2 and R′OCO) would be very rapid.[15]

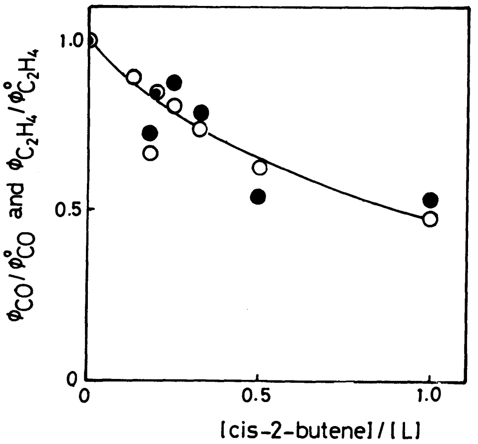

Fig. 6. Quantum yields of CO (○) and ethylene (●) in the cadmium-photosensitized reaction of γ-butyrolactone in the presence of *cis*-2-butene.

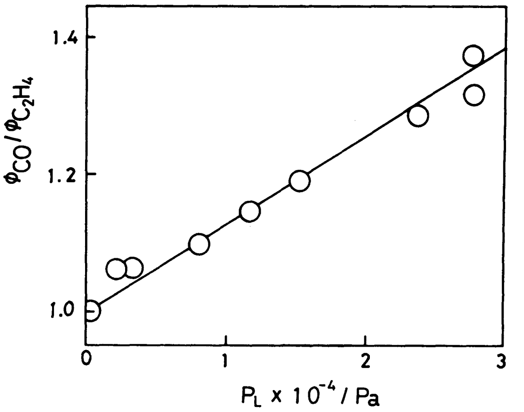

Fig. 7. Plots of $\phi_{CO}/\phi_{C_2H_4}$ against lactone pressure.

$$
\begin{aligned}
&RCOOR' + h\nu \\
&\longrightarrow RCO_2 + R' \ (\longrightarrow R + CO_2 + R'), \quad \text{I} \\
&\longrightarrow R + CO_2R' \ (\longrightarrow R + CO_2 + R'), \quad \text{II} \\
&\longrightarrow RCO + OR' \ (\longrightarrow R + CO + OR'). \quad \text{III}
\end{aligned}
$$

Mercury-photosensitized reaction of lactone seems to proceed by process I and/or II, while cadmium-photosensitized reaction seems to proceed by process III. The bond dissociation energies of some bonds in lactone were estimated by thermochemical data given by Benson:[16]

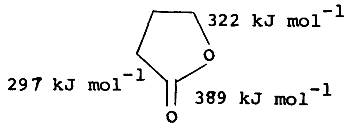

TABLE 2. ENTHALPY CHANGES FOR SOME REACTIONS BETWEEN γ-BUTYROLACTONE AND $Cd(^3P_1)$[a]

Reaction		ΔH kJ mol^{-1}
$CH_2CH_2CH_2OCO + Cd(^3P_1)$	$\rightarrow \cdot COCH_2CH_2CH_2O\cdot + Cd$	22.2
	$\rightarrow \cdot COCH_2CH_2CH_2O\text{-}Cd\cdot$	−350.3
	$\rightarrow CO + \cdot CH_2CH_2CH_2O\cdot + Cd$	56.9
	$\rightarrow CO + \cdot CH_2CH_2CH_2O\text{-}Cd.$	−315.6

a) We used the value of 372.5kJ mol^{-1} for the bond energy of Cd-O. J. C. Bailar, H. J. EMeteus, Sir Ronald Nyholm, and A. F. Trotman-Dickenson, "Comprehensive Inorganic Chemistry," Vol. III, Pergamon Press, Oxford (1973).

It is easy to understand the mercury-photosensitized reaction of lactone, since the excitation energy of Hg($^3P_1$) is sufficiently large. Although the excitation energy of Cd($^3P_1$) is smaller than the bond energy of CO–O, the CO–O bond must break at first to produce carbon monoxide. Therefore, we assumed formation of an O–Cd bond in Reaction 16.

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