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Cadmium-photosensitized Reaction of γ-Valerolactone and α-Methyl-γ-butyrolactone

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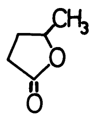
The cadmium-photosensitized reactions of γ-valerolactone and α-methyl-γ-butyrolactone have been investigated. The obtained products in both cases were carbon monoxide, ethylene, propylene, acetaldehyde, and 2-methyloxetane. The dependence of the yields of ethylene and propylene on the total pressure suggests the existence of a biradical and an energized intermediate. Possible mechanisms are discussed.

While the photochemistry of aliphatic esters and cyclic ketones has been investigated in some detail, there have been only a few quantitative studies on the photo-decomposition of simple aliphatic lactones in the gas phase.

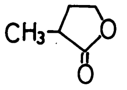
Simonaitis and Pitts[1)] investigated the direct photolysis and the mercury-photosensitized decomposition of γ-butyrolactone(BL) in the gas phase and observed that lactone (1) isomerizes to succinaldehyde, (2) decomposes to ethylene, carbon monoxide, and formaldehyde, and (3) decomposes to propylene or cyclopropane and carbon dioxide. They pointed out that succinaldehyde and ethylene are probably singlet-state products, whereas cyclopropane and propylene are probably triplet-state products.

Recent work[2)] in our laboratory on BL has shown that quite different products are obtained in mercury- and cadmium- photosensitized reactions. We concluded that the decomposition of lactone takes place through different intermediates, that is, a triplet state of lactone in the mercury-photosensitized reaction and an excited complex between an excited cadmium atom and a lactone molecule in the cadmium-photosensitized reaction. A rational mechanism has been proposed for the mercury-photosensitized reaction. However, the mechanism regarding the cadmium-photosensitized reaction has remained somewhat obscure.

In order to obtain further information on the cadmium-photosensitized reaction of lactone, we investigated the effect of a methyl group in the α- and γ-positions regarding primary processes, quantum yields, and rates of decomposition. In this paper we report on the cadmium-photosensitized reactions of γ-valerolactone(VL) and α-methyl-γ-butyrolactone (ML).



VL



ML

Experimental

The apparatus and techniques were similar to those used previously.[2)] An analysis of products was performed using simple fractionation at 77 and 190 K, measurements with a gas burette, and gas chromatography. The light absorbed by cadmium atoms at 326.1 nm was determined by *cis*-2-butene actinometry.[3)]

VL (aldrich, 98%) and ML (Tokyo Kasei Ind., E.P. grade) were used after drying using a molecular sieve (5A) and several trap-to-trap distillations. Known amounts of liquid lactone were injected into the reaction cell with a microsyringe and were fully degassed after many careful freeze-pump cycles. *cis*-2-Butene (Nihon Tokushu Gasu K.K., pure grade) snd N_2 (Takachiho Shoji., pure grade) were used as supplied.

The cadmium-photosensitized reaction was carried out at 300 °C in order to obtain a sufficient cadmium vapor pressure. A thermal decomposition occurred at this temperature and yielded carbon dioxide, methylcyclopropane and other minor products. However, the amounts of these products were very small and the influence of the thermal decomposition on the results of the cadmium-photosensitized reaction was negligible.

Results

The major observed volatile products in the cadmium-photosensitized reaction were carbon monoxide, ethylene, propylene and acetaldehyde. These products are different from those obtained during thermal decomposition. Yields of these products increased linearly with reaction time, showing that they are primary products. The quantum yields of carbon monoxide, ethylene, and propylene are shown in Fig. 1 as a function of lactone pressure. All of them decreased with an increasing lactone pressure, showing the existence of a collisional deactivation process. The amount of acetaldehyde was always roughly equal to that of ethylene.

Only small amounts of 2-methyloxetane were obtained for pure lactone systems. In the presence of a large nitrogen pressure, however, we obtained considerably more 2-methyloxetane and found that the yield increased with pressure.

When *cis*-2-butene was added to lactone, the

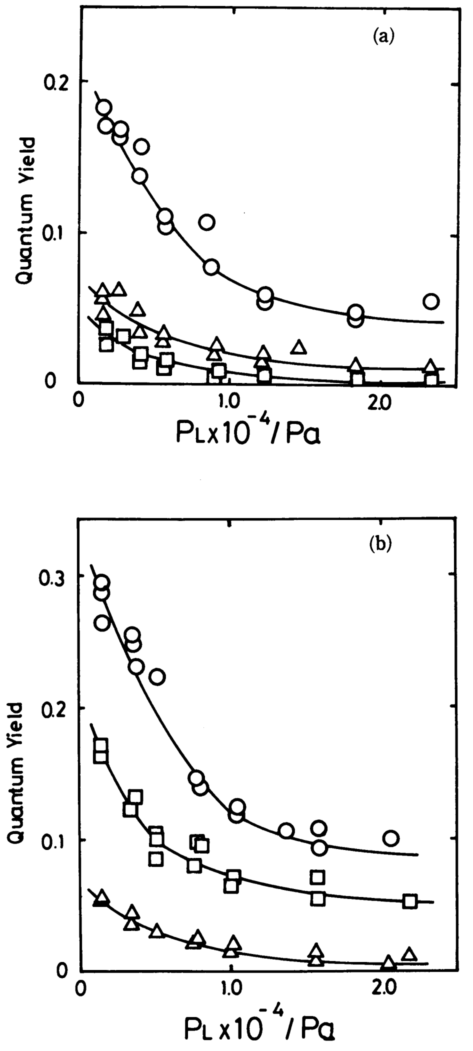


Fig. 1. Pressure dependence of quantum yields of carbon monoxide (○), ethylene (△), and propylene (□) in the cadmium-photosensitized reaction of (a) VL and (b) ML.

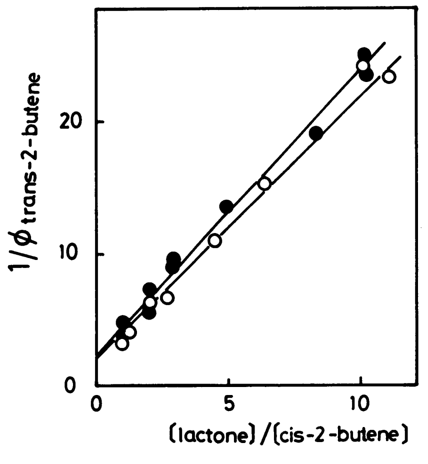
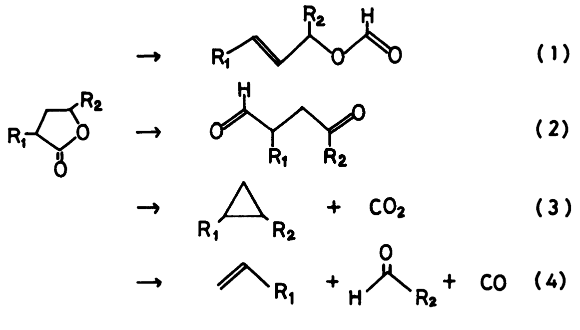


Fig. 2. Plots of the reciplocal of the quantum yield of *trans*-2-butene against the lactone/*cis*-2-butene pressure ratio for VL (●) and ML (○).

quantum yields of the decomposition products decreased as the quantum yield of *trans*-2-butene formation increased. From the slopes of the reciprocal plots of the quantum yield of *trans*-2-butene *vs.* the lactone/*cis*-2-butene ratio (Fig. 2), the quenching efficiencies of VL and ML relative to that of *cis*-2-butene were estimated to be 1.00±0.10 and 1.10±0.10. These values are close to that of BL (0.92±0.10).[2]

Discussion

Simonaitis and Pitts[4] investigated the photolysis of BL, VL, and ML in the liquid phase. They proposed primary processes (1)-(4) to explain major products.



As they pointed out, process (4) is minor regarding liquid-phase photolysis and is important for the vapor-phase photolysis of BL.[1] In the cadmium-photosensitized reactions of BL, VL, and ML, however, products considered to arise from process (4) alone were observed. This suggests the possibility that the cadmium-photosensitized reaction occurs through a different state from those for the direct photolysis.

In the photolysis of *trans*-2,3-dimethylcyclopentanone, Frey and Lister[5] obtained ethylene and butene as well as 1,2-dimethylcyclobutane as products. They pointed out that C_2+C_4 hydrocarbons and 1,2-dimethylcyclobutane are formed by independent pathways and that the former are not formed from a "hot" 1,2-dimethylcyclobutane molecule because (in the latter case) propylene must also be formed. The photolysis of cyclopentanone-2,2,5,5-d_4 gave evidence for the same conclusion.[6] In the present cases, however, ethylene and propylene were observed. Propylene (for VL) and ethylene (for ML) can not be directly formed from the biradicals produced by the elimination of carbon monoxide from VL and ML. This indicates that these products must be formed from "hot" oxetane molecules.

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

$$\mathrm{Cd}(^1S_0) + h\nu(326.1\ \mathrm{nm}) \rightarrow \mathrm{Cd}^*(^3P_1) \qquad I_a \qquad (5)$$

$$\mathrm{Cd}^* \rightarrow \mathrm{Cd} + h\nu(326.1\ \mathrm{nm}) \qquad k_1 \qquad (6)$$

$$\mathrm{Cd^* + L \rightarrow CdL^*} \qquad k_1 \qquad (7)$$

$$\mathrm{CdL^* + L \rightarrow Cd + 2L} \qquad k_2 \qquad (8)$$

$$\left.\begin{array}{l}\mathrm{CdL^* \rightarrow \alpha(CO + R_1\underset{\cdot}{C}HCH_2CHR_2\underset{\cdot}{O}\text{-}Cd)} \quad (9)\\ \qquad \rightarrow (1-\alpha)\ \text{other processes} \quad (10)\end{array}\right\} k_3$$

$$\mathrm{R_1\underset{\cdot}{C}HCH_2CHR_2\underset{\cdot}{O}\text{-}Cd}$$

$$\rightarrow \mathrm{R_1\underline{CHCH_2CHR_2O}^* + Cd} \qquad k_4 \qquad (11)$$

$$\left.\begin{array}{l}\rightarrow \gamma(\mathrm{R_1CH{=}CH_2 + R_2CH{=}O + Cd}) \quad (12)\\ \rightarrow (1-\gamma)\text{other processes} \quad (13)\end{array}\right\} k_5$$

$$\mathrm{R_1\underline{CHCH_2CHR_2O}^* \rightarrow R_1CH{=}CH_2 + R_2CH{=}O} \qquad k_6 \qquad (14)$$

$$\rightarrow \mathrm{R_1CH{=}O + R_2CH{=}CH_2} \qquad k_7 \qquad (15)$$

$$\mathrm{R_1\underline{CHCH_2CHR_2O}^* + L}$$

$$\left.\begin{array}{l}\rightarrow \mathrm{R_1\underline{CHCH_2CHR_2O} + L} \quad (16)\\ \rightarrow \text{other processes} \quad (17)\end{array}\right\} k_8$$

$$\mathrm{VL;\ R_1{=}H,\ R_2{=}CH_3}$$

$$\mathrm{ML;\ R_1{=}CH_3,\ R_2{=}H}$$

Here, CdL* stands for a transient complex between the excited cadmium atom and a lactone molecule. As mentioned previously,[2)] since the triplet state of BL lies at about 439 kJ/mol above the ground state, it can not be formed by a reaction of Cd($^3P_1$), which has an energy of only 367 kJ/mol. Therefore, we proposed that the complex is formed in the cadmium-photosensitized reaction of BL in order to explain the difference between the mercury- and cadmium-photosensitized reactions. This complex was also assumed for the present cases because the triplet energies of VL and ML are also probably larger than the excitation energy of excited cadmium atom. The formation of an O–Cd bond in Reaction (5) was assumed since the excitation energy of Cd($^3P_1$) alone is not sufficient to produce biradical $R_1\underset{\cdot}{C}HCH_2CHR_2\underset{\cdot}{O}$, as has been shown in a previous paper.[2)]

In a pure lactone system, a few minor products other than those previously mentioned were observed (some of them are the same as those observed during thermal decomposition). From their retention times, these minor products seem to be C_4- or higher compounds. Since their gas-chromatogram peaks were very small and overlapped in a complex way, we could not make assignments. In the presence of a large nitrogen pressure, a considerable amount of 2-methyloxetane was obtained (as previously mentioned). In this case, most of the peaks for minor products diminished. These findings indicate that in the presence of a large nitrogen pressure, intermediates seem to be stabilized by collisions with nitrogen molecules and give 2-methyloxetane, while in the pure lactones, most of the intermediates must react with lactone and yield other products (Reaction 17).

From the above mechanism, the following relations can be derived:

$$\frac{1}{\phi_{\mathrm{CO}}} = \frac{1}{\alpha} + \frac{1}{\alpha}\frac{k_2}{k_3}[\mathrm{L}] \qquad (18)$$

$$\frac{\phi_{\mathrm{CO}}}{\phi_{\mathrm{R_2CH=CH_2}}} = \left(1+\frac{k_5}{k_4}\right)\left(1+\frac{k_6}{k_7}\right) + \left(1+\frac{k_5}{k_4}\right)\frac{k_8}{k_7}[\mathrm{L}] \qquad (19)$$

From plots of $1/\phi_{\mathrm{CO}}$ *vs.* lactone pressure (Fig. 3), values of α and k_2/k_3 were obtained for VL and ML. These values are listed in Table 1, together with those for BL. The values of α for VL and ML are similar to that for BL, while the value of k_2/k_3 for VL is somewhat larger than those for ML and BL. This seems to show that the VL complex is a little less stable than those of ML and BL due to a steric hindrance of the methyl group at the γ-position, and more easily decomposes to a cadmium atom and a lactone molecule by collision with lactone molecules.

The quantum yields of carbon monoxide (extrapolated to zero pressure) were 0.31 and 0.37 for VL and ML. These small values suggest that most of the excited lactone that was formed underwent other reaction (Reaction 10). The amount of products volatile at 190 K (other than carbon monoxide, ethylene, propylene, acetaldehyde, and 2-methyloxetane) were negligibly small (see above). Therefore, isomerization to 4-oxopentanal, 2-methylsuccinaldehyde and other substances which were observed in

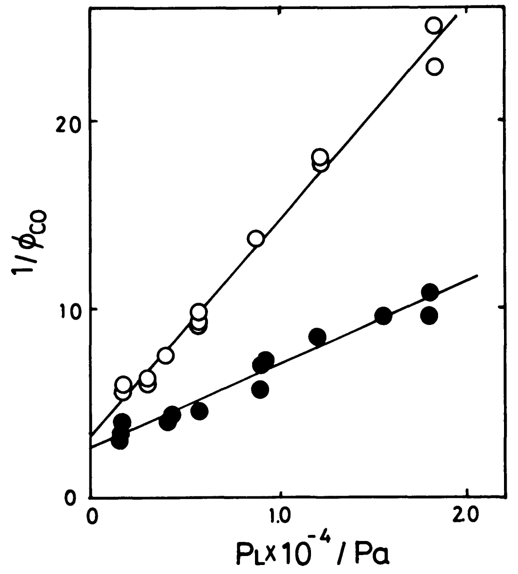


Fig. 3. Plots of $1/\phi_{\mathrm{CO}}$ against lactone pressure for VL (○) and ML (●).

TABLE 1. CONSTANT AND RATIO OF RATE CONSTANTS INVOLVED IN Eq. 18

	BL[1)]	VL	ML
α	0.27±0.02	0.31±0.02	0.37±0.02
$10^{-4}\,k_2/k_3$ Pa^{-1}	1.1±0.1	3.6±0.3	1.6±0.1

1) Calculated from the data shown in Ref. 2.

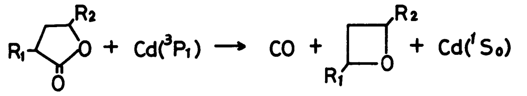
the photolysis of VL and ML in the liquid phase,[4] and the process in which excited lactones lose their energy without forming any products seem to be important (Reaction 10). The ratios of the other reaction (α) are almost equal for three lactones.

It was shown that in the thermal decomposition of 2-methyloxetane, both ethylene and propylene are obtained and the ratio of propylene/ethylene (1.31) is independent of temperature.[7] In our cases, $R_2CH=CH_2$ and a part of $R_1CH=CH_2$ are possibly formed from a "hot" oxetane as shown in Reactions (14) and (15). If so, the ratio of k_6/k_7 can be set at 1/1.31 for VL and 1.31 for ML. Plots of $\phi_{CO}/\phi_{R_1CH=CH_2}$ *vs.* lactone pressure are presented in Fig. 4. From the intercepts and the slopes of the straight lines, the values of k_5/k_4 and k_8/k_7 were obtained using k_6/k_7 (mentioned above). $k_8/(k_6+k_7)$ can be also calculated from the intercepts and the slopes. These values are listed in Table 2. k_5/k_4 for VL is similar to that for ML and $k_8/(k_6+k_7)$ for VL is considerably larger than for ML. The experimental values of $k_8/(k_6+k_7)$ give $k_d=k_6+k_7$ as $(5.9\pm1.6)\times10^8\,s^{-1}$ for VL and $(3.2\pm1.3)\times10^9\,s^{-1}$ for ML by adopting $8.0\times10^4\,s^{-1}$ as the kinetic collision frequency at 1 Pa and 300 °C and by assuming a collision-deactivation efficiency of unity for lactone.

The excess energy of energized 2-methyloxetane can be estimated using

$$k_d(E) = A\left(1-\frac{E_a}{E}\right)^{s-1} \tag{20}$$

Here, $k_d(E)$ is the rate constant regarding decomposition when the excess energy is E, A is the frequency factor, E_a is the critical energy, and s is the number of effective oscillators in the molecule. Using experimental values of k_d and substituting $A=10^{14.89}\,s^{-1}$ and $E_a=249.8$ kJ/mol (taken from the experiment of Hammond and Holbrook[7]) and $s=16$ (about half of the number of the modes of vibration), the values of E were found to be (410±5) kJ/mol for VL and (444±10) kJ/mol for ML. These excess energies are much larger than the enthalpy changes for the following reaction which are estimated to be 173 and 180 kJ/mol for VL and ML according to thermochemical data given by Benson.[8]



(21)

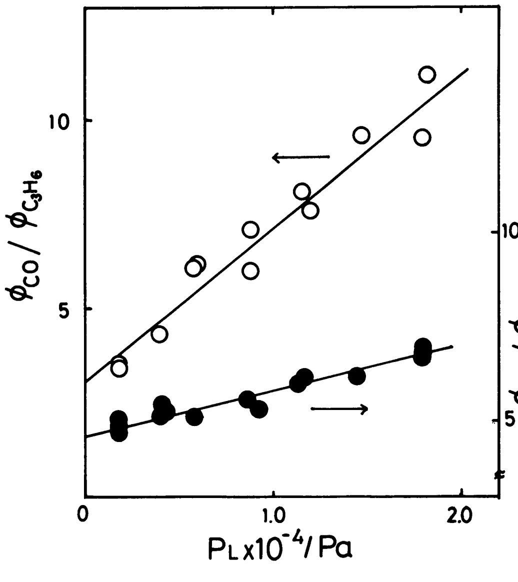
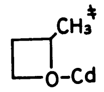


Fig. 4. Plots of $\phi_{CO}/\phi_{C_3H_6}$ (○) for VL and $\phi_{CO}/\phi_{C_2H_4}$ (●) for against lactone pressure.

TABLE 2. RATIOS OF RATE CONSTANTS INVOLUVED IN Eq. 19

	VL	ML
k_5/k_4	0.73±0.15	1.0±0.1
$10^4\,k_8/k_7$ Pa^{-1}	2.40±0.30	0.58±0.10
$10^4\,k_8/(k_6+K_7)$ Pa^{-1}	1.36±0.30	0.25±0.10

The estimation of the excess energy is also dependent on the collision-deactivation efficiency and the value of s. For example, an efficiency of 1/10, which is an unlikely small efficiency for lactone, results in a decrease of excess energy by about 34 kJ/mol. If a value of $s=14$ is adopted, the value of E is found to be 377 kJ/mol for VL. Even in these cases, the excess energy is still much larger than the enthalpy change shown above. Thus, the possibility that the dissociating intermediate is an energized 2-methyloxetane must be eliminated. As has been described in a previous paper,[2] the formation of an O–Cd bond must play an important role in the cadmium-photosensitized reaction of lactone. In order to explain the large rate constant regarding the decomposition of intermediates, we proposed the following intermediate as another possibility:



The excess energy of the above intermediate must be larger than that estimated thermochemically for an energized oxetane because of the additional energy of the O–Cd bond. If this is the case, the "hot" oxetane in the above mechanism should be replaced by this intermediate. It is notable that Eq. 19 holds regarding this case. Unfortunately, since it is difficult to estimate the excess energy of the above intermediate, no quantitative conclusions can be drawn about the thermochemistry.

From the above mechanism, the following relation can be derived:

$$\frac{\phi_{R_1CH=CH_2}}{\phi_{R_2CH=CH_2}} = \frac{k_5}{k_4}\left(\frac{k_6+k_7}{k_7}\right) + \frac{k_6}{k_7} + \frac{k_5k_8}{k_4k_7}[L] \tag{22}$$

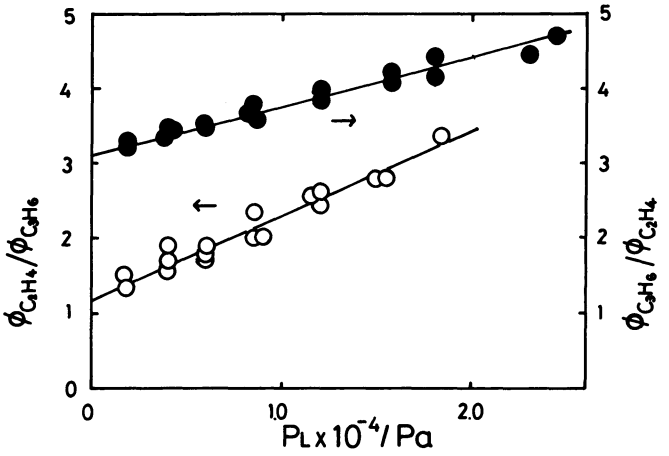


Fig. 5. Plots of $\phi_{C_2H_4}/\phi_{C_3H_6}$ (○) for VL and $\phi_{C_3H_6}/\phi_{C_2H_4}$ (●) for ML against lactone pressure.

From the intercepts and the slopes of the lines shown in Fig. 5, $k_8/(k_6+k_7)$ can be obtained using the following equation:

$$\frac{k_8}{k_6+k_7}=\frac{\text{slope}}{\text{intercept}-k_6/k_7} \tag{23}$$

The values for VL and ML obtained by using 1/1.31 and 1.31 for k_6/k_7 are $(1.79\pm0.30)\times10^{-1}$ and $(0.35\pm0.10)\times10^{-4}$ Pa^{-1}, respectively. These values are in fair agreement with those obtained from Fig. 4 (Table 2). The small discrepancy may be due to the use of these k_6/k_7 values for oxetane instead of those for the above intermediate.

In conclusion, the present results give further evidence for the formation of an O–Cd bond and the presence of an excited complex between the excited cadmium atom and the lactone molecule (discussed in a previous paper[2]).

References

1) R. Simonaitis and J. N. Pitts, Jr., *J. Phys. Chem.*, **75**, 2733 (1971).

2) S. Yamamoto, S. Matsuda, C. Ozaki, H. Takahoso, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **57**, 3408 (1984).

3) S. Tsunashima and S. Sato, *Bull. Chem. Soc. Jpn.*, **41**, 284 (1968).

4) R. Simonaitis and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **91**, 108 (1969).

5) H. M. Frey and D. H. Lister, *J. Chem. Soc.* (A), **1970**, 627.

6) R. Srinivasan, *Adv. Photochem.*, **1**, 83 (1963).

7) P. Hammonds and K. A. Holbrook, *J. Chem. Soc., Faraday Trans. 1*, **78**, 2195 (1982).

8) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," NSRDS-NBS, 21 U.S. 1970.