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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 studied. The gaseous products obtained in the mercury-photosensitized reaction were carbon dioxide, cyclopropane, and propylene. On the other hand, the products obtained in the cadmium-photosensitized reaction were carbon monoxide and ethylene.

Cadmium-photosensitized reaction has often been compared with mercury-photosensitized reaction 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 cadmium-sensitized reactions of γ-butyrolactone and found quite different products in these reactions. This seems to be very interesting.

The mercury-sensitized reaction was studied at 125 °C in a cylindrical quartz cell, 10 cm in diameter and 10 cm long, fitted with plane quartz windows. A spiral mercury discharge lamp filled with 670 Pa Ar was used. Absorbed light intensity at 253.7 nm was determined by ethylene actinometry.[1] The cadmium-sensitized 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.[2] Butyrolactone (E.P. grade) was purified by trap-to-trap distillation. Liquid butyrolactone was injected into the cell by a microsyringe because of its low vapor pressure and was fully degassed. Gases noncondensable at 77 K were collected by a Toepler pump. Condensable products were collected through a trap held at −60

°C, which retained most of lactone, and analysed by gas chromatography, using a 5 m column of VZ-7 (Gasukuro Kogyo Co., LTD) at 0 °C.

Mercury-photosensitized reaction

Mercury-photosensitized reaction of γ-butyrolactone has been reported before only briefly by Simonaitis and Pitts, Jr.[3] and Krull and Arnold.[4] Both of them observed carbon dioxide, cyclopropane, and propylene as main products. Gaseous products observed by us were also carbon dioxide, cyclopropane, and propylene. These products are the same as those which originate from the triplet manifold of lactone in the direct photolysis.[3] This is reasonable, because sensitization by $Hg(^3P_1)$ is expected to give triplet lactone due to spin conservation. Quantum yields of these products are shown in Fig. 1 as a function of lactone pressure. Fig. 1 shows that the quantum yield of carbon dioxide does not change with lactone pressure. On the other hand, the quantum yield of cyclopropane increases, while that of propylene decreases with increasing lactone pressure. The time dependence of these quantum yields pointed out by Simonaitis and Pitts, Jr. was not observed in this study.

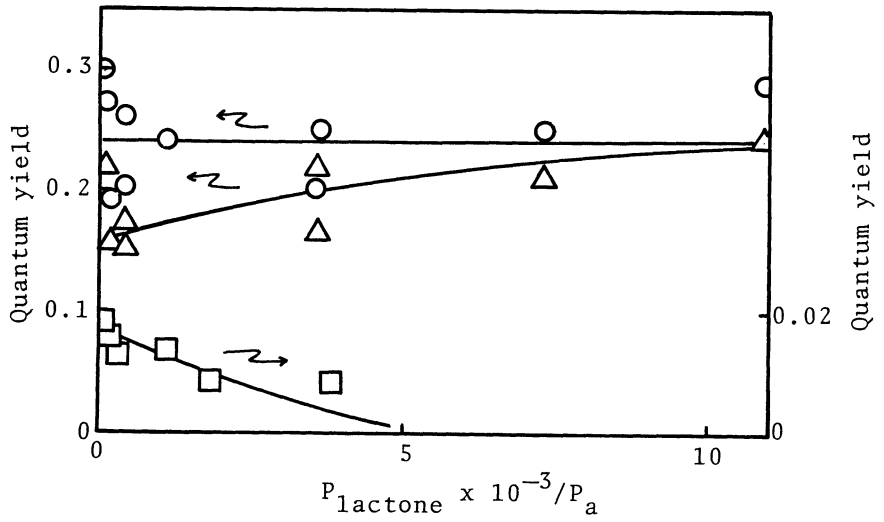

Fig. 1. Pressure dependence of quantum yields of CO_2(○), cyclopropane(△), and propylene(□).

The following set of reactions is proposed to explain the above findings.

$$Hg + h\nu(253.7\ nm) \longrightarrow Hg(^3P_1) \quad (1)$$

$$Hg(^3P_1) + L \longrightarrow Hg + L^3 \quad (2)$$

$$L^3 \longrightarrow CO_2 + C_3H_6^* \quad (3)$$

$$L^3 \longrightarrow \text{other reactions} \quad (4)$$

$$C_3H_6^* \longrightarrow CH_3CH{=}CH_2 \quad (5)$$

$$C_3H_6^* + L \longrightarrow \text{cyclo-}C_3H_6 + L \quad (6)$$

Here, L^3 denotes triplet lactone and $C_3H_6^*$ is a "hot" cyclopropane intermediate.

From this mechanism the quantum yields of products can be given by

$$\phi_{CO_2} = k_3/(k_3 + k_4) \quad (7)$$

$$\phi_{CH_3CH=CH_2} = (k_3/(k_3 + k_4))(k_5/(k_5 + k_6[L])) \quad (8)$$

$$\phi_{cyclo\text{-}C_3H_6} = (k_3/(k_3 + k_4))(k_6[L]/(k_5 + k_6[L])) \quad (9)$$

These equations explain well the pressure dependences of quantum yields mentioned above.

Reaction, L $\longrightarrow$ cyclo-C_3H_6 + CO_2, is endothermic by about 29 kJ/mol.[3] Since the excitation energy of $Hg(^3P_1)$ is 469 kJ/mol, the energy to be distributed among the products can be greater than about 440 kJ/mol. This value is almost the same as that estimated for the average energy transferred to the cyclobutanone molecule from the $Hg(^3P_1)$ atom.[5] Photosensitized reaction of cyclobutanone has been reported to yield vibrational excited cyclopropane and carbon monoxide, and the former was known to isomerize to propylene. In this case the propylene/cyclopropane ratio of 0.58 at about 1330 Pa was obtained. As is shown in Fig. 1, however, propylene was produced only about one-fifteenth of cyclopropane at same pressure. Although the reason of this discrepancy is not fully understood, it is tentatively proposed that if triplet carbone dioxide (the triplet state energy of carbon dioxide is about 356 kJ/mol[6]) is formed in Reaction (3), the energy content of cyclopropane is greatly reduced, making the isomerisation impossible.

Cadmium-photosensitized reaction

Gaseous products were carbon monoxide and ethylene. These products are quite different from those for mercury-photosensitized decomposition. If the triplet state of lactone lies at about 439 kJ/mol above the ground state, as has been estimated by Simonaitis and Pitts, Jr.,[7] it can not be formed in the cadmium-photosensitized reaction (excitation energy of $Cd(^3P_1)$ is 367 kJ/mol). As was mentioned above, however, in the mercury-photosensitized reaction the triplet state of lactone must be formed. This is probably responsible for the difference in products between mercury- and cadmium-photosensitized reactions of lactone.

Quantum yields of products are shown in Fig. 2 as a function of lactone pressure. The value of ethylene decreases a little more rapidly than that of carbon monoxide with increasing the pressure.

The follwing set of reactions is proposed.

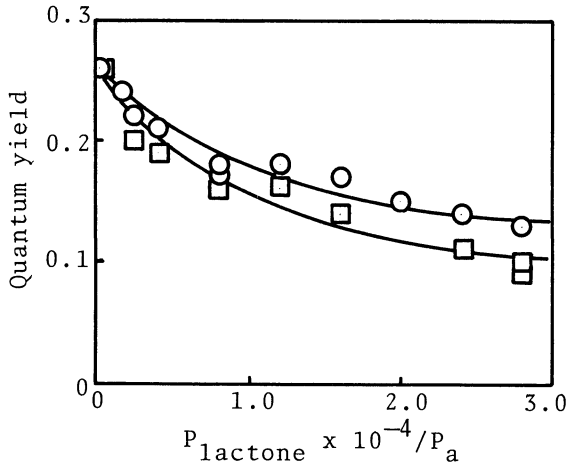

Fig.2. Pressure dependence of quantum yields of CO(○) and ethylene(□).

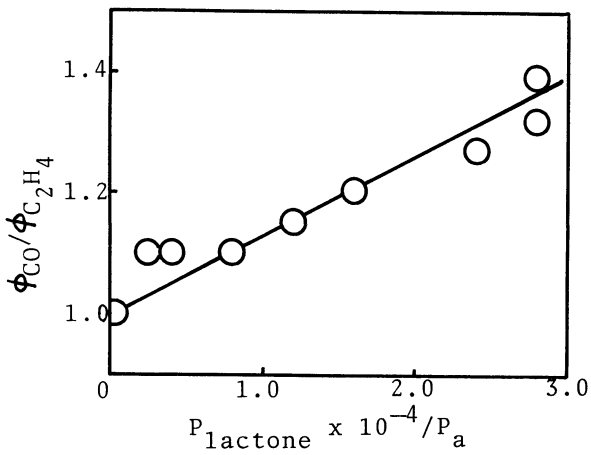

Fig. 3. $\phi_{CO}/\phi_{C_2H_4}$ vs. pressure of lactone

$$Cd + h\nu(326.1\ nm) \longrightarrow Cd(^3P_1) \quad (10)$$

$$Cd(^3P_1) + L \longrightarrow CdL^* \quad (11)$$

$$CdL^* \longrightarrow Cd + CO + \cdot CH_2CH_2CH_2O\cdot \quad (12)$$

$$CdL^* \longrightarrow \text{other reaction} \quad (13)$$

$$CdL^* + L \longrightarrow Cd + 2L \quad (14)$$

$$\cdot CH_2CH_2CH_2O\cdot \longrightarrow CH_2{=}CH_2 + CH_2O \quad (15)$$

$$\cdot CH_2CH_2CH_2O\cdot + L \longrightarrow \underbrace{CH_2CH_2CH_2O} + L \quad (16)$$

Here, CdL* stands for a transient complex between the excited cadmium atom and the lactone molecule. Such a complex was recognized between excited cadmium atom and saturated alcohols and ethers.[8)]

From this mechanism the following relation can be derived

$$\phi_{CO}/\phi_{C_2H_4} = 1 + k_{16}[L]/k_{15} \quad (17)$$

A plot of $\phi_{CO}/\phi_{C_2H_4}$ vs. lactone pressure is presented in Fig. 3. From the slope we get $k_{16}/k_{15} = 1.31 \times 10^{-5}\ P_a^{-1}$. The low collision efficiency implies a relative short lifetime of biradical.

References

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