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Mercury-Photosensitized Decomposition of *β*-Butyrolactone

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The mercury-photosensitized decomposition of *β*-butyrolactone has been investigated at temperatures between 353 and 393 K and pressures from 450 to 13600 Pa. The products were carbon dioxide, propylene, carbon monoxide, propylene oxide, acetone, and acetaldehyde. The yields of these products increased linearly with reaction time and light internsity, while they were independent of the lactone pressure. Three decomposition processes were proposed to explain the formation of the products. The decrease in the quantum yields of carbon dioxide, carbon monoxide, and acetaldehyde observed in the presence of *cis*-2-butene can be explained by the competitive quenching of the triplet mercury atom by the lactone and *cis*-2-butene (the quenching efficiency of lactone relative to that of *cis*-2-butene was estimated to be 0.61). The decrease in the quantum yields of carbon dioxide, propylene, and acetaldehyde by the addition of oxygen can again be explained only by the competitive quenching of the triplet mercury atoms by lactone and oxygen (k_Q(lactone)/k_Q(oxygen)=1.36). The quantum yields of propylene oxide and acetone, however, decrease more rapidly than predicted for competitive quenching. This indicates the existence of a reaction between oxygen and a biradical, which is a precursor of propylene oxide and acetone.

Recently, we have studied the mercury- and cadmium-photosensitized decompositions of *γ*-butyrolactone (*γ*-BL)[1] and *β*-propiolactone (PL)[2] and found the different kinetic behavior in the two photosensitized reactions. We have concluded that the mercury-photosensitized reaction proceeds through a lactone triplet state, while the cadmium-photosensitized reaction proceeds through an excited complex between an excited cadmium atom and a lactone molecule.

Recently, Frey and Watts[3,4] studied the thermal decomposition of *β*-butyrolactone (*β*-BL) and PL and pointed out that the introduction of a methyl group into the 4 position on the lactone ring accelerates the thermal decomposition rate, and that the rate acceleration can be attributed to the stabilization of a positive-charge center (by the methyl group) which develops on C_4 in the compex. We have investigated the mercury-photosensitized decomposition of *β*-BL in order to compare the results with those of the mercury-photosensitized reaction of PL and to test some of the mechanistic ideas developed for PL.

Experimental

The apparatus and techniques are similar to those used previously.[1,2]

An analysis of the products was performed using simple fractionation at 77 and 190 K, measurements with a gas burette, and gas chromatography. The light intensity absorbed by the mercury atoms at 253.7 nm was determined by *cis*-2-butene actinometry.

β-BL (Tokyo Kasei Ind., GR grade) was 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. The pressure of *β*-BL in the cell was calculated by the perfect-gas equation. *cis*-2-Butene (NihonTokushu Gasu K.K., pure grade), O_2 (Takachiho Shoji, pure grade) were used as supplied.

Results and Discussion

Since the vapor pressure of *β*-BL is low at room temperature, it is necessary to elevate the reaction temperature in order to obtain sufficient vapor pressure. The mercury-photosensitized reaction was studied at 353, 373, and 393 K. The thermal decomposition at these temperatures and the direct photolysis at 253.7 nm were found to be negligible.

The major products of the mercury-photosensitized decomposition of *β*-BL were carbon dioxide, propylene, carbon monoxide, propylene oxide, acetone, and acetaldehyde. Yields of these products increased linearly with reaction time and light intensity, showing that they are primary products.

The yields of the products are shown in Fig. 1 as a function of lactone pressure. As Fig. 1 shows, the yields of all products are independent of the lactone pressure. The relative product yields to that of carbon dioxide at 353, 373, and 393 K are shown in Table 1. The ratios of the product yields are independent of temperature. The quantum yields (Φ) of products

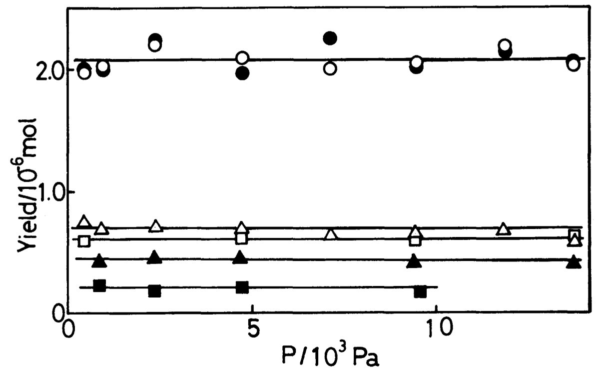


Fig. 1. Pressure dependence of product yields. CO_2 (○), propylene (●), acetaldehyde (□), CO (△), propylene oxide (▲), and acetone (■).

Table 1. Temperature Dependence of Yields of Products Relative to That of CO_2

T/K	C_3H_6	CH_3CHO	CO	C_3H_6O	$(CH_3)_2CO$
353	1.01	0.084	0.086	0.054	0.017
373	1.04	0.078	0.096	0.056	0.013
393	1.04	0.087	0.091	0.051	0.012

Table 2. Quantum Yields of Products in the Mercury-Photosensitized Decomposition of β-BL at 373 K

Products	CO_2	C_3H_6	CH_3CHO	CO	C_3H_6O	$(CH_3)_2CO$
	0.89±0.05	0.90±0.05	0.07±0.01	0.08±0.01	0.05±0.01	0.02±0.01

obtained at 373 K are listed in Table 2. The fact that the prodcut yields are independent of lactone pressure shows that the decomposition of β-BL may occur from the triplet state of the lactone. If the decomposition occurs from the vibrationally excited-electronic ground state which is produced by intersystem crossing, the product yields are expected to be largely pressure-dependent.

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

$$Hg(^1S_0) + h\nu(253.7\,\text{nm}) \rightarrow Hg(^3P_1) \quad (1)$$

$$Hg(^3P_1) \rightarrow Hg(^1S_0) + h\nu(253.7\,\text{nm}) \quad (2)$$

$$Hg(^3P_1) + L \rightarrow Hg(^1S_0) + {}^3L \quad (3)$$

$$^3L \rightarrow CO_2 + CH_3CH{=}CH_2 \quad (4)$$

$$^3L \rightarrow CO + \alpha CH_3\underline{CHCH_2O} + (1-\alpha)CH_3COCH_3 \quad (5)$$

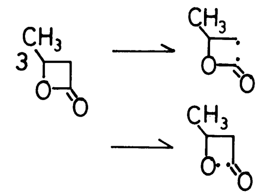
$$^3L \rightarrow CH_3CHO + CH_2CO \quad (6)$$

Here, ^3L denotes a triplet lactone.

As Table 2 shows, $\Phi(CO_2)+\Phi(CO)+\Phi(CH_3CHO)=1.05\pm0.05$. This shows that the decomposition from the excited triplet state leads to processes (4), (5), and (6).

Recently, Frey and Watts[3,4] investigated the thermal unimolecular decompositions of β-BL and PL and found relatively small energies of activation (163.4 and 180.5 kJ mol^{-1}). They pointed out that a biradical mechanism can be ruled out and a concerted pathway must be involved. Unlike the thermal decomposition, excitation in the mercury-photosensitized reaction undoubtedly provides sufficient energy to produce biradicals, which could then decompose.

If β-BL undergoes Norrish type I cleavage which is common in carbonyl compounds, the following biradicals are formed:

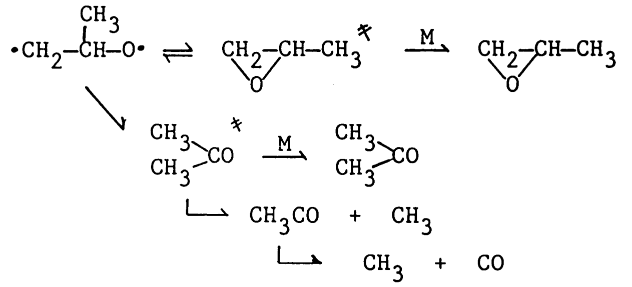


(7)

(8)

Reaction (7) is followed by elimination of carbon dioxide by breakage of the C_4–O bond and produces propylene. The biradical produced by Reaction (8) can either produce carbon monoxide and a biradical, $\cdot CH_2CH(CH_3)O\cdot$, by breakage of the O=C–C_3 bond or produce acetaldehyde and ketene by breakage of the C_3–C_4 bond.

The biradical, $\cdot CH_2CH(CH_3)O\cdot$, can either close to form propylene oxide or isomerize by hydrogen transfer to acetone, as shown by the following scheme:

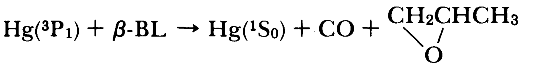


Scheme 1.

From the large exothermicity of the reactions, β-BL+$Hg(^3P_1)$→CO+propylene oxide+$Hg(^1S_1)$ and β-BL+$Hg(^2P_1)$→CO+acetone+$Hg(^1S_0)$, propylene oxide and acetone will be formed with large excess energy and may dissociate to CO and CH_3 radicals.

As described previously,[2] for the mercury-photosensitized reaction of PL yields of ethylene oxide and acetaldehyde, which are correspond to propylene oxide and acetone in the present case, show pressure dependence at lower pressures. From the pressure dependence of yields of ethylene oxide and acetaldehyde, we have estimated the excess energy of energized ethylene oxide and obtained the value of 272 kJ mol^{-1} which corresponds to about 78% of the enthalpy change for the reaction, PL+$Hg(^3P)$→ethylene oxide+CO+$Hg(^1S_0)$.

Here, we assume that almost the same fraction (75—80%) of the enthalpy changes of the following reactions are partitioned to propylene oxide and acetone:



$$\mathrm{Hg(^3P_1)} + \beta\text{-BL} \rightarrow \mathrm{Hg(^1S_0)} + \mathrm{CO} + \mathrm{CH_2CHCH_3}\text{ (}\diagdown\text{O}\diagup\text{)} \qquad (9)$$

$$\mathrm{Hg(^3P_1)} + \beta\text{-BL} \rightarrow \mathrm{Hg(^1S_0)} + \mathrm{CO} + \mathrm{(CH_3)_2CO} \qquad (10)$$

The excess energies of hot propylene oxide and acetone are 267—285 and 360—384 kJ mol^{-1} respectively.

The rate constant, $k(E)$ for the decomposition of the hot molecules, when its energy is E, is calculated by the following equation:[5]

$$k(E) = A\left(1 - \frac{E_a}{E}\right)^{s-1} \qquad (11)$$

where A is the frequency factor, E_a is the critical energy, and s is the number of effective oscillators in the molecules. Using the experimental values, A=3.7×10^{12} s^{-1} and E_a=217 kJ mol^{-1} for propylene oxide (taken from the experiment of Hardwick[6]) and A=1.83×10^{16} s^{-1} and E_a=339 kJ mol^{-1} for acetone (the values recomended by Benson and O'Neal[7]) and s=11 (half of the number of the modes of vibration) and substituting E=267—285 kJ mol^{-1} for propylene oxide and E=360—384 kJ mol^{-1} for acetone, the values of $k(E)$ were found to be 3.67×10^{4}—5.28×10^{5} s^{-1} and 4.87×10^{2}—1.05×10^{6} s^{-1}. These values are smaller than the value of the collision frequency (ω) even at 450 Pa which is the lowest pressure we examined and much smaller than those at higher pressures (ω=3.6×10^{7} s^{-1} at 450 Pa and 1.1×10^{9} s^{-1} at 13600 Pa are obtained when 8.0×10^{4} s^{-1} is adopted as the kinetic collision frequency at 1 Pa and 373 K). This explains why the yields of propylene oxide and acetone are independent of the lactone pressure.

The relative rate of Reactions (7) and (8) (R_7/R_8) is estimated by the ratio of the yield of carbon dioxide to the sum of those of carbon monoxide and acetaldehyde. Table 3 shows the comparison of R_7/R_8 in the mercury-photosensitized decomposition of PL, β-BL, and γ-BL, together with the difference in the bond dissociation energies of OC–C and OC–O bonds in lactones. These were estimated from the thermochemical data of Benson.[7] As Table 3 shows, the value of R_7/R_8 decreases in this order, PL β-BL γ-BL, and this order agrees with the order of the increase in ΔE-value.

Table 3. Ratios of Products and Primary Processes in the Mercury-Photosensitized Decomposition

Compound	CO / CO$_2$	$R_7$$^{a)}$ / R_8	$\Delta E$$^{b)}$ / kJ mol^{-1}
PL$^{c)}$	0.40	0.40	46.4
β-BL	0.09	0.17	54.8
γ-BL$^{d)}$	0	0	92.0

a) Relative rates of Reactions (7) and (8) (Reactions corresponding to Reactions (7) and (8) for PL and γ-BL). b) Difference in the bond dissociation energies of OC–C and OC–O bonds in lactones. c) Ref. 2. d) Ref. 1.

This shows that the ease of cleavage of α-bonds in triplet lactones seems to be determined by the bond strength. This tendency must be greater in the ground state, since carbon monoxide is not produced in the thermal decomposition of PL and β-BL.[3,4]

When *cis*-2-butene was added to β-BL, the quantum yield of the products from β-BL decreased and that of *trans*-2-butene formation increased with the increase in the *cis*-2-butene/β-BL ratio. From the slope of the reciprocal plot of the quantum yield of *trans*-2-butene vs. the β-BL/*cis*-2-butene ratio, the quenching efficiency of β-BL relative to that of *cis*-2-butene was estimated to be 0.61. This value is almost equal to that for PL(0.62).[2] Figure 2 shows the effect of *cis*-2-butene on the yields of carbon dioxide, carbon monoxide, and acetaldehyde. The solid line shows the value of Φ°/Φ (Φ° denotes the quantum yield in the absence of *cis*-2-butene) calculated using the relative quenching efficiency of β-BL obtained above. As Fig. 2 shows, the decrease in the quantum yields observed in the presence of *cis*-2-butene can be explained by the competitive quenching of the triplet mercury atom by the lactone and butene. This finding shows that the mode of formation of these products was not affected by the addition of *cis*-2-butene.

The addition of oxygen to the photosensitization

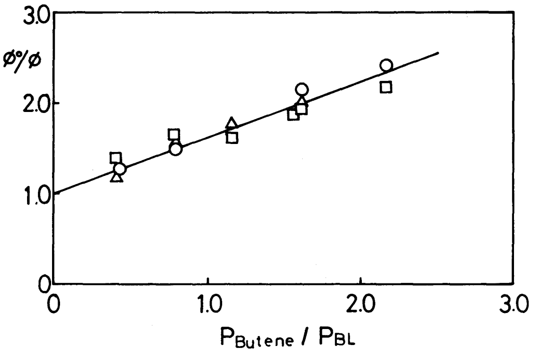


Fig. 2. Plots of Φ°/Φ for CO$_2$ (○), CO (△), and acetaldehyde (□) against the *cis*-2-butene/β-BL pressure ratio.

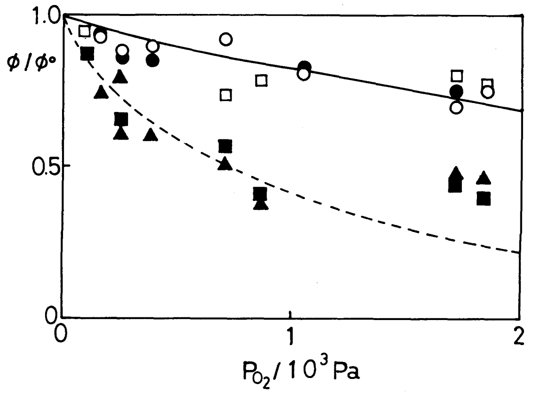


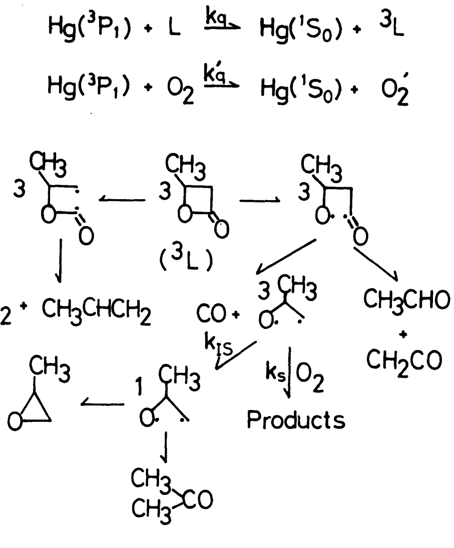
Fig. 3. Quantum yields of products in the presence of oxygen. CO$_2$ (○), propylene (●), acetaldehyde (□), propylene oxide (▲), and acetone (■).

system suppressed the formation of products. Figure 3 shows the effect of oxygen on the yields of products. As Fig. 3 shows, yields of all products decrease with increasing oxygen pressure. The solid line shows the relative quantum yields calculated using the following relative quenching efficiencies for β-BL and oxygen:

$k_Q(\beta\text{-BL})/k_Q(O_2)=1.36$ (obtained from $k_Q(\beta\text{-BL})/k_Q(cis\text{-2-butene})=0.61$ and $k_Q(O_2)/k_Q(cis\text{-2-butene})=0.45$[8])

The decrease in the quantum yields of carbon dioxide, propylene, and acetaldehyde can be explained by the competitive quenching of the triplet mercury atom by the lactone and oxygen. The decreases in the yields of propylene oxide and acetone, however, are steeper than those of other products. This shows that oxygen has additional effects on the formation of propylene oxide and acetone. As mentioned above, the biradical, $\cdot COCH_2(CH_3)O\cdot$, is a common intermediate for the formation of acetaldehyde and propylene oxide (and acetone). The difference in the effect of oxygen on the formation of acetaldehyde and that of propylene oxide and acetone shows that oxygen does not scavenge this biradical, but may scavenge another intermediate which locates between the biradical and propylene oxide and acetone (the final products).

The effect of oxygen on product yields can be discussed in terms of reactions schematically depicted in Scheme 2.



Scheme 2.

From this mechanism, the following equations can be derived:

$$\frac{\Phi_{CO_2}}{\Phi^{\circ}_{CO_2}}=\frac{\Phi_{CH_3CHCH_2}}{\Phi^{\circ}_{CH_3CHCH_2}}=\frac{\Phi_{CH_3CHO}}{\Phi^{\circ}_{CH_3CHO}}=\frac{k_q[L]}{k_q[L]+k_q'[O_2]} \tag{12}$$

$$\frac{\Phi_{CH_3\underline{CHCH_2O}}}{\Phi^{\circ}_{CH_3\underline{CHCH_2O}}}=\frac{\Phi_{(CH_3)_2CO}}{\Phi^{\circ}_{(CH_3)_2CO}}$$

$$=\frac{k_q[L]}{k_q[L]+k_q'[O_2]}\,\frac{k_{IS}}{k_{IS}+k_s[O_2]} \tag{13}$$

The relationship between $\Phi_{CO2}/\Phi^{\circ}_{CO_2}$, $\Phi_{CH_3CH=CH_2}/\Phi^{\circ}_{CH_3CH=CH_2}$, and $\Phi_{CH_3CHO}/\Phi^{\circ}_{CH_3CHO}$ vs. oxygen pressure has been already discussed above. The additional effect of oxygen on the yields of propylene oxide and acetone mentioned above is expressed by the term $k_{IS}/(k_{IS}+k_s[O_2])$. The ratio of the rate constants, k_s/k_{IS}, was evaluated by fitting Eq. 13 to the experimental measurements ($k_s/k_{IS}=7.5\times10^{-1}$ Pa). The dashed curve in Fig. 3 shows the calculated values of Φ/Φ° for propylene oxide and acetone. If k_s has a typical value of $1.0\times10^{13}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ similar to that suggested for the analogous reaction of alkyl monoradicals,[9] then k_{IS} can be calculated to be $3.2\times10^6\ \mathrm{s^{-1}}$. This value is in reasonable agreement with that proposed by Montague for intersystem crossing of alkyl biradicals ($3\times10^6<k_{IS}<4.5\times10^8\ \mathrm{s^{-1}}$).[10]

According to recent kinetic studies[11–14] of the reaction of ethylene with the ground-state oxygen atom($O(^3P)$), the reaction proceeds via two main channels: one yielding $CH_2=CHO\cdot+H$ (a) and the other, CH_3+HCO (b). The primary process is the addition of the oxygen atom to the C=C double bond to form a triplet biradical, $\cdot CH_2CH_2O\cdot$. Hunziker et al.[11] proposed a schematic potential energy diagram for the O+ethylene reaction and pointed out that the shift of a hydrogen atom in the triplet biradical to give triplet acetaldehyde requires a high activation energy. They also suggested that by collision it can be converted into an isoenergetic singlet biradical which would have low activation energy pathways available to give hot ground state oxide and aldehyde. Koda et al.,[15] however, pointed out that this mechanism cannot explain the pressure independence of the branching ratio over a wide range. They proposed a rapid collision-free intersystem crossing to interpret their experimental results. They assumed that the branching ratio of (b)/(a) is determined by the unimolecular dissociation rate of the triplet intermediate yielding $CH_2=CHO\cdot+H$ compared with the rate of the intersystem crossing to the singlet surface and can interpret the enhancement of the branching ratio by the deuterium substitution of ethylene.

The biradical produced in the mercury-photosensitized reaction of β-BL seems to be a triplet as shown above and to behave similarly to the triplet biradical formed in the oxygen–ethylene reaction and is converted into a singlet biradical by a collision-free intersystem crossing. The fate of the singlet biradical has already been discussed above.

References

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

2) S. Yamamoto, R. Gohda, R. Morikawa, H. Takahoso, Y. Sueishi, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, **59**, 2559 (1986).

3) H. M. Frey and H. P. Watts, *J. Chem. Soc., Faraday Trans. 1*, **79**, 1659 (1983).

4) H. M. Frey and I. M. Pidgeon, *J. Chem. Soc., Faraday Trans. 1*, **81**, 1087 (1985).

5) L. S. Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928).

6) T. J. Hardwick, *Can. J. Chem.*, **46**, 2454 (1968).

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

8) R. J. Cvetanovic, "Mercury Photosensitized Reactions," Progress in Reaction Kinetics, Vol. 2, ed. by G. Porter, The Macmillan Co., New York (1964), p. 39.

9) For example, R. P. Ruiz and K. D. Bayes, *J. Phys. Chem.*, **88**, 2592 (1984).

10) D. C. Montague, *J. Chem. Soc., Faraday Trans. 1*, **74**, 277 (1978).

11) H. E. Hunziker, H. Kneppe, and H. R. Wendt, *J. Photochem.*, **17**, 377 (1981).

12) J. F. Smalley, F. L. Nesbitt, and R. B. Klemm, *J. Phys. Chem.*, **90**, 491 (1986).

13) K. Mahmud, P. Marshall, and A. Fontijn, *J. Phys. Chem.*, **91**, 1568 (1987).

14) Y. Endo, S. Tsuchiya, C. Yamada, E. Hirota, and S. Koda, *J. Chem. Phys.*, **85**, 4446 (1986).

15) S. Koda, Y. Endo, E. Hirota, and S. Tsuchiya, *J. Chem. Phys.*, **91**, 5840 (1987).