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Thermal and Infrared Multiphoton Decompositions of γ-Butyrolactone in the Vapor Phase

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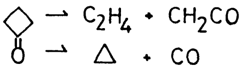
The thermal decomposition of γ-butyrolactone was studied in a static system at temperatures from 690 to 833 K and pressures from 70 to 4300 Pa. The major products were CO, CO_2, ethylene, propylene, and cyclopropane. The first-order rate constant for the apparently homogeneous formation of CO is described in terms of Arrhenius parameters $\log A$ (s^{-1})=16.44±0.04 and E_a=310.0±4.2 kJ mol^{-1}. Under the same conditions the ratio of CO_2/CO increased with decreasing temperature, corresponding to an activation energy of about 294 kJ mol^{-1} for CO_2 formation and a frequency factor of about 60-times lower than that for CO formation. The decomposition induced by a pulsed CO_2 laser was also studied; the same decomposition products were observed and the dependences of their yields on the fluence were examined.

Molecules which undergo simple unimolecular decomposition photochemically or thermally by two (or more) channels are of interest from several points of view. A comparison of the activation energies and frequency factors for different channels can sometimes determine whether or not these channels involve a common transition state or intermediate. Regarding photolysis, measurements of the ratios of the quantum yields for the different channels as a function of the wavelength, pressure, and added quenching gases can give information about the electronic and vibrational excitation of the dissociating molecules.

It has been well-established that there are two nonradical unimolecular reaction modes in the thermal and infrared multiphoton decompositions of cyclobutanone:[1-8)]



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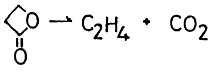
The thermal and infrared multiphoton decompositions of β-propiolactone (PL), however, were found to yield only ethylene and carbon dioxide in equal amounts:[9-11)]



(3)

This decomposition pathway is a concerted one which has a much smaller activation energy than the lowest-energy biradical pathway may have.[9,10)]

The thermal decomposition of γ-butyrolactone (γ-BL), which apparently has not been studied before, is interesting for a comparison with the thermal decompositions of PL[9,10)] and β-butyrolactone (β-BL)[12)] which have been quatitatively studied; it is also interesting for a comparison with the photolysis[13)] and mercury-photosensitized decomposition[14)] of γ-BL which have also been studied previously.

Experimental

γ-BL (Tokyo Kasei Ind., GR grade) was used after drying over calcium hydride and several trap-to-trap distilations.

The thermal decomposition was studied in a conventional static system using a cylindrical quartz vessel (about 4 cm in diameter, 20 cm long, with round ends, and about 100 cm^3 in volume) mounted in a tube furnace controlled to ±0.5 K. The gas-handling manifold, a Baratron pressure gauge, and a reagent storage trap were all enclosed in an air thermostat held at 393 K, which permitted operation at vapor pressures of up to 6000 Pa. The reaction was started by admitting lactone vapor to the hot reaction vessel and terminated by opening a valve leading through a cold trap (77 K) to a Toepler pump.

In order to obtain reproducible kinetic data it was necessary to age the quartz reaction vessel. Some small improvement resulted from attempts to age the vessel by repeated pyrolyses of 1-ethylcyclopentene and isobutene. However, a more successful aging procedure proved to be successive pyrolysis of the γ-BL to high-percentage decomposition. Frey and Watts also found a large surface effect in the thermal decomposition of β-BL,[12)] which could be eliminated by seasoning the vessel by repeated prolonged pyrolysis of the β-BL. To test for any surface effect, a similar vessel, packed with some 4 mm od quartz tubes, which increased the surface/volume ratio by a factor of 6.3, was used.

Infrafed laser experiments were carried out in a cylindrical Pyrex vessel (10 cm long and 4 cm in diameter) fitted with NaCl windows at each end. The light source used for IR photolysis was an Ushio CO_2 TEA laser. The output energy of a typical laser pulse ranged from 1.0 to 1.5 J and the pulse was operated at a repetition rate of 1 Hz. Since the CO_2 TEA laser was operated with He, CO_2, and N_2 as flowing gases, the pulse profile showed an initial spike of about 80-ns fwhm with a long tail of about 1-μs fwhm. The laser was tuned to the R(20) line of the 9.6-μm CO_2 band at 1078 cm^{-1}. Laser irradiation was performed in a tightly-focussed geometry, where the beam was focussed at the center of the cell by a BaF_2 lenes with a focal length of 25 cm after passing through a teflon iris with an 8-mm diameter. The beam area at the focus was estimated to be 0.0133 cm^2 from the beam divergence of 2.6 mrad. The laser fluence at the focus was calculated from the beam area and the laser energy. The fluence was extremely inhomogeneous along the beam within the cell. The fluence could be changed by inserting calibrated NaCl absorbers just before the lens. The cell and a reagent storage trap were enclosed in an air thermostat held at 325 K, at which temperature the sample pressure was 350 Pa.

Product analysis was carried out by measurements with a gas buret and gas chromatography after fractionation at 77 and 184 K. The first portion, noncondensable at 77 K, was collected using a Toepler pump. This portion comprised CO; its amount was measured with a gas buret. The second portion, which was not condensable at 184 K, was analyzed by means of gas chromatography using a 6-m column of VZ-7 (Gasukuro Kogyo Co., Ltd.) at 273 K and a 2-m column of Gasukuro-pack 55 (Gasukuro Kogyo Co., Ltd.) at 413 K. The third portion, which was condensable at 184 K, contained a large amount of γ-BL; it was not analyzed. Noncondensable products from the decomposition induced by a pulsed laser was analyzed by means of gas chromatography using a 5-m column of Molecular sieves 4A (Gasukuro Kogyo Co., Ltd.) at 373 K.

Results

Thermal Decomposition. The thermal decomposition was studied at temperatures of 690—833 K and pressure from 70 to 4300 Pa. The observed products were CO, CO_2, ethylene, propylene, and cyclopropane, whose productions were linear with time (Fig. 1). The only other minor product detected was propionaldehyde.

Figure 2 shows an Arrhenius plot of the first-order rate constant for the formation of CO. Since the rate constant did not depend on the pressure at between 2000 and 4300 Pa, all of the data shown in Fig. 2 were obtained within this range. At lower pressure the rate constant decreased substantially (Fig. 3). Similar pressure dependences were observed for other products. The production of CO showed some enhancement in the packed vessel, in which the surface/volume ratio was increased by a factor of 6.3 (Fig. 2). The surface reaction clearly makes a sizeable contribution at lower temperatures; a correction was made for this to the values of k_{CO} obtained in the unpacked cell, based on the usual assumption that the gas-phase and surface reactions were simply additive and that the latter was proportional to the surface area. The contribution for the surface reaction to the value of k_{CO} was nearly zero at 833 K and about 20% at 733 K. A larger contribution was obtained at lower temperatures. An Arrhenius plot of the corrected values of k_{CO} obtained at temperatures between 733 and 833 K gave $\log A$ (s^{-1})=16.44 ($\pm$0.04) and E_a=310.0 ($\pm$4.2) kJ mol^{-1}. A similar surface effect was observed for the formations of other products.

Figure 4 shows an Arrhenius plot of the products ratio (CO_2/CO) obtained after the correction for the surface reaction. The product ratio CO_2/CO (i.e., $k(CO_2)/$

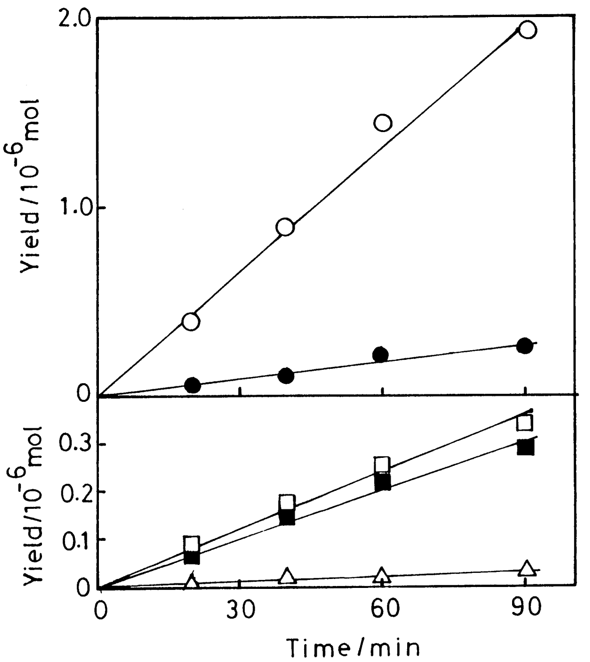


Fig. 1. Time dependence of the products in the thermal decomposition of γ-BL. ○: CO, ●: ethylene, □: CO_2, ■: propylene, △: cyclopropane.

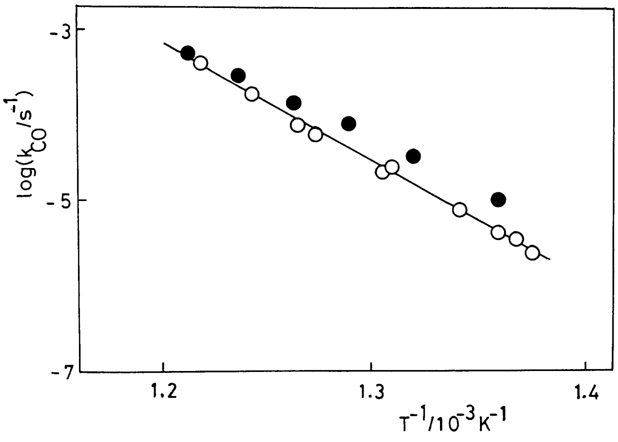


Fig. 2. Arrhenius plot for the first-order rate constant for the formation of CO in the thermal decomposition of γ-BL: ○: unpacked reaction vessel; ●: packed reaction vessel, S/V increased by factor of 6.3.

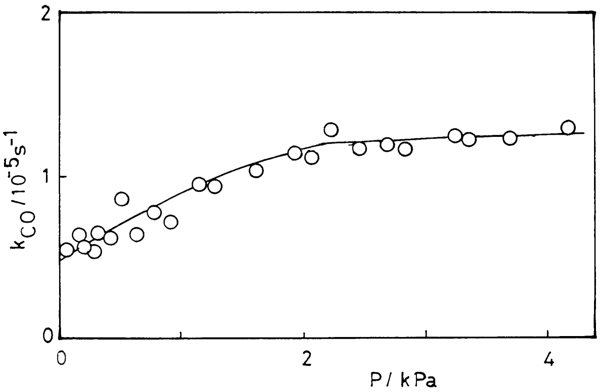


Fig. 3. Pressure dependence of the first-order rate constant for the formation of CO.

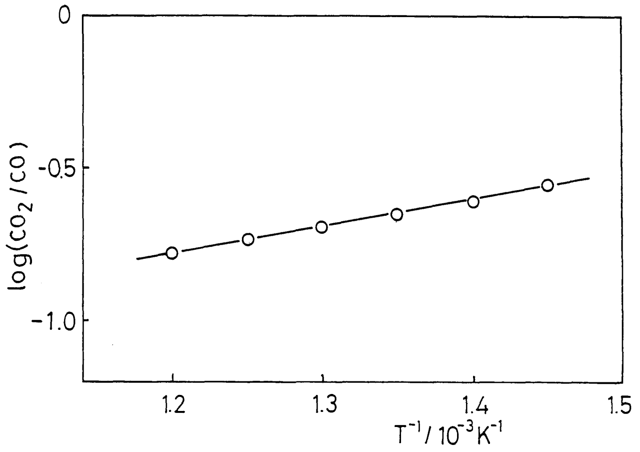


Fig. 4. Arrhenius plot of the product ration CO_2/CO from the thermal decomposition of γ-BL.

k(CO)) increased with decreasing temperature. The relative rate expression derived from these data is

$$\log k(CO_2)/k(CO) = 16000(\mathrm{J\ mol^{-1}})/2.303RT - \log 60; \quad (4)$$

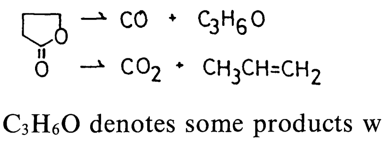
this results in an E_a of 294 kJ mol^{-1} and a log A (s^{-1}) of 14.66 for CO_2 formation.

Infrared Multiphoton Decomposition. The products were the same as those in the thermal decomposition. The yields per pulse were independent of the number of pulses for all of the products, indicating that these products were primary.

Figures 5 and 6 show the yields of the products (moles per pulse) as a function of the fluence (the fluence was measured at the focal point).

Discussion

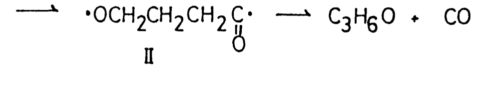
Thermal Decomposition. Since CO, CO_2, ethylene, and propylene were the main products, the production of CO and CO_2 can be mainly described by the following two parallel unimolecular reactions:



(5)

(6)

Here, C_3H_6O denotes some products which are formed with CO and partly decompose to give ethylene (see below). The following reactions including the intermediate biradicals (I and II) for the formation of CO can be advanced:



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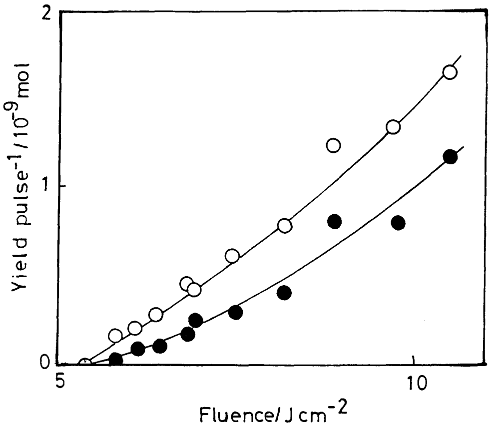


Fig. 5. Effect of the fluence on the yields per pulse of CO (○) and ethylene (●).

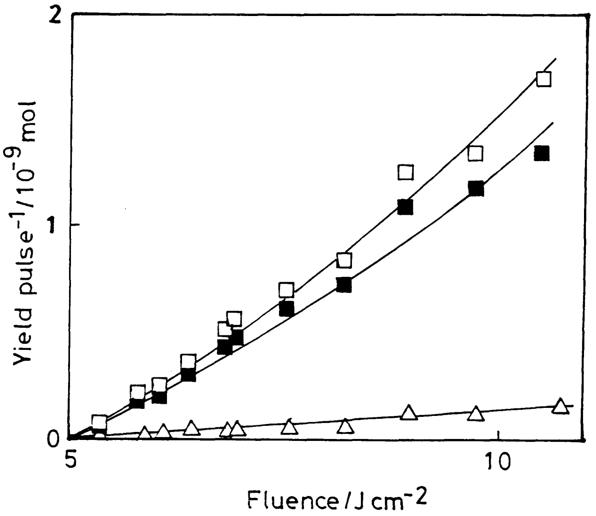


Fig. 6. Effect of the fluence on the yields per pulse of CO_2 (□), propylene (■), and cyclopropane (△).

The activation energies for the formations of biradicals I and II, estimated by the method of Benson,[15] are 309 and 360 kJ mol^{-1} (the activation energies of the back reactions of these reactions were neglected). The observed activation energy (310.0 kJ mol^{-1}) for the formation of CO agrees well with the estimated value for Reaction (7), showing that the formation of CO is a biradical pathway.

Although oxetane, propionaldehyde, allyl alcohol, cyclopropanol, and propylene oxide are possible products (C_3H_6O) with CO, only proprionaldehyde was detected. The thermal decomposition of oxetane was studied in detail and is known to produce ethylene.[16,17] The rate constant for the decomposition of oxetane is much larger than that of γ-BL in the temperature ranges of this study: (k(ox)/k(γ-BL)=270 at 750 K and 130 at 830 K; k(ox)[17] and k(γ-BL) are the rate constants for the decomposition of oxetane and γ-BL). This shows that even if oxetane was produced as a primary product of the decomposition of γ-BL, it must be decomposed

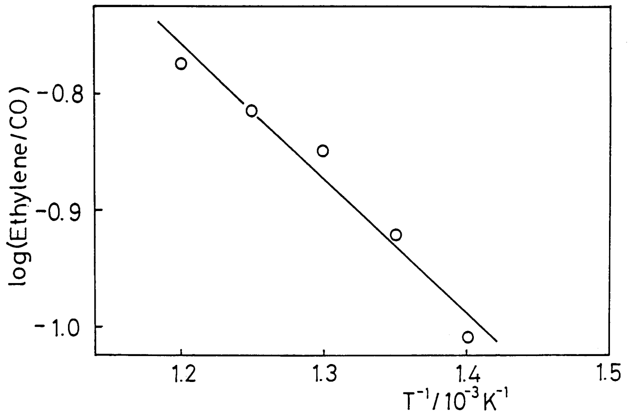
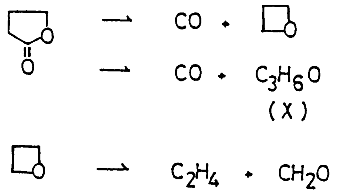


Fig. 7. Arrhenius plot of the product ratio ethylene/CO.

effectively to give ethylene. Since the rate for the decomposition of oxetane is very fast compared with that for γ-BL, ethylene behaves like a primary product in regard to the time dependence of its yield.

In order to explain the findings that the ratio of ethylene/CO was always smaller than unity and that the ratio increased with increasing temperature (Fig. 7), the following reactions are considered:



(9)

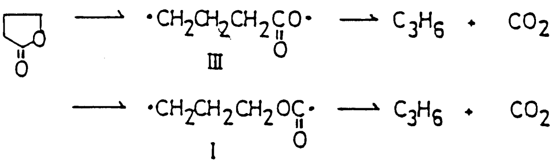
(10)

(11)

It is assumed that the product (X) does not decompose, or, if it dose, it does not give ethylene. The possible compounds for X are propionaldehyde, allyl alcohol, cyclopropanol, and propylene oxide. As mentioned above, although propionaldehyde was detected, its observed amount was very small (less than 10% of that of CO). Allyl alcohol and propylene oxide were not observed (cyclopropanol was not available, and its production could not be checked). Although the amount of X should be about 80% of that of CO, we could not specify X. It seems likely that X (or its precursor) was lost by polymerization or a reaction with γ-BL. Since oxetane decomposes completely, the ratio of k_9/k_{10} must increase with increasing temperature.

The formation of CO_2 is accompanied by either propylene or cyclopropane. Since the ratio of (propylene+cyclopropane)/CO_2 is always nearly equal to unity, there must be only two reactions for the formation of CO_2. Since the ratio of cyclopropane/propylene was found to increase with increasing temperature, the activation energy for the formation of cyclopropane is a little larger than that for the formation of propylene.

The observed activation energy for the formation of CO_2 (as well as propylene) is slightly smaller than the predicted activation energies for the decompositions of γ-BL via biradicals III and I (303 and 309 kJ mol^{-1}; the heat of formation of biradical III was estimated using the method of Benson[15] by including the resonance energy (20 kJ mol^{-1}) for biradical III and by neglecting the activation energies for the back reactions).



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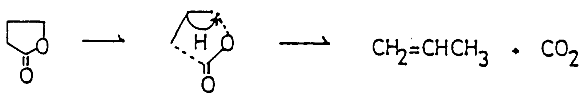
(13)

This shows that the pathway of the formation of CO_2 and propylene is not a pure biradical one, and the following concerted pathway which involves the 1,2-hydrogen transfer is postulated:



(14)

This concerted reaction can explain the results that propylene is a main product.

Simonatis and Pitts reported that the decomposition products from the direct phorolysis of γ-BL in the vapor phase were CO, CO_2, ethylene, propylene, and cyclopropane.[13] They pointed out that ethylene and CO originate from the singlet manifold and that the other products originate from the triplet manifold of γ-BL. The latter products were also observed in the mercury-photosensitized reaction of γ-BL.[13,14] Further, since the formation of CO and ethylene was pressure quenched, they concluded that these products arised from a vibrationally excited ground-state of the lactone. The decomposition from the vibrationally excited ground-state generally corresponds to the thermal decomposition. Only ethylene and CO, which are products from the process of the higher activation energy in the thermal decomposition, were observed as products from the vibrationally excited ground-state in direct photolysis. This probably reflects the higher energy content of the decomposing molecules in direct photolysis.

Infrared Multiphoton Decomposition. The products were the same as those in the thermal decomposition, with large ratios of CO_2/CO and ethylene/CO. As shown in Figs. 5 and 6, the production of all the products strongly depends on the fluence. Figures 8 and 9 show the variation with fluence of the ratios of CO/CO_2 and ethylene/CO. The results that the ratios of CO/CO_2 and ethylene/CO increase with increasing fluence are consistent with the fact that these ratios increase with increasing temperature in the thermal decomposition. The large value of ethylene/CO compared with that in the thermal decomposition shows that decomposition

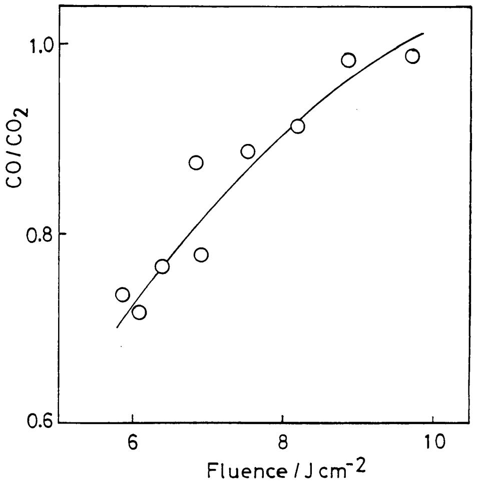


Fig. 8. Effect of the fluence on the product ratio CO/ CO$_2$.

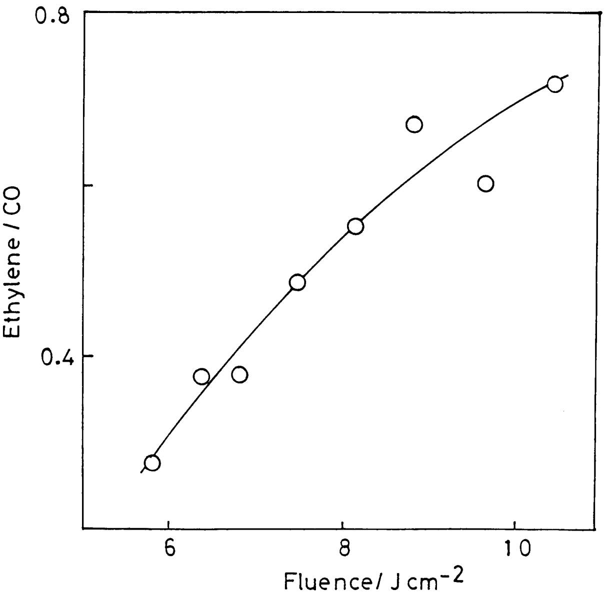


Fig. 9. Effect of the fluence on the product ratio ethylene/CO.

occurs with high energies in the infrared multiphoton decomposition. This is not consistent, however, with the large ratio of CO$_2$/CO, compared with that in the thermal decomposition. For the formation of CO, few molecules decomposed per pulse, but apparently did so with high energies; for the formation of CO$_2$, however, many more decomposed, but at much lower average energy. As mentioned above, laser irradiation was performed in a tightly-focussed geometry; the fluence was then extremely inhomogeneous along the beam. Since the decomposition probability depends strongly on the fluence, the reaction zone is difficult to determine for irradiation with an inhomogeneous fluence. A possible explanation for the above-mentioned findings is that the reaction which produces CO and ethylene occurred in a small region in which the fluence was very high, while the reaction producing CO$_2$ and propylene occurred in a larger and low-fluence region.

The large difference in the product ratios of CO$_2$/CO and ethylene/CO between the infrared multiphoton and thermal deconpositions can be brought about by surface reactions which occur in the latter. However, this is not the case, since almost the same values of CO$_2$/CO and ethylene/CO were obtained in both unpacked and packed cells at temperatures higher than 770 K, indicating that the influence of the surface reactions on the product ratios can be neglected at these temperatures.

There seems to be some posibilities why oxetane was not observed in the infrared multiphoton decomposition. As mentioned above, the yields of all the products per pulse were independent of the number of pulses, indicating that a secondary decomposition of oxetane does not occur. The decomposition of vibrationally excited oxetane formed in Reaction (9) is also ruled out, since the ratio ethylene/CO was independent of the lactone pressure from 190 to 490 Pa. The most plausible explanation is that biradical I or hot oxetane reacts with γ-BL effectively and does not give a detectable amount of oxetane. This is also possible in thermal decomposition.

The more complex behavior of γ-BL, compared with PL and β-BL, may reflect a less easy decarboxylation for γ-BL by concerted pathways. For PL and β-BL, the concerted decarboxylation has much smaller activation energies compared with biradical pathways, and only this concerted reaction occurs. For γ-BL, however, the activation energy for concerted decarboxylation is similar to that for the biradical pathway which produces CO; more than two channels were observed.

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