Gas Phase Pyrolysis of γ-Butyrolactone and γ-Thiobutyrolactone†

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In the gas phase the title lactone pyrolyses *via* decarboxylation, while the thiolactone pyrolyses *via* decarbonylation, as the major modes of decomposition.

Pyrolysis of esters commonly results in elimination to give an alkene and an acid, through a 1,5-hydrogen shift in a six-membered cyclic transition state.[1] Lactones of ring size larger than six atoms pyrolyse in a similar way at ~ 520 °C to yield an unsaturated acid.[2] In contrast, the relatively unstable four-membered ring β-lactones are known to readily undergo concerted stereospecific elimination of CO_2 at moderate temperatures (140–160 °C) to give an olefin.[3,4] In the case of lactones of intermediate ring size, the only reported attempt to pyrolyse the five-membered γ-butyrolactone and γ-valerolactone up to 590 °C was unsuccessful.[2] We now report the first complete pyrolysis of γ-butyrolactone (at 980 °C) and γ-thiobutyrolactone (at 800 °C) and find that not only are their major modes of decomposition different from each other, but their decomposition mechanisms differ from the larger lactones.

A flow system was used for pyrolysis and the products were detected by HeI photoelectron (PE) spectroscopy, with spectra recorded on a Leybold-Heraeus UPG-200 spectrometer. Pyrolysis of the gaseous compounds was carried out in a quartz tubing with the heating applied through a temperature controlled oven.[5] The sample pressure was maintained at approximately 0.7 mbar,‡ a condition conducive to the occurrence of unimolecular processes. Progress of the pyrolysis was monitored by on-line recording of the PE spectrum of the heated gas. In some cases, a liquid nitrogen cold trap placed downstream from the quartz tube was employed to trap condensables. To measure the spectra of the individual products, the trapped components were released differentially by using a cold bath of liquid N_2–EtOH mixture.

The PE spectral changes for the pyrolysis of γ-butyrolactone are shown in Fig. 1. The onset of decomposition was 980 °C as seen from the emerging CO_2 bands at 13.8 and 18.1 eV [Fig. 1(*b*)]. Fig. 1(*c*) shows the composite spectrum at 1050 °C, the presence of other products, propene, ethene, formaldehyde and acrolein are indicated. Although the bands overlap in the region from 10–11 eV, the assignments given[6] have been confirmed by cold-trapping the condensables at liquid nitrogen temperature and differentially evaporating the individual products.

Fig. 2 illustrates the spectral changes for the pyrolysis of γ-thiobutyrolactone. The onset of decomposition occurred at 800 °C as shown by the appearance of the PE bands of CO, ethene and thioformaldehyde [Fig. 2(*b*)]. These bands became more prominent at 850 °C, and bands attributed to COS, C_3H_6, H_2S and CS_2 also appeared. At 950 °C, decomposition was largely complete. The products were confirmed through their individual spectra recorded *via* cold-trapping and differential vapourization.

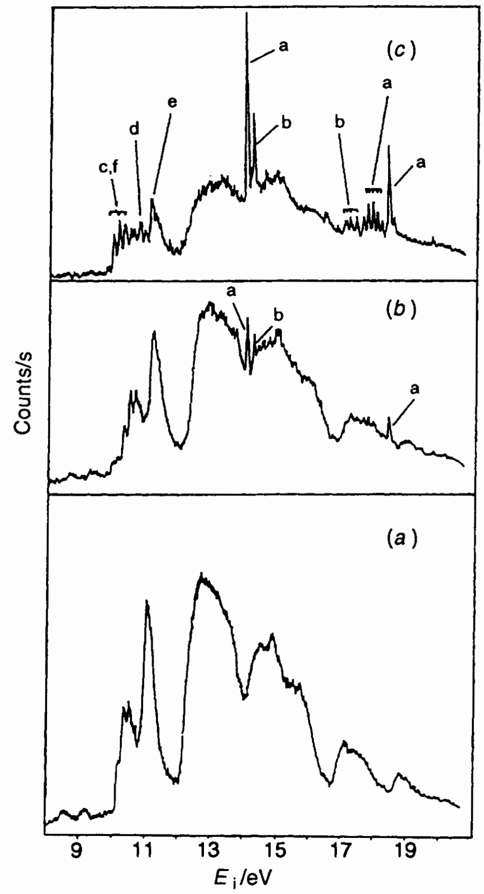
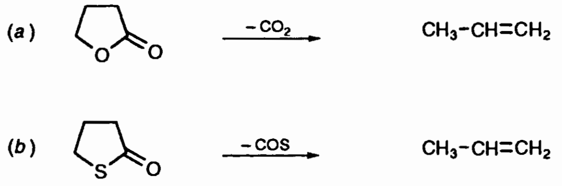


Fig. 1 Spectral changes during pyrolysis of γ-butyrolactone at (*a*) room temp.; (*b*) 980 °C; and (*c*) 1050 °C. Products: a, CO_2; b, CO; c, C_3H_6; d, C_2H_4; e, HCHO; and f, acrolein.

The product distribution as shown in Table 1 suggests that decarboxylation with the formation of propene is the major mode of decomposition for the lactone, while loss of COS is a minor mode of decomposition in the case of the thiolactone, in agreement with the expectation that CO_2 is a better leaving group than COS. The reaction probably proceeds through the formation of a $CH_2CH_2CH_2$ biradical species, which subsequently rearranges to give propene. The formation of cyclopropane as another intermediate cannot be ruled out. If formed, it would isomerize to propene under the conditions of our experiment. Indeed, cyclopropane has been observed in the



Scheme 1

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† 4,5-Dihydrothiophen-2(3*H*)-one.

‡ 1 bar = 10^5 Pa.

Table 1 Pyrolysis products of γ-butyrolactone and γ-thiobutyrolactone

	Major	Minor
γ-Butyrolactone	CO_2, C_3H_6	CO, HCHO, C_2H_4, CH_2=CHCHO
γ-Thiobutyrolactone	CO, HCHS, C_2H_4	COS, C_3H_6, H_2S, CS_2

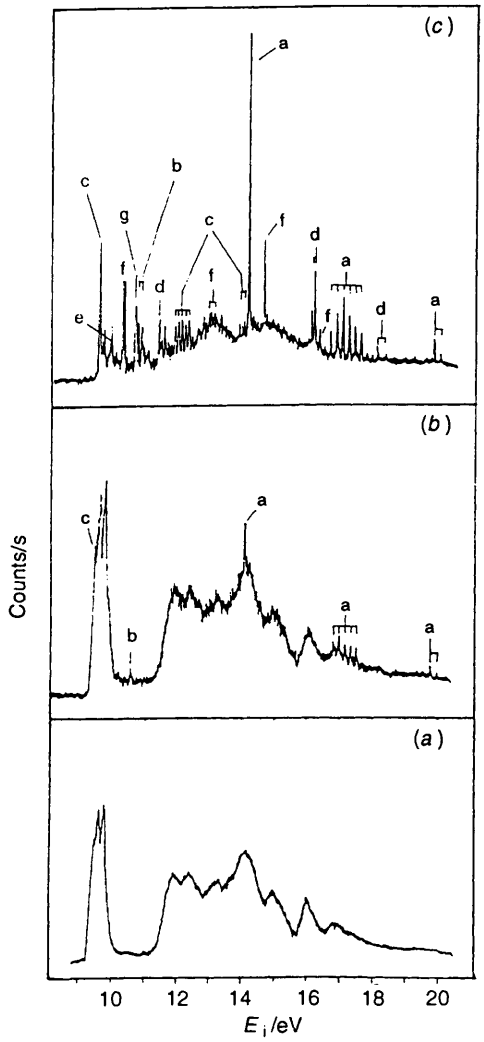
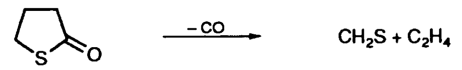


Fig. 2 Spectral changes during pyrolysis of γ-thiobutyrolactone at (*a*) room temp.; (*b*) 800 °C; and (*c*) 950 °C. Products: a, CO; b, C_2H_4; c, HCHS; d, COS; e, C_3H_6; f, CS_2; and g, H_2S.

photolysis, while a peak at *m*/*z* 42 was postulated as the cyclopropyl ion in the mass spectrometric studies of γ-butyrolactone.[7,8]



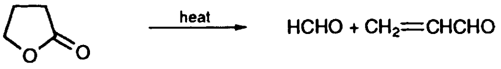
Scheme 2

For γ-thiobutyrolactone, decarbonylation with formation of ethene and thioformaldehyde appears to be the major mode of decomposition. The reaction may proceed through the intermediacy of either a $CH_2CH_2CH_2S$ biradical species or thietane. When we pyrolysed thietane under the same experimental conditions, ethene and thioformaldehyde were observed at 600 °C, the commencement of decomposition. At 850 °C, thietane decomposition was complete and besides the two products mentioned, H_2S and CS_2 were detected as secondary products.

Alternatively the decarbonylation reaction may proceed through a concerted pathway involving a six-electron transition state; here the process is analogous to the reverse of a cheletropic reaction.

Scheme 3

A minor mode of decomposition for the lactone may proceed through decarbonylation, analogous to Scheme 2, yielding CO, ethene and formaldehyde. But the detection of acrolein points to yet another competitive path for decomposition yielding the same products as decarbonylation. It has been reported previously that under similar experimental conditions, acrolein decomposed into CO and ethene.[5]



Scheme 4

Acknowledgements

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