

Thermal decomposition of methylated γ -thiobutyrolactones: a photoelectron spectroscopic study

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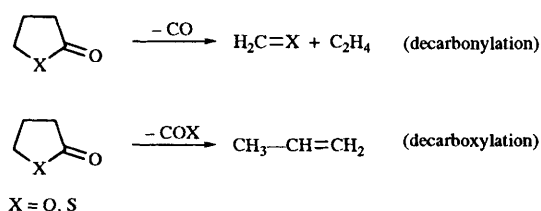
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The thermal decomposition of γ -thiovalerolactone, α -methyl- γ -thiobutyrolactone and β -methyl- γ -thiobutyrolactone has been studied in a gaseous flow system, by monitoring the changes in the photoelectron spectra recorded during the course of the reactions. Three modes of decomposition were observed, two involve loss of carbon monoxide (decarbonylation) and one involves loss of carbonyl sulfide (decarboxylation). The decarbonylation reaction producing an olefin and a thioaldehyde and the decarboxylation producing an olefin are similar to those observed for the unsubstituted thiobutyrolactone. The third reaction, observed only in the methylated compounds, is decarbonylation with the formation of hydrogen sulfide and butadiene. It is proposed that the last reaction can be attributed to the relatively facile elimination reaction of a butenethiol intermediate.

Introduction

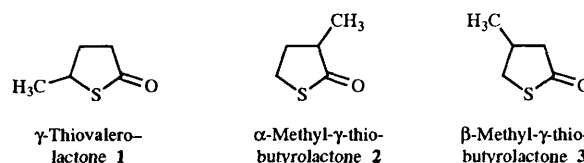
Lactones of different ring sizes undergo thermal decomposition through different reaction channels. Thus, lactones containing more than six atoms in the ring pyrolyse to give unsaturated acids,¹ similar to esters,² while the relatively unstable four-membered β -lactones undergo elimination of CO_2 to give olefins.^{3,4}

In a recent investigation we found that the five-membered rings, γ -butyrolactone and γ -thiobutyrolactone, show two modes of decomposition, a decarbonylation reaction which gives CO, ethene and formaldehyde (or thioformaldehyde), and a decarboxylation giving CO_2 (or COS) and propene.⁵



Decarboxylation was found to be the main reaction for the lactone, and decarbonylation the main reaction for the sulfur analogue.⁵ While the modes of reaction could be readily inferred from the intensity of spectral bands and the pressure of individual product species, the detailed pathways of the processes are less tractable experimentally, and in order to gain some mechanistic insights we have carried out semi-empirical SCF MO calculations on potential energy hypersurfaces of the systems.⁶ The results of the calculations are in qualitative agreement with experiments concerning the relative importance of the decomposition modes; the calculations also predict a stepwise pathway for the decarboxylation process, and, more tentatively, a concerted pathway for decarbonylation.⁶

In the present work the decomposition of three methylated thiolactones, compounds 1–3, were investigated in the hope of obtaining further mechanistic information, in particular the importance of the thietane intermediate in the decarbonylation process.⁵ The results indicate that thietane is an intermediate, though of minor importance. More interestingly, the results show that in the presence of a methyl group a new decarbonylation process becomes a dominant channel for decomposition, irrespective of the position of substitution.



Among the analytical methods suitable for the study of gaseous reactions, photoelectron spectroscopy offers the advantages of small sample size, ready identification of products with characteristic bands and detection of semi-stable species.¹⁰

Experimental

Compounds 1–3 were synthesised by using the corresponding lactones as starting materials, according to the method of Kharash and Langford⁹ for the conversion of γ -butyrolactone into its sulfur analogue. Compounds 2 and 3 are novel, while compound 1 has been extracted from natural products before.¹⁰

γ -Thiovalerolactone 1

Yield 67.0%, bp 84–87 °C/5 mmHg; δ_{H} 1.50 (3 H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH_3), 1.86, 2.40 (2 H, m, α -H), 2.63 (2 H, m, β -H), 3.95 (1 H, m, γ -H); m/z 116 (M^+ , 100%), 101 (8), 60 (12), 59 (12), 56 (26), 45 (14), 41 (67); ν/cm^{-1} (KBr) 2800–3000 (CH_3 , CH_2), 1698 ($\text{C}=\text{O}$), 1450 (CH_3 , CH_2) (Found: C, 51.43; H, 7.01; S, 27.51. $\text{C}_5\text{H}_8\text{OS}$ requires C, 51.69; H, 6.94; S, 27.60%).

α -Methyl- γ -thiobutyrolactone 2

Yield 55.6%, bp 85–87 °C/5 mmHg; δ_{H} 1.19 (3 H, d, $^3J_{\text{HH}} = 6.7$ Hz, CH_3), 1.88 (1 H, m, α -H), 2.50 (2 H, m, β -H), 3.29 (2 H, m, γ -H); m/z 116 (M^+ , 100%), 69 (15), 60 (11), 56 (25), 55 (14), 45 (13), 41 (20); ν/cm^{-1} (KBr) 2800–3000 (CH_3 , CH_2), 1697 ($\text{C}=\text{O}$), 1450 (CH_3 , CH_2) (Found: C, 51.75; H, 6.70; S, 27.43%).

β -Methyl- γ -thiobutyrolactone 3

Yield 62.9%, bp 88–90 °C/5 mmHg; δ_{H} 1.23 (3 H, d, $^3J_{\text{HH}} = 6.3$ Hz, CH_3), 2.23 (1 H, m, β -H), 2.63 (2 H, m, α -H), 3.06, 3.43 (2 H, m, γ -H); m/z 116 (M^+ , 100%), 69 (88), 56 (16), 46 (20), 41 (57); ν/cm^{-1} (KBr) 2800–3000 (CH_3 , CH_2), 1703 ($\text{C}=\text{O}$), 1448, 1405 (CH_3 , CH_2) (Found: C, 51.76; H, 7.00; S, 27.55%).

Pyrolysis was conducted in a gaseous flow system at low

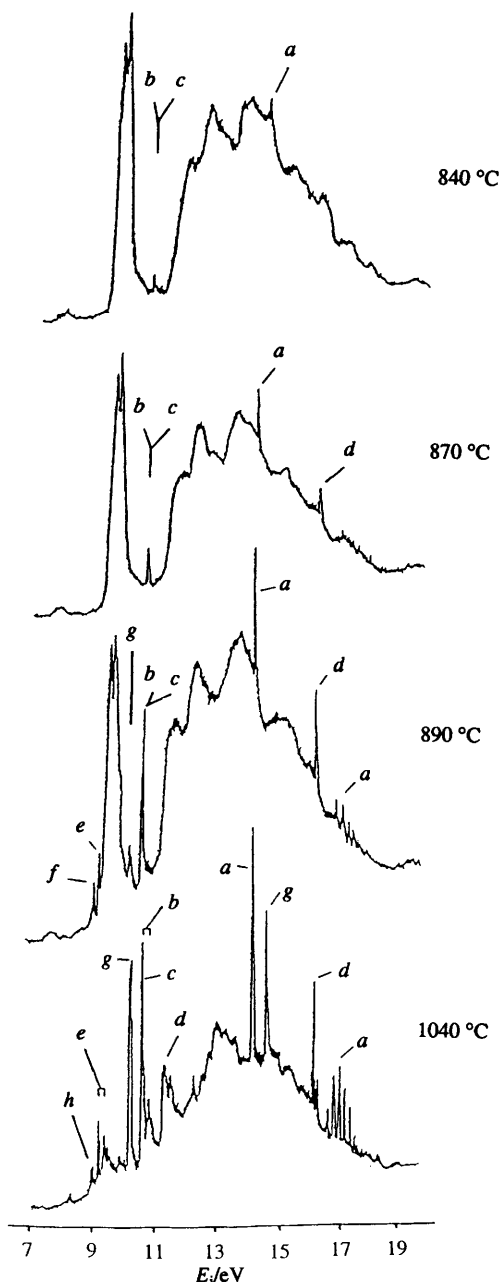


Fig. 1 Photoelectron spectral changes observed during pyrolysis of **1**. Apart from the small product signals indicated, the spectrum recorded at 840 °C corresponds to that of **1**: (a) CO; (b) C₂H₄; (c) H₂S; (d) COS; (e) butadiene; (f) CH₃CHS; (g) CS₂; (h) ethenethiol.

pressures. The experimental set-up consisted of a quartz tube 45 cm × 1.2 cm inner diameter. Heating was achieved by using a tube-oven which was 30 cm in length. One end of the quartz tube was connected to a sample container and the other to the inlet system of a Leybold-Heraeus UPG-200 photoelectron spectrometer. The vapour pressure of the sample gas was maintained at about 1 mbar with a needle valve. The progress of the reaction was monitored by the on-line recording of photoelectron (PE) spectra. A liquid nitrogen cold trap placed downstream from the heated zone was occasionally employed to collect the condensables. For identification of individual products, the components in the trapped mixture were released through differential vaporization, by using a cold bath of liquid N₂-EtOH slurry.

The resolution of the photoelectron spectrometer was ca. 22–30 meV. Spectra were calibrated with the first bands of argon and methyl iodide.

¹H NMR spectra were measured on a Bruker ACF300 or a Bruker AMX500 spectrometer operating at 300.13 and 500.13

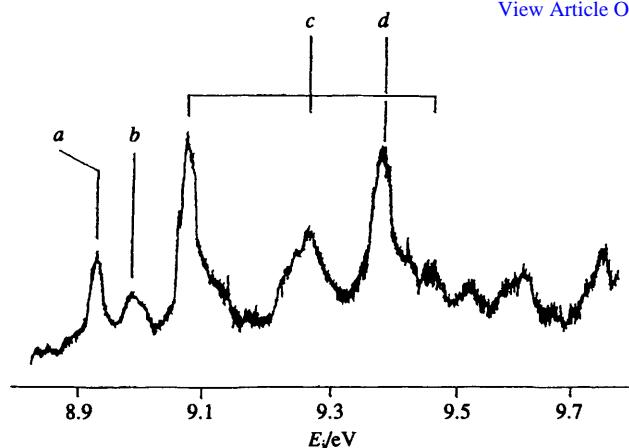


Fig. 2 Expanded spectrum recorded at 1040 °C during pyrolysis of **1**: (a) ethenethiol; (b) thioacetaldehyde; (c) butadiene; (d) thioformaldehyde

MHz respectively, using deuteriochloroform as solvent and tetramethylsilane as internal reference. COSY experiments were performed on the ACF300 instrument using a standard pulse program from the Bruker library. Mass spectra were recorded on a VG Micromass 7035E spectrometer or a Hewlett Packard 5890 GC/MS instrument. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. Microanalyses of samples were carried out using a Perkin-Elmer CHN analyser, Model 2400. Sulfur contents were determined by the oxygen flask method.

Semi-empirical SCF MO calculations on energy profiles of reactions were performed by using the PM3 Hamiltonian¹¹ available in the AMPAC 5.0 program package,¹² on a Silicon Graphics Personal Iris IRIX work station, Model 4. The PM3 method has been shown to give results superior to MNDO and AM1 methods in predicting the heats of formation and geometrical parameters of five-membered heterocycles.¹³ To accommodate possible radical character of intermediate species, the UHF formalism was employed throughout. Transition states were located by using the eigenvector following (EF) routine and were characterised by having one and only one negative force constant in the Hessian matrix.

Results and discussion

Changes observed during pyrolysis

γ-Thiovalerolactone 1. The PE spectral changes observed during the pyrolysis of **1** at different temperatures are shown in Fig. 1. Heating up to 800 °C produced no observable changes. The onset of decomposition occurred at 840 °C, when a weak signal at 14.01 eV due to carbon monoxide, and another one at 10.50 eV due to overlapping bands of ethene and hydrogen sulfide were observed.¹⁴ At 870 °C the spectrum showed an additional band at 16.05 eV attributed to the presence of carbonyl sulfide.¹⁵ More products were detected at 890 °C; thus, the formation of butadiene and carbon disulfide was indicated by the appearance of bands at 9.06 and 10.06 eV, respectively. Furthermore a sharp peak at 8.98 eV attributed to the first band of thioacetaldehyde¹⁶ was also observed.

Decomposition was largely completed at 1040 °C. Besides the various products mentioned, a small and sharp signal at 8.92 eV was observed at this temperature, corresponding to the first band of ethenethiol.¹⁷ When the spectrum was expanded (see Fig. 2), it became evident that the ethenethiol was formed at the expense of the isomeric thioacetaldehyde, suggesting interconversion of the two.¹⁷ The presence of another product, thioformaldehyde, is also indicated by a peak at 9.38 eV in the expanded spectrum.¹⁸

With the exception of the thioaldehydes, the presence of the various products mentioned was readily confirmed by PE spectral identification of the individual species following

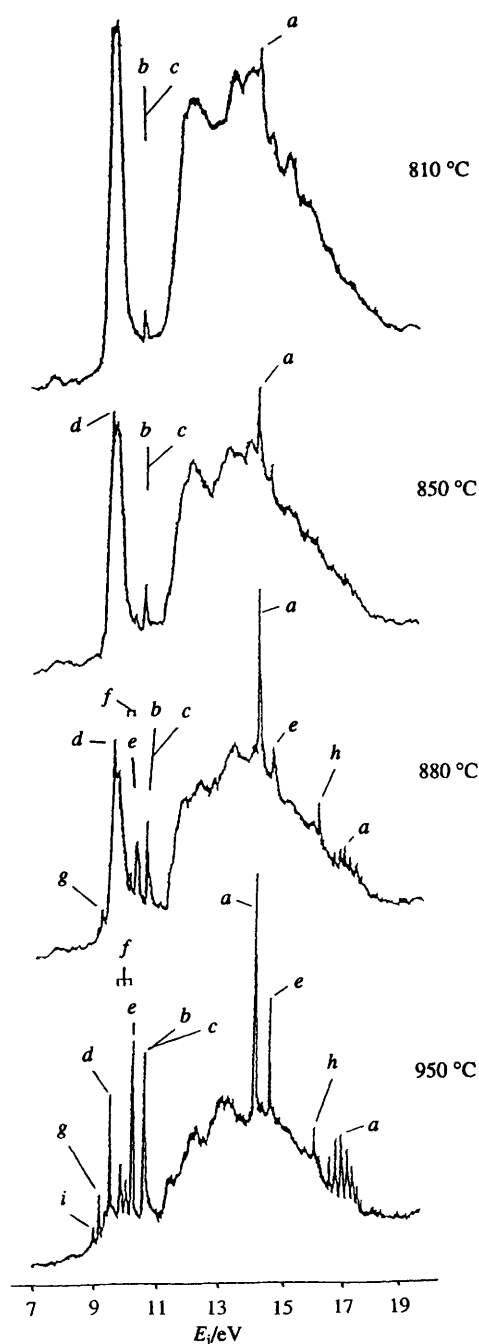


Fig. 3 Spectral changes observed during pyrolysis of **2**. Apart from the product signals indicated, the spectrum recorded at 810 °C corresponds to that of **2**: (a) CO; (b) H₂S; (c) C₂H₄; (d) CH₂S; (e) CS₂; (f) C₃H₆; (g) butadiene; (h) COS; (i) ethenethiol.

differential evaporation of the condensed mixture. The formation of propene, which could not be detected in the composite spectrum, was established in this way. The thio aldehydes are known to undergo polymerization easily,¹⁹ and only weak spectral signals of monomers could be observed from the trapped mixture.

α -Methyl- γ -thiobutyrolactone 2. The onset of decomposition of **2** occurred at 810 °C with the appearance of the sharp bands of carbon monoxide and hydrogen sulfide. The PE spectral changes at increasing temperatures are shown in Fig. 3. At 850 °C the first band of thioformaldehyde at 9.38 eV can be detected as a small sharp peak at the position of the first band of the parent compound, becoming more prominent at higher temperatures. At 880 °C carbonyl sulfide, butadiene and carbon disulfide were detected through the appearance of their characteristic bands. Close inspection revealed a small peak at 9.8 eV which was partially masked by the first ionization band

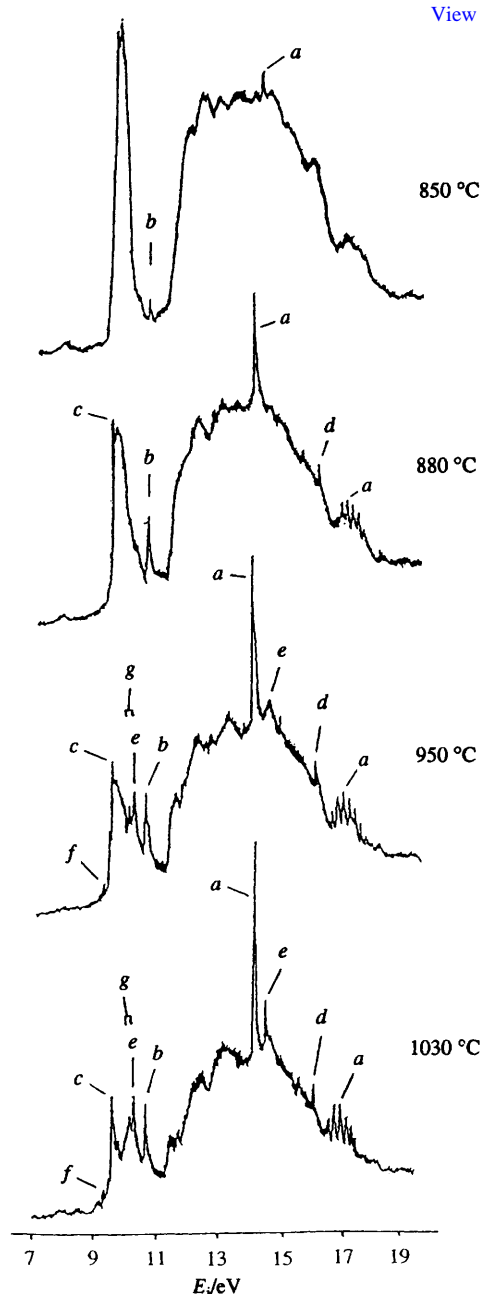


Fig. 4 Spectral changes observed during pyrolysis of **3**. Apart from the product signals indicated, the spectrum recorded at 850 °C corresponds to that of **3**: (a) CO; (b) H₂S; (c) CH₂S; (d) COS; (e) CS₂; (f) butadiene; (g) C₃H₆.

of carbon disulfide. It corresponded to the first band of propene. At 950 °C decomposition was largely complete. Besides the prominent sharp bands of the products mentioned, the first band of ethenethiol at 8.92 eV, though small, was noticeable in the composite spectrum obtained at this temperature.

As in the case for **1**, the formation of the products mentioned was confirmed in the PE spectra of the individual species following differential evaporation of the condensed mixture. Minute quantities of acetylene and methylacetylene were also detected in this process.

β -Methyl- γ -thiobutyrolactone 3. Heating **3** up to 800 °C did not result in observable spectral changes. Decomposition was only noticeable at 850 °C with the appearance of the bands due to carbon monoxide and hydrogen sulfide at 14.01 and 10.50 eV, respectively. These changes and others observed at higher temperatures are illustrated in Fig. 4. At 880 °C the sharp bands of thioformaldehyde and carbonyl sulfide, at 9.38 and 16.05 eV,

Table 1 Products of pyrolysis^a

Reactant	Main products	Minor products
1	CO, C ₂ H ₄ , C ₄ H ₆ H ₂ S, CS ₂	COS, C ₄ H ₈ , C ₃ H ₆ , H ₂ C=CHSH CH ₃ (H)C=S, H ₂ C=S
2	CO, C ₃ H ₆ , H ₂ C=S C ₄ H ₆ , H ₂ S, CS ₂	COS, C ₂ H ₄ , C ₄ H ₈ , H ₂ C=CHSH C ₂ H ₂ , CH ₃ CCH
3	CO, C ₃ H ₆ , C ₄ H ₆ H ₂ C=S, H ₂ S, CS ₂	COS, C ₄ H ₈

^a C₃H₆, Propene; C₄H₆, butadiene; C₄H₈, butenes.

respectively, emerged while those due to CO and H₂S became more pronounced. The first bands of butadiene and propene at 9.06 and 9.75 eV, respectively, were discernible only at 950 °C. At 1030 °C decomposition of **3** was nearly complete.

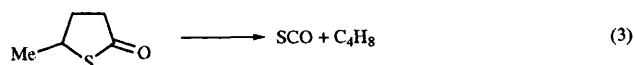
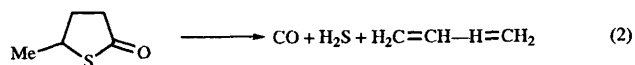
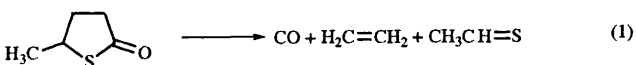
In the pyrolysis of **1–3**, the formation of butenes as decomposition products was not detected in the PE spectra because of their low concentrations and overlap of spectral bands with butadiene. However, their presence was revealed in NMR spectra. During differential evaporation of the condensables, obtained by pyrolysis of each thiolactone, at the temperature of the first appearance of CS₂, a fraction released between –90 and –75 °C was collected in a chilled second U-tube. The NMR and COSY spectra of the solution of the trapped mixture in deuteriated chloroform confirmed the presence of *cis*- and *trans*-but-2-ene, but-1-ene and isobutene, along with butadiene, by spectral data agreement with literature values.^{20–22} The NMR spectra further showed that in each case butadiene was a major product, its abundance being more than the combined total of the butenes. Under the experimental conditions interconversion of the butenes took place readily. Thus, when a sample of pure *trans*-but-2-ene was heated by passing the gas through the flow tube at 800 °C, isomerization occurred with the formation of an appreciable amount of the *cis* isomer along with minor quantities of but-1-ene and isobutene.

The products of decomposition can be approximately classified as major and minor based on the relative band intensities in the composite spectra as well as the vapour pressures of the individual species obtained during differential evaporation. The results, given in Table 1, show that in each case carbon monoxide, hydrogen sulfide and butadiene are among the main products, while carbonyl sulfide and the butenes are among the minor products.

Among the major products, carbon disulfide was mainly observed at high temperatures. As the temperature was raised beyond the point of complete decomposition of the parent compounds, the yield of carbon disulfide became increasingly high, suggesting that the compound was formed through secondary processes.

Modes of decomposition and mechanisms

The product distributions in the pyrolyses of **1–3** suggest that there are three modes of decomposition, *viz.* two involve loss of carbon monoxide (decarbonylation) and one with loss of carbonyl sulfide (decarboxylation). Thus decomposition of **1** proceeds through reactions (1) to (3). The product distribution

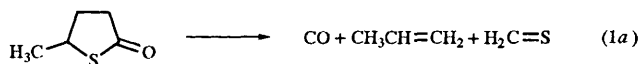


C₄H₈ = butenes

also suggests decarbonylation as the main process while decarboxylation is relatively minor. Similar results were obtained for the unsubstituted thiobutylolactone, although in this case decarbonylation led only to formation of thioformaldehyde and ethene,⁵ corresponding to reaction (1).

The same processes occurred in the decomposition of compounds **2** and **3**, for which the equivalent of reaction (1) yielded carbon monoxide, propene and thioformaldehyde.

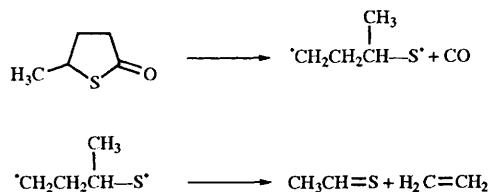
For compounds **1** and **2**, a minor variant of reaction (1) was also detected, giving rise to slightly different products. Thus, for **1** this minor mode led to formation of CO, propene and thioformaldehyde [reaction (1a)]. In the case of **2** the



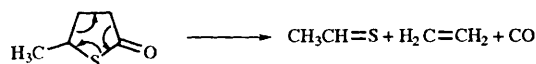
corresponding reaction produced ethene and thioacetaldehyde, the latter has the tendency to undergo tautomerism to ethenethiol because of ineffective p_π–p_π overlap in the C=S bond.^{19,23} For **3** such an alternative reaction was not observed, as expected.

The formation of hydrogen sulfide and butadiene as a major decarbonylation reaction is common to all the three compounds, irrespective of the position of the methyl substituent. Another common reaction is decarboxylation with the formation of carbonyl sulfide and butenes.

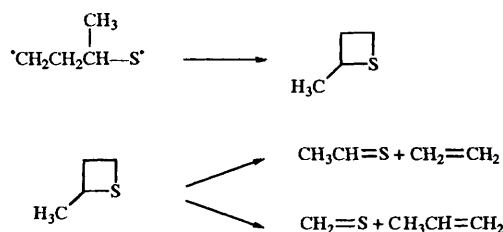
Reaction (1) may proceed either through a stepwise pathway involving biradical intermediates



or through a concerted pathway.

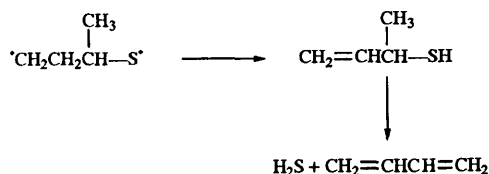


Semi-empirical UHF-PM3 calculations of reaction energy profiles for the unsubstituted γ -thiobutylolactone showed that the barrier height for the stepwise pathway is about 20% higher than that for the concerted pathway.⁶ The occurrence of reaction (1a), however, is indicative of the stepwise mechanism, since ring closure of the diradical species may result in the formation of another intermediate, 2-methylthietane, from which propene and thioformaldehyde can be derived.

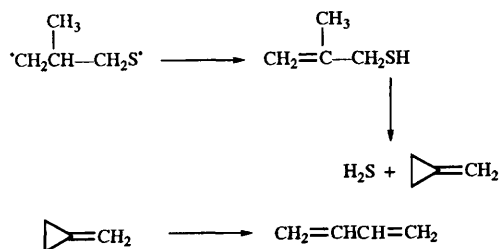


2-Methylthietane, once formed, is expected to undergo fragmentation readily under the experimental conditions.⁵ As the two modes of fragmentation of 2-methylthietane are probably of similar competitiveness, the smaller yields of propene and thioformaldehyde, as compared to those of ethene and thioacetaldehyde, indicate that ring closure of the diradical to form the thietane is a relatively minor process.

The formation of carbon monoxide, hydrogen sulfide and butadiene in reaction (2) involves intramolecular hydrogen transfers and can be accounted for by the stepwise mechanism. Thus, for compound **1** the process may proceed through a 1,3-hydrogen shift of the biradical intermediate, forming but-1-ene-3-thiol, followed by an elimination reaction of the thiol to give the final products.



Similar processes could be proposed for compounds **2** and **3**. In the case of **3**, consecutive hydrogen transfers may lead to the formation of methylenecyclopropane, which subsequently isomerises to butadiene.²⁴



The formation of butenes and carbonyl sulfide in reaction (3) involves a 1,2-hydrogen shift. For compounds **1** and **2** the hydrogen transfer may proceed in two ways, giving but-1-ene or but-2-ene, while for **3** only isobutene is expected. The detection of all the isomeric butenes in the pyrolysis of the three compounds indicates the occurrence of butene isomerisation, as already mentioned.

Information from MO calculations

Previous UHF-PM3 calculations on the potential energy profiles for the decarboxylation reaction showed that the stepwise pathway is favoured energetically as compared to the concerted route by 120 and 91 kJ mol⁻¹ for the unsubstituted γ -butyrolactone and γ -thiobutyrolactone, respectively.⁶ Since a stepwise pathway was also envisaged to be a possible route for reaction (2), calculations were performed for compound **1** with respect to the stepwise pathways for reactions (2) and (3), for a comparison of the energetics of the two processes. The detailed pathways are illustrated in Scheme 1.

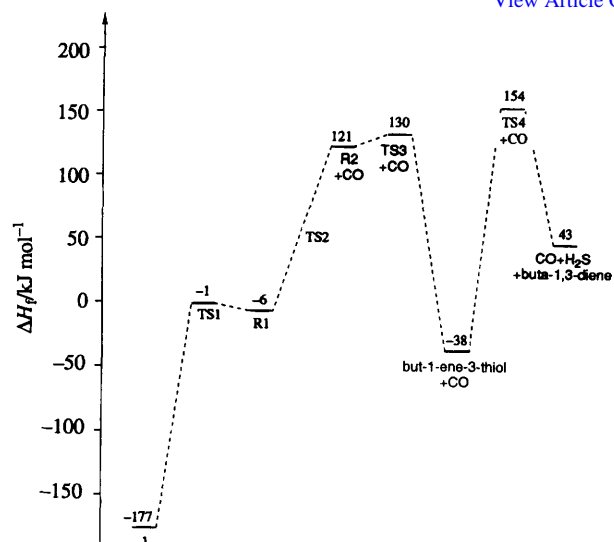
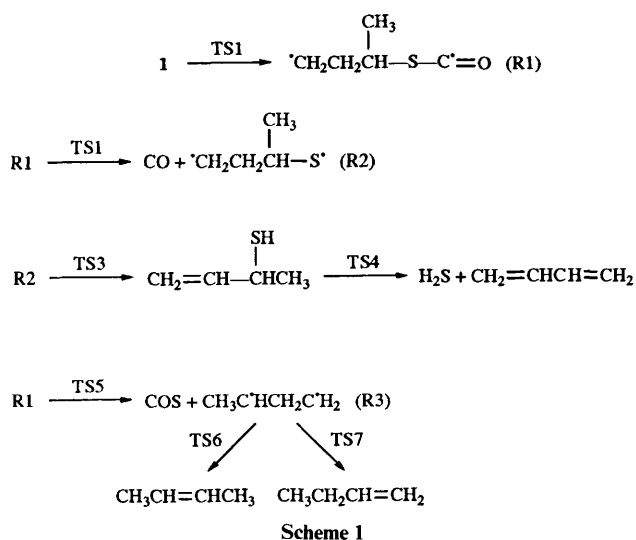


Fig. 5 UHF-PM3 energy profile for decarboxylation of **1**, leading to formation of hydrogen sulfide and butadiene

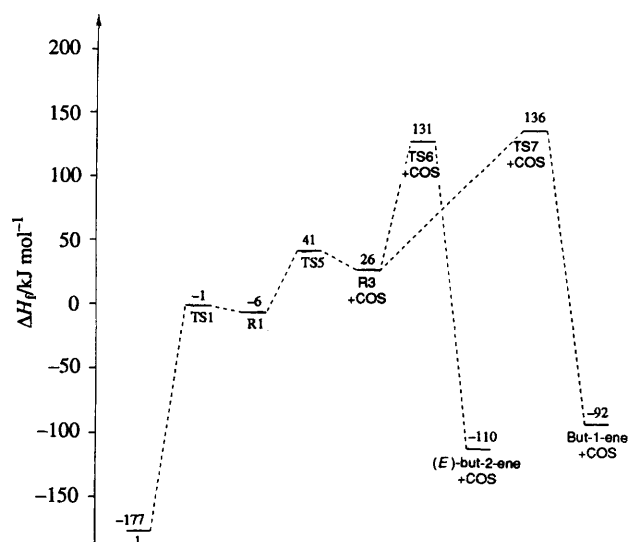


Fig. 6 UHF-PM3 energy profile for decarboxylation of **1**

R1–R3 are three biradical intermediates, TS1–TS7 are the transition states associated with the respective steps. The UHF-PM3 calculations indicated that the C–C bond at the carbonyl position is the weakest in the cyclic structure of the parent compound; thus the first step is bond breaking with formation of the species R1. The energy profiles of the processes are illustrated in Figs. 5 and 6, and the optimized structures of the biradical and transition state species are given in Fig. 7. Also shown in the last figure are the calculated heats of formation and the $\langle S^2 \rangle$ values of the species. Note that the $\langle S^2 \rangle$ values of the biradicals and the related transition states vary between 0.82 to 1.04, indicating some spin contamination.

In the decarboxylation leading to formation of hydrogen sulfide and butadiene (Fig. 5), the barrier for but-1-ene-3-thiol formation is approximately 100 kJ mol⁻¹ higher than that for the dissociation of the thiol into the final products. Thus, the formation of the thiol is rate controlling. Attempts to locate TS2 were not successful. However, the heat of formation of TS2 should be very close to the combined value for R2 + CO, judging from the results obtained for γ -butyrolactone.⁶ In the decarboxylation reaction (Fig. 6) the overall barrier heights for formation of the two butenes are about the same. They are also comparable to that for the formation of but-1-ene-3-thiol shown in Fig. 5.

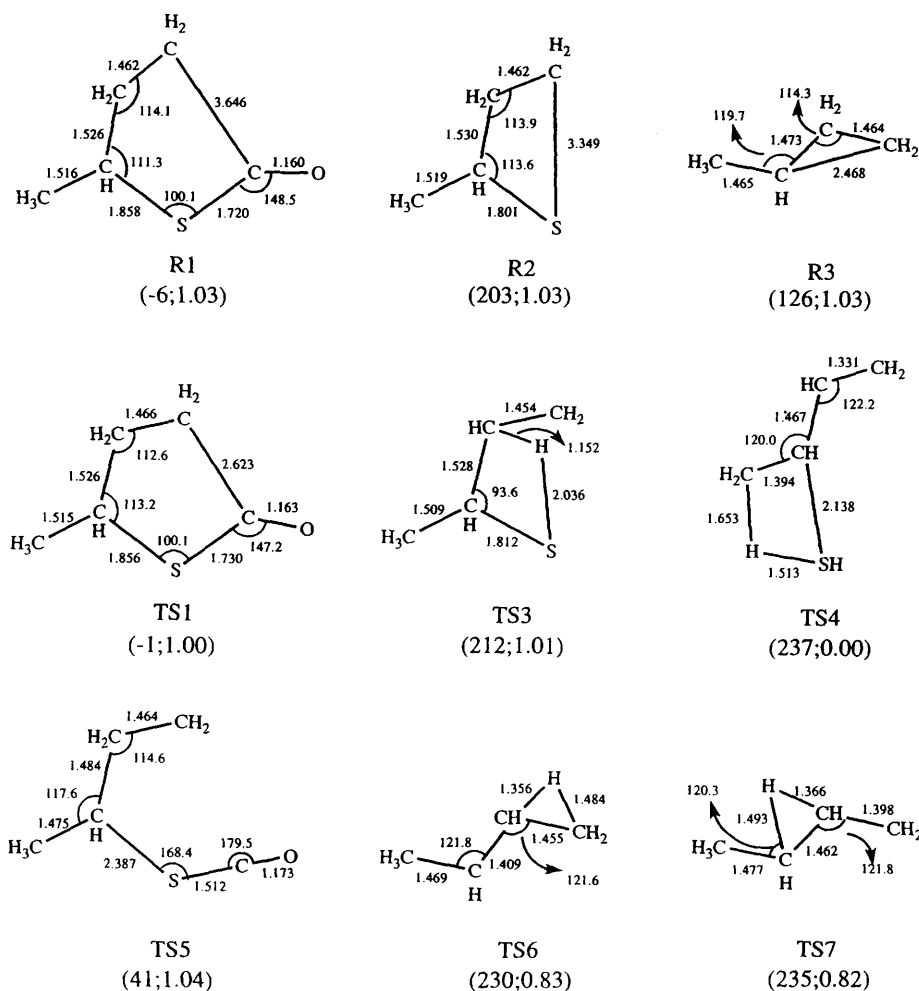


Fig. 7 UHF-PM3 optimized geometries of biradicals and transition state species. The values in parentheses are the calculated heats of formation and the $\langle S^2 \rangle$ value, respectively, for each species.

Conclusions

The thermal decomposition of the methylated thiobutyrolactones occurred through decarbonylation and decarboxylation, with the former as the major process. This general behaviour is the same as that exhibited by the unsubstituted compound. However, a new mode of decarbonylation with the formation of hydrogen sulfide and butadiene becomes a dominant process for the substituted compounds. This mode of reaction probably proceeds through the intermediacy of a butenethiol, which undergoes relatively facile elimination to form the final products. The presence of a methyl group made it possible to distinguish between the two routes for decarbonylation leading to the formation of an olefin and a thioaldehyde. The presence of the 2-methylthietane intermediate was also suggested by the results.

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