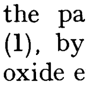
Gas Phase Thermolyses. Part 4.[1a] Gas Phase Thermolyses of Thietan 1-Oxide and 1,2-Oxathiolan 2-Oxide. Evidence for the Intermediacy of 1,2-Oxathiolan

By **Lars Carlsen** * and **Helge Egsgaard,** Chemistry Department, Risø National Laboratory, DK–4000 Roskilde, Denmark
David N. Harpp, Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A2K6

The unimolecular gas phase thermolyses of thietan 1-oxide, 1,2-oxathiolan 2-oxide, and dimethyl sulphoxide have been studied by the flash vacuum thermolysis–field ionization mass spectrometry technique in the temperature range 783—1 404 K. The reactions are rationalized in terms of atomic oxygen extrusions and sulphoxide–sulphenate rearrangements. Evidence is presented for the common intermediacy of 1,2-oxathiolan from the thermolyses of both thietan 1-oxide and 1,2-oxathiolan 2-oxide.

We have previously reported on the thermal [2,3] and photolytic [4] generation of the simplest cyclic sulphenates, the three-membered oxathiirans, which are found to be thermally highly labile compounds. The corresponding four- and five-membered cyclic sulphenates, 1,2-oxathietans, and 1,2-oxathiolans, respectively, are not known. The former has, however, been studied theoretically within the CNDO/B and CNDO/S frameworks.[5] To our knowledge only one example of a stable cyclic sulphenate has been reported,[6] the compound being highly substituted. Attempts to synthesize the parent five-membered sulphenate, 1,2-oxathiolan (1), by deoxygenation of the corresponding stable *S*-oxide employing a series of reagents commonly used for reduction of sulphoxides were unsuccessful.[7] However, evidence has been obtained for the isolation of (1) by cyclization of *S*-phthalimido-3-mercaptopropan-1-ol. Compound (1) exhibits a half-life of *ca.* 3 h at room temperature.[8]

As a part of our current interest in the unimolecular gas phase thermolytic decompositions of organic sulphur compounds,[1] we now report our results on the unimolecular gas phase thermolyses of thietan 1-oxide (2) and 1,2-oxathiolan 2-oxide (3) as possible precursors to the unknown 1,2-oxathiolan (1). The thermolyses of (2) and (3) were studied since sulphoxides are known thermally to rearrange to the corresponding sulphenates,[9] and organic *S*-oxides have been shown to extrude atomic oxygen under pure unimolecular gas phase thermolytic conditions.[3] To elucidate the presence of these two reactions we also studied the unimolecular gas phase thermolysis of dimethyl sulphoxide (4).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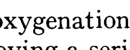
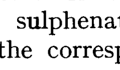
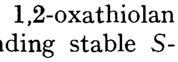

(2)


(3)


$CH_3-\overset{+}{S}(-\bar{O})-CH_3$

(4)

The thermolyses were studied by the flash vacuum thermolysis–field ionization mass spectrometry (f.v.t.–f.i.m.s.) method,[10] which secures detection of unimolecularly formed products only.

EXPERIMENTAL

Compounds (2) [11] and (3) [12] were synthesised according to published procedures.

Flash Vacuum Thermolysis Technique.—The f.v.t. technique, described in detail elsewhere,[10] is based on the direct combination of a thermolysis unit with a double focusing Varian MAT CH 5D mass spectrometer, equipped with a combined electron impact ionization–field ionization–field desorption (e.i.–f.i.–f.d.) ion source. The thermolysis unit is connected directly to the ion source of the mass spectrometer *via* a heatable line-of-sight inlet system. Samples (*ca.* 50 μg) of the pure compounds were introduced (microsyringe) into the hot zone (reactor) *via* a heated injection block. The contact time in the reactor has been estimated to be *ca.* 10^{-3}—10^{-4} s. The internal geometry of the reactor (length 40 mm, internal diameter 2 mm) combined with a low actual pressure (*P ca.* 10^{-4} Torr) assures a very low frequency of intermolecular collisions relative to the molecule–hot surface collision frequency, *i.e.* only unimolecular reactions take place. However, it should be remembered that surface catalytic effects may operate.

The thermolysis products are detected by recording the field ionization mass spectra immediately after the thermolyses. F.i. gives rise to molecular ions (even of very unstable substances) accompanied only by few, if any, fragment ions.[13]

Further identification of the single compounds formed by the gas phase thermolyses are obtained by recording the collision activation (c.a.) mass spectra [14] of the corresponding molecular ions.[10]

RESULTS

Several authors have recently reported on the gas phase thermolysis of dimethyl sulphoxide (4).[15-17] From this work a rather complicated decomposition pattern could be expected upon thermolysis of (4). Two papers by Block and his co-workers caught our attention as they reported the formation of sulphine (thioformaldehyde *S*-oxide) [16] and methanesulphenic acid.[17] However, these studies do not report on the unimolecular decomposition of (4). The same is true in a study by Thyrion [15] who rationalized a complete degradation of (4) in terms of a series of speculative radical reactions. The f.i.–m.s. spectrum of (4) following thermolysis (1 404 K), is however very simple, as only three reaction products, dimethyl sulphide (5) (*M* 62), methanethiol (6) (*M* 48), and formaldehyde (7) (*M* 30), are observed (Figure 1). The identity of these compounds was verified by studying the corresponding thermolysis of dimethyl $[^2H_6]$sulphoxide, which resulted in the formation of products with molecular weights of 68, 52, and 32, respectively. No peak corresponding to $[^2H_2]$sulphine (*M* 64) was observed. Thermolysis of (4) at lower temperatures did not afford new products, as only the above three reaction products were observed, albeit, in lower overall yield.

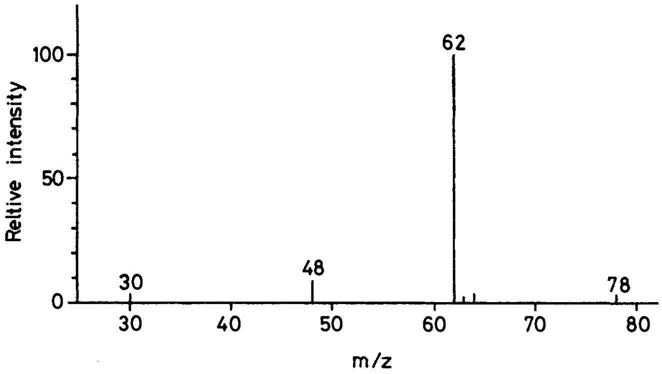


FIGURE 1 Field ionization mass spectrum of dimethyl sulphoxide following unimolecular gas phase thermolysis at 1 404 K

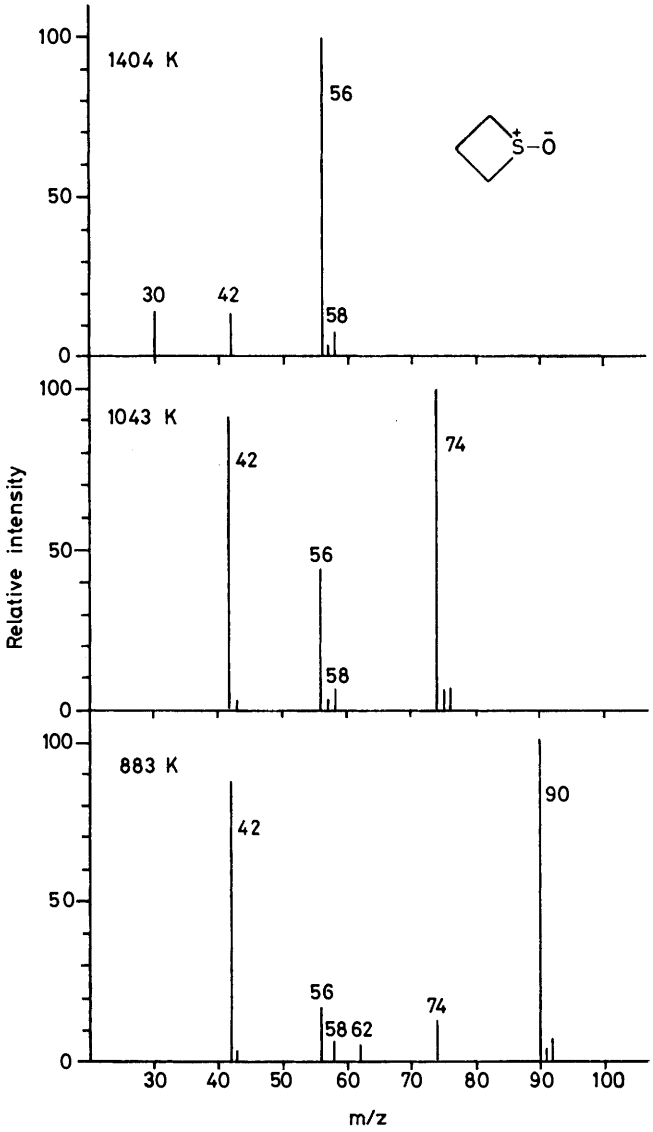


FIGURE 2 Field ionization mass spectra of thietan 1-oxide following unimolecular gas phase thermolyses at 883, 1 043, and 1 404 K, respectively

In the case of thietan 1-oxide (2) (*M* 90) we found that the product composition is somewhat dependent on the thermolysis temperature. Figure 2 depicts the f.i.–m.s. spectra following thermolyses of (2) at 883, 1 043, and 1 404 K, respectively. On the basis of these spectra, complementary with collision activation mass spectra of authentic samples, a product assignment of thietan (8) (*M* 74), acrolein (11) (*M* 56), sulphine (9) (*M* 62), and products with the molecular compositions C_3H_6O (10) (*M* 58) and C_3H_6 (12) (*M* 42), respectively are observed. Due to the low intensity of the peak with *m/e* 58 it has, unfortunately, not been possible to obtain satisfactory c.a.–m.s. spectra for a conclusive identification.* Neither has it, by the c.a. method applied here, been possible to distinguish between propene and cyclopropane (12) (*M* 42). Figure 3 depicts the f.i.–c.a. spectra of thietan and acrolein obtained after thermolysis of (2) at 1 043 K. The spectra are identical to those recorded from authentic samples.

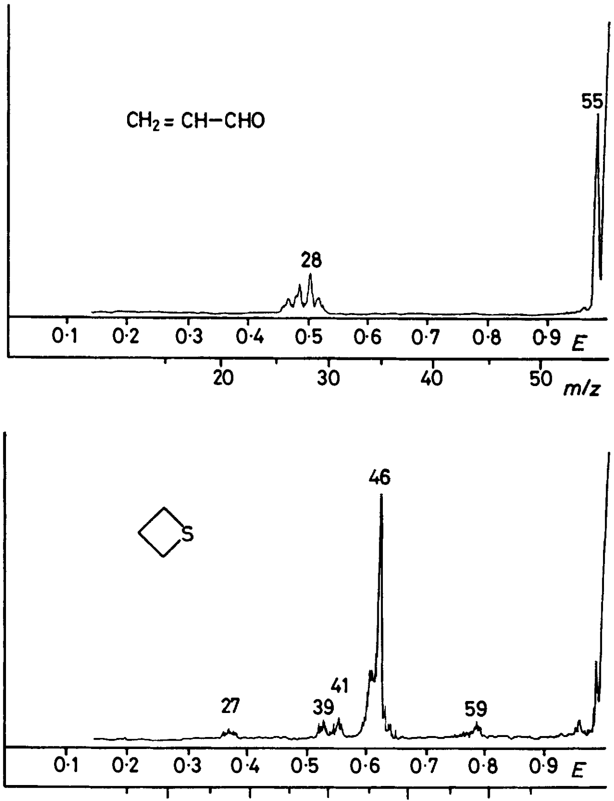


FIGURE 3 Collision activation spectra of field ionized thietan and acrolein obtained after thermolysis of thietan 1-oxide at 1 043 K

In Figure 4, the product composition following thermo-

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* C.a.–m.s. spectra of authentic samples only exhibit minor quantitative differences.

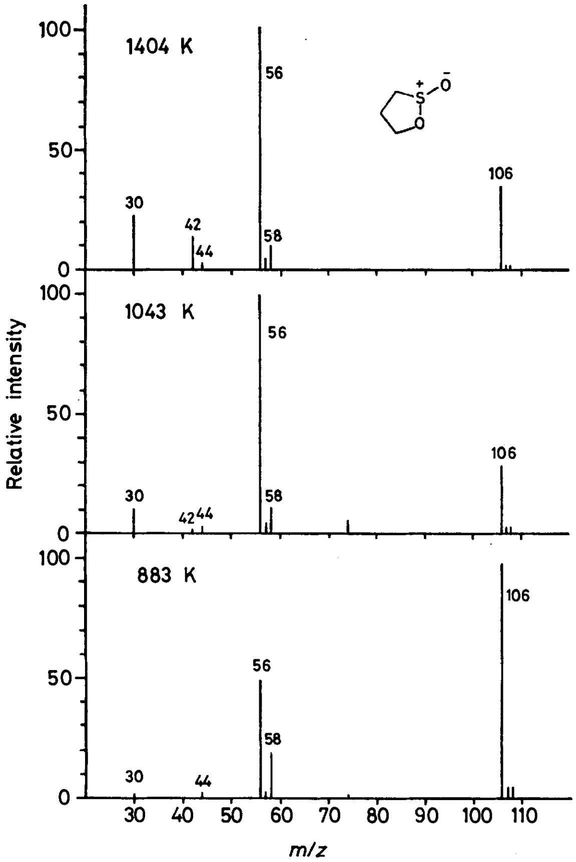


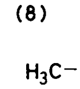
FIGURE 4 Field ionization mass spectra of 1,2-oxathiolan 2-oxide following unimolecular gas phase thermolysis at 883, 1 043, and 1 404 K, respectively

lyses of 1,2-oxathiolan 2-oxide (3) (*M* 106) at 883, 1 043, and 1 404 K, respectively, is very similar to the thermolysis of (2). Additionally formaldehyde (7) (*M* 30) is found in low abundance. An f.i.–c.a. spectrum of acrolein identical to that mentioned above was obtained.

It is not possible to calculate the yields of the single species directly from the f.i.–m.s. spectra, as the single compounds may exhibit rather different f.i. sensitivities.[13] However, the relative f.i.-sensitivities of (12), (11), (10), and (8) were determined using the gas inlet system of the mass spectrometer. Tentatively the sensitivities for propene and oxetan, as representatives for (12) and (10), respectively, were used. From Figures 2 and 4, supplemented by the relative f.i.-sensitivities, the relative yields of these compounds were estimated (Table).

CH_3SH (6)

H_2CO (7)



(8)

H_2CSO (9)

C_3H_6O (10)

$H_2CCHCHO$ (11)

C_3H_6 (12)

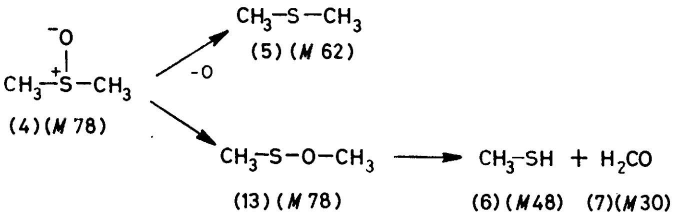
$H_3C{-}S{-}O{-}CH_3$ (13)

$HSCH_2CH_2CHO$ (14)

DISCUSSION

The product formation reported above can be discussed in terms of the two possible reactions mentioned in the Introduction, *i.e.* atomic oxygen extrusion * and rearrangement of sulphoxides to the corresponding sulphenate coupled with consecutive sulphenate decomposition reactions.

The existence of these types of reactions is easily rationalized in the case of dimethyl sulphoxide (4) (Figure 1). It has previously been reported that sulphoxides that do not possess β-hydrogens thermally can be rearranged to the corresponding sulphenates, the latter consecutively fragmenting into a thiol and a carbonyl compound.[9] In the present case this reaction would result in the formation of methanethiol (6) and formaldehyde (7) likely *via* methyl methanesulphenate (13).



However, a c.a.–m.s. analysis of the peak with *m*/*z* 78, following thermolysis of (4) at temperatures between 883 and 1 404 K only showed unchanged (4). No signals corresponding to a contribution of (13) to the peak of *m*/*z* 78 were observed, indicating the instability of the latter under the conditions used.

Relative yields of (7), (12), (11), (10), and (8) following unimolecular gas phase thermolyses of (2) and (3) at 783, 883, 1 043, and 1 404 K, respectively. The figures are averages for three experiments

			783 K		883 K		1 043 K		1 404 K	
Compound	*M*	*S* [a]	(2)	(3)	(2)	(3)	(2)	(3)	(2)	(3)
(7)	30	1.00 [b]				0.02		0.10	0.05	0.08
(12)	42	0.17	0.39		0.89		0.61	0.04	0.37	0.37
(11)	56	1.00	0.04	0.34	0.04	0.58	0.11	0.70	0.47	0.46
(10)	58	0.52	0.04	0.66	0.02	0.40	0.02	0.16	0.11	0.09
(8)	74	0.63	0.53		0.04		0.26			
Approx. overall yield			0.10	0.05	0.50	0.40	1.00	0.80	1.00	0.80

[a] Relative f.i. sensitivities. [b] Assumed value equal to that of acrolein.

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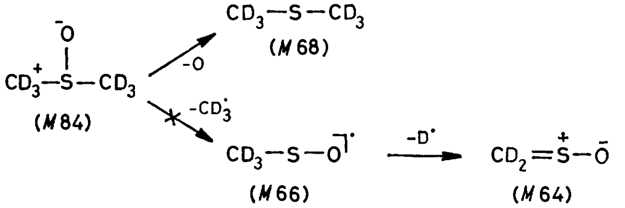
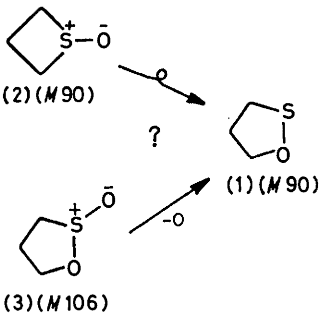
* Since rupture of the semipolar S–O bond in (4) appears to require 86.6 kcal mol^{-1} (S. W. Benson, *Chem. Rev.*, 1978, **78**, 23) the apparent presence of this mechanism suggests that the atomic oxygen extrusion reaction may involve surface catalysis. However, since the hot filaments in the reactor are wires of different alloys (the actual composition being determining for the Curie temperature of a given wire) different surface catalytic effects may operate (*cf.* Y. Nishiyama and Y. Tamai, *Chemtech.*, 1980, **10**, 680), not of necessity giving rise to a smooth variation in yield with temperature.

A possible unimolecular formation of sulphine (9) *via* a pathway involving primary loss of a methyl radical from (4) followed by a loss of a hydrogen radical from the resulting MeSO radical is effectively ruled out due to the above mentioned deuterium labelling experiment.



In the case of (2) (Figure 2) atomic oxygen extrusion evidently results in the formation of thietan (8) (*M* 74),* whereas the sulphoxide–sulphenate rearrangement would afford formation of the unknown 1,2-oxathiolan (1); the latter, on the other hand, would also be a result of atomic oxygen extrusion from the *S*-oxide (3).

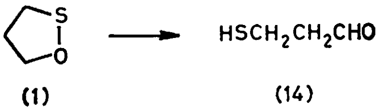
However, when (3) was thermolysed (Figure 4) no product with molecular weight 90 is observed. This could be explained by a consecutive quantitative degradation of (1). It furthermore suggests that, if formed, (1) exhibits a half-life $<10^{-3}$ s under the reaction conditions.[10] Furthermore, formation of (10) and (11) by rearrangements and/or fragmentations directly from both (2) and (3) can be explained only in terms of highly speculative reaction mechanisms, whereas a



straightforward rationalization is possible assuming the existence of the common intermediate (1).

To elucidate the possible degradation pathway of (1), we shall turn to a discussion of the formation of (10) and acrolein (11), the common products for the thermolyses of both (2) and (3). There is a remarkable constancy in the (10) : (11) ratios, when comparing the product distributions following thermolyses of (2) and (3) at the single temperatures (Table). This supports an assumption that these products are formed *via* the same species.

Acrolein formation can be explained in terms of a fragmentation of sulphenate (1), analogous to that observed for (13), resulting in the formation of methanethiol and formaldehyde. However, as the sulphenate moiety in the case of (1) is fixed in a five-membered ring system the fragmentation would lead to generation of 3-mercaptopropanal (14), the latter only being known as its oligomer.[18] We find, however, that the oligomer of (14) at *ca.* 400 K (*in vacuo*) is smoothly cracked into the monomeric species.[19] Cracking the oligomeric species under conditions where thermolysis of the initially formed (14) would closely mimic those for the thermolyses of (2) and (3), we found that (14) very easily eliminates hydrogen sulphide affording acrolein (Figure 5). The c.a.–m.s. spectrum of the latter is identical with that obtained from authentic acrolein. We find that even at 631 K [200 K below the temperature where (2) and (3) thermolyse to an observable extent] a high degree of H_2S elimination from (14) is observed, and at 1 043 K only very minor amounts of (14) are recovered. In addition, it is seen (Figure 5) that (10) (*M* 58) is formed in low yield; the above mentioned (10) : (11) ratio is also found here to be 0.23 (1 043 K). For comparison, the (10) : (11) ratios following thermolysis of (2) and (3) at 1 043 K are calculated to be 0.18 and 0.23, respectively.



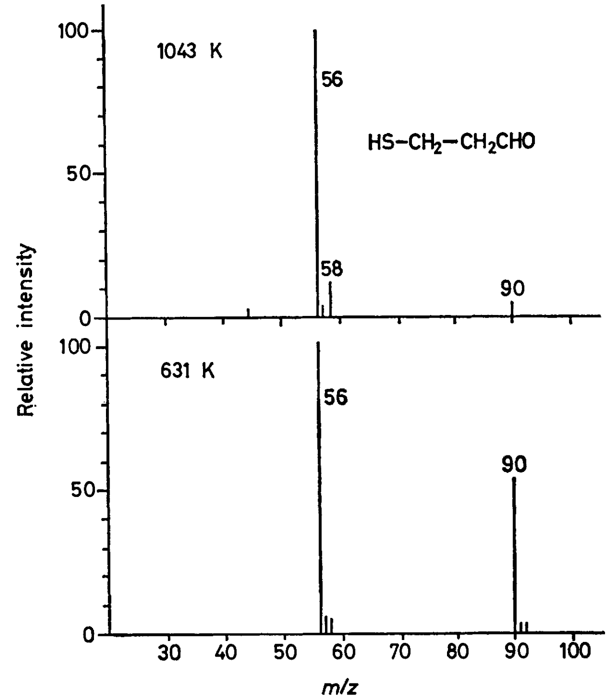


FIGURE 5 Field ionization mass spectra of 3-mercaptopropanal following unimolecular gas phase thermolyses at 631 and 1 043 K, respectively

It should finally be mentioned that the electron impact ionization mass spectrum of monomeric (14) suggests some content of the isomeric thietan-2-ol,[19,20] which similarly may contribute to the peak with *m*/*z* 90 (Figure 5), as well as be responsible for the thermal formation of (10) by sulphur extrusion. From the above,

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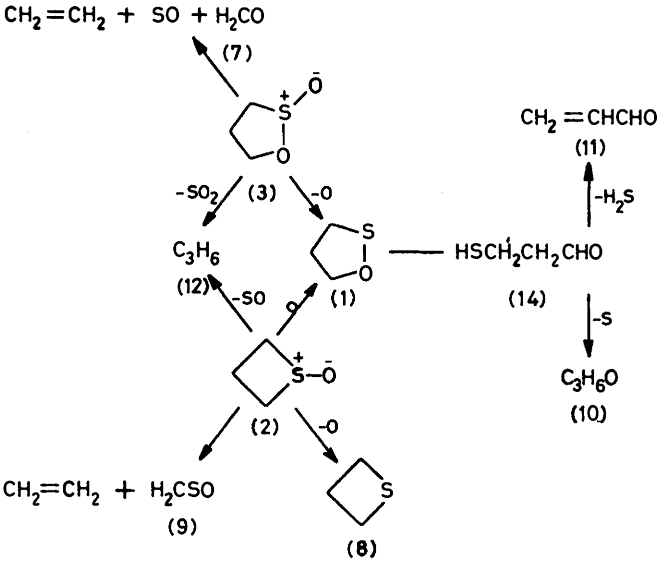
* Same footnote as on p. 1168.

it is not surprising that we are unable to detect sulphenate (1) and/or the rearranged product (14), but only the corresponding decomposition products, acrolein and (10).

Remaining to be discussed, concerning the thermolysis of (2), is the formation of C_3H_6 (12) (*M* 42), apparently generated by simple sulphur monoxide extrusion, and sulphine (9) (*M* 62), which is likely due to a 2 + 2-retrocycloaddition of ethylene and sulphine, as previously reported by Block.[16] Since sulphine is formed only in very minor amounts (Figure 2) the apparent lack of a peak corresponding to ethylene (*M* 28) is not unreasonable owing to a very low f.i.-sensitivity of the latter.[13]



SCHEME

In connection with the thermolysis of (3), the two undiscussed products, (12) and (7), are apparently generated by sulphur dioxide extrusion and a simple rearrangement analogous to the recently reported sulphinate thermolyses by Durst *et al.*[21]

In summary we rationalize the unimolecular gas phase thermolyses of (2) and (3) as depicted in the Scheme, taking the results reported into account for the intermediacy of (1). Although cumulative evidence for the intermediacy of 1,2-oxathiolan in the gas phase thermolyses of thietan 1-oxide and 1,2-oxathiolan 2-oxide is high, direct experimental verification under such conditions does not seem likely.

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