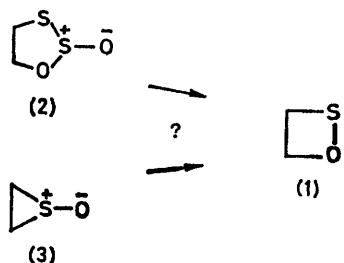


Gas-phase Thermolyses. Part 7.¹ Gas-phase Thermolysis of 1,2,3-Oxadithiolan 2-Oxide and Thiiran 1-Oxide. On the Intermediacy of 1,2-Oxathietan¹

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The unimolecular gas-phase thermolyses of 1,2,3-oxadithiolan 2-oxide and thiiran 1-oxide have been studied by the flash vacuum thermolysis-field ionization mass spectrometry (f.v.t.-f.i.m.s.) technique in the temperature range from 1 043 to 1 404 K. The reactions are rationalized in terms of sulphoxide-sulphenate rearrangement and atomic oxygen, sulphur monoxide, and sulphur dioxide extrusions. Evidence is presented for the common intermediacy of 1,2-oxathietan from the thermolyses of both 1,2,3-oxadithiolan 2-oxide and thiiran 1-oxide.

VERY recently we reported on the intermediacy of 1,2-oxathiolan² in the gas-phase thermolyses of 1,2-oxathiolan 2-oxide and thietan 1-oxide,³ the five-membered cyclic sulphenate being characterized partly based on its thermal decomposition into acrolein and allyl alcohol. We have likewise in a series of papers reported on features of the three-membered cyclic sulphenates, *i.e.* the oxathiirans.⁴ However, to our knowledge, no reports on the corresponding four-membered sulphenates, the 1,2-oxathietans, have appeared.† In the present study we report investigations on the possible intermediacy of the parent 1,2-oxathietan (1) in the gas-phase thermolyses of 1,2,3-oxadithiolan 2-oxide (2), and thiiran 1-oxide (ethylene sulphoxide) (3).



The choice of the compounds (2) and (3) as possible 1,2-oxathietan precursors was based on the following assumptions. It has previously been reported that cyclic sulphites upon thermolysis eliminate sulphur monoxide;⁵ hence, an analogous sulphur monoxide extrusion from (2) seems feasible, apparently leading to (1). In connection with our recent study on 1,2-oxathiolan we reported on the thermally induced ring expansion of thietan 1-oxide into the five-membered sulphenate;³ analogously, the three-membered sulphoxide (3) was expected to afford (1) by ring expansion.

EXPERIMENTAL

1,2,3-Oxadithiolan 2-oxide (2)⁶ and thiiran 1-oxide (3)⁷ were synthesized according to previously reported procedures.

Flash Vacuum Thermolysis Technique.—The f.v.t. tech-

† The parent 1,2-oxathietan has been studied theoretically by semi-empirical CNDO methods (J. P. Snyder and L. Carlsen, *J. Am. Chem. Soc.*, 1977, **99**, 2931).

nique used has been described in detail elsewhere⁸ and 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 μ g) 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 (*l* 40 mm, *i.d.* 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.⁹

Further identification of the single compound formed by the gas-phase thermolyses is obtained by recording the collision activation (c.a.) mass spectra¹⁰ of the corresponding molecular ions.⁸ The oxiran and acetaldehyde ions are distinguishable by c.a.m.s.¹¹ However, the conclusive discrimination between the possible C_2H_4O isomers is strongly facilitated by a study of the unimolecular metastable ion spectra.¹² In the present case DADI (Direct Analysis of Daughter Ions) spectra of the molecular ion (*m/z* 44) of oxiran and acetaldehyde, obtained by 70 eV electron impact ionization, have been applied.

RESULTS

The thermolyses of compounds (2) and (3) have been studied by the flash vacuum thermolysis-field ionization mass spectrometry (f.v.t.-f.i.m.s.) technique⁸ in the temperature range from 1 043 to 1 404 K.

In Figure 1 the f.i.m.s. spectra recorded after thermolysis of the monothiosulphite (2) (*M* 124) at 1 043, 1 253, and 1 404 K, respectively, are shown. Based on these spectra and by comparison (c.a.m.s. or DADI, *cf.* Experimental section) with authentic samples, the following products have been identified: ethylene (4) (*M* 28), formaldehyde (5) (*M* 30), keten (6) (*M* 42), acetaldehyde (7) (*M* 44), and thiiran (ethylene sulphide) (8) (*M* 60).

In recent years several authors have reported on the gas-phase thermolysis of thiiran 1-oxide.^{13,14} It was concluded that the main reaction was the extrusion of sulphur monoxide, affording ethylene in high yield. Additionally, Saito¹⁴ reported the formation of minor amounts of C_2H_4S ,

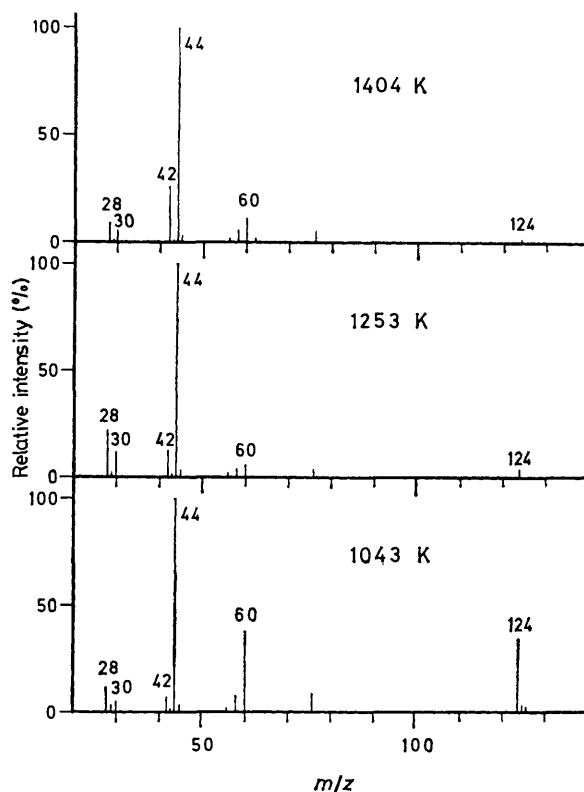


FIGURE 1 Field ionization mass spectra after gas-phase thermolysis of 1,2,3-oxadithiolan 2-oxide at 1 043, 1 253, and 1 404 K

C_2H_4O , and formaldehyde. It should, however, be emphasized that the thermolyses were carried out under conditions where bimolecular reactions certainly could not be excluded. The thermolysis of (3) under pure unimolecular conditions results, nevertheless, in a product composition qualitatively quite similar to that reported by Saito.¹⁴

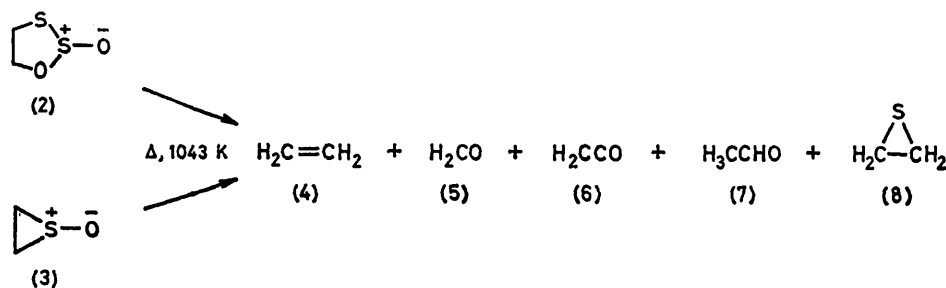


Figure 2 shows the product composition obtained after thermolysis of (3) at 1 043 K. The products are shown to be identical to those generated by thermolysis of (2).*

* It should be noted that the C_2H_4O isomer (M 44), unequivocally established by the DADI technique to be acetaldehyde, was reported by Saito¹⁴ as ethylene oxide. However, the present study revealed no evidence for the presence of ethylene oxide among the products.

Scrutiny of the spectra depicted in Figures 1 and 2 reveals the presence of a peak at m/z 76. In the case of (3) the peak was *a priori* assigned to undecomposed sulphoxide. However, careful c.a.m.s. analyses disclosed that in both the case of (2) and (3) the correct assignment of m/z 76 was carbon disulphide. The appearance of CS_2 among the reaction products seems rather obscure, but the authors are convinced that catalytic effects on the hot surface in the reactor play an important role.†

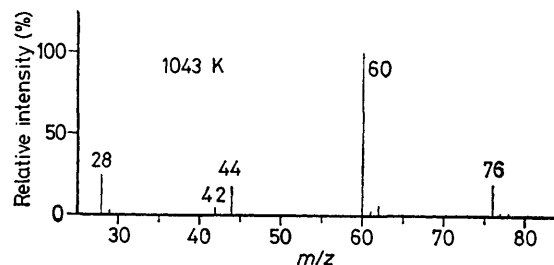


FIGURE 2 Field ionization mass spectrum after gas-phase thermolysis of thiiran 1-oxide at 1 043 K

In addition, it should be emphasized that c.a.m.s. analyses of the m/z 76 peak following thermolyses of (3) at temperatures between 631 and 1 043 K showed, besides an increasing amount of carbon disulphide, only unchanged (3). No signals corresponding to a contribution of other possible C_2H_4OS isomers, *e.g.* the sulphenate (1), to the peak m/z 76 were observed.

DISCUSSION

The above reported product formation is discussed in terms of sulphoxide-sulphenate rearrangement, atomic oxygen extrusion, and sulphur mono- or di-oxide elimination. The latter reaction, however, cannot be distinguished from an atomic oxygen extrusion consecutively accompanied by a rapid sulphur monoxide elimination, as the f.i.m.s. technique does not enable us to verify the possible existence of small inorganic fragments such as O, S, and SO † among the reaction products.⁸

The presence of an atomic oxygen extrusion reaction is obvious in the case of thiiran 1-oxide (3), resulting in the

formation of a considerable amount of thiiran (8) (M 60) (*cf.* Figure 2). We have previously reported extrusions of atomic oxygen from organic S-oxides;^{3,4,15} however,

† Tentatively it is suggested that sulphur monoxide is involved, since we have not been able to detect SO, obviously eliminated at least from (3), by normal 70 eV electron impact mass spectrometry.

rupture of the semipolar S-O bond apparently requires *ca.* 90 kcal mol⁻¹,¹⁶ which may suggest that surface catalytic effects are operating by this reaction. Evidence for an analogous reaction in the case of (2), which apparently would result in formation of 1,2,3-oxadithiolan, is not obtained, since no signal corresponding to the latter (*M* 108) was detected. Thus, we conclude that, if formed, the 1,2,3-oxadithiolan exhibits a half-life < *ca.* 1 ms under the actual conditions used.⁸ However, a rapid series of consecutive reactions, the primary one being a sulphur extrusion from 1,2,3-oxadithiolan, cannot be excluded.

Apart from the ethylene formation from (3), by SO extrusion, (4) may additionally originate from ethylene sulphide (8). Thermolysis of (8) at 1 043 K revealed nearly quantitative ethylene formation which led us to suggest that formation of the latter by thermolysis of (2) most probably appears as a secondary product originating from primarily generated thiiran (8), the latter being a result of sulphur dioxide elimination from (2).

We shall now turn to a discussion of the formation of keten and acetaldehyde. It has previously been reported that sulphoxides that do not possess β -hydrogens can be rearranged thermally into the corresponding sulphenate, the latter consecutively fragmenting into a thiol and a carbonyl compound.^{3,17} In the case of (3) a sulphoxide-

sulphenate rearrangement evidently would result in the formation of the unknown 1,2-oxathietan (1). On the other hand, a chelotropic elimination of sulphur monoxide from the monothiosulphite (2) analogously would lead to (1).

As mentioned above, we have not been able to detect any product with molecular weight *M* 76, corresponding to C₂H₄OS, other than thiiran 1-oxide (1). It is, however, obvious that (1) formed under the present reaction conditions will be generated in a vibrational excited state. Analogous to 1,2-oxathiolan^{2,3} it is highly likely that the vibrational relaxation of (1) will lead to a quantitative degradation of the latter. This indicates that, if formed, (1) exhibits a half-life < *ca.* 10⁻³ s under the actual reaction conditions.⁸

Formation of keten (6) and acetaldehyde (7) by rearrangements and/or fragmentations directly from both (2) and (3) can be explained only in terms of highly speculative mechanisms, whereas a straightforward rationalization is possible assuming the common intermediacy of 1,2-oxathietan (1).

Drawing a parallel to the previously reported thermal decomposition of 1,2-oxathiolan^{2,3} the first step on the decomposition path for (1) is suggested to be a ring opening to mercaptoacetaldehyde (9), consequently followed by loss of sulphur and hydrogen sulphide to give acetaldehyde and keten, respectively. It has been reported that mercaptoacetaldehyde (9) is generated by cracking the corresponding dimer 2,5-dihydroxy-1,4-dithian.¹⁸ Smooth cracking of the latter *in vacuo* followed by flash vacuum thermolysis of the generated (9) indeed affords a mixture of (6) and (7) (Figure 3), the (6) : (7) intensity ratio being qualitatively in accord with those observed following thermolysis of (2) and (3), respectively.

With this background we rationalize the unimolecular gas-phase thermolyses of (2) and (3) as visualized in the Scheme, taking the above results into account for the intermediacy of (1). Although cumulative evidence for the intermediacy of (1) in the gas-phase thermolyses of 1,2,3-oxadithiolan 2-oxide and thiiran 1-oxide is high a direct experimental verification under such conditions does not seem feasible.

Finally the appearance of formaldehyde (5) shall be discussed. The unimolecular decomposition of 1,2-dioxetans affords the formation of two carbonyl compounds,¹⁹ in general as the only products. By analogy to this it might have been expected that 1,2-oxathietan would lead to formaldehyde and thioformaldehyde, at least to a reasonable extent. However, only very minor amounts of formaldehyde are detected, and it is believed that thioformaldehyde formed in equimolar amounts may well have escaped detection owing to a lower sensitivity of the latter relative to formaldehyde. It is generally assumed that the first step in the case of decomposition of 1,2-dioxetans is a homolytic cleavage of the O-O bond. The driving force in the consecutive cleavage of the carbon-carbon bond to form the two carbonyl compounds may well be the high energy gain by generation of the carbon-oxygen double bonds. In

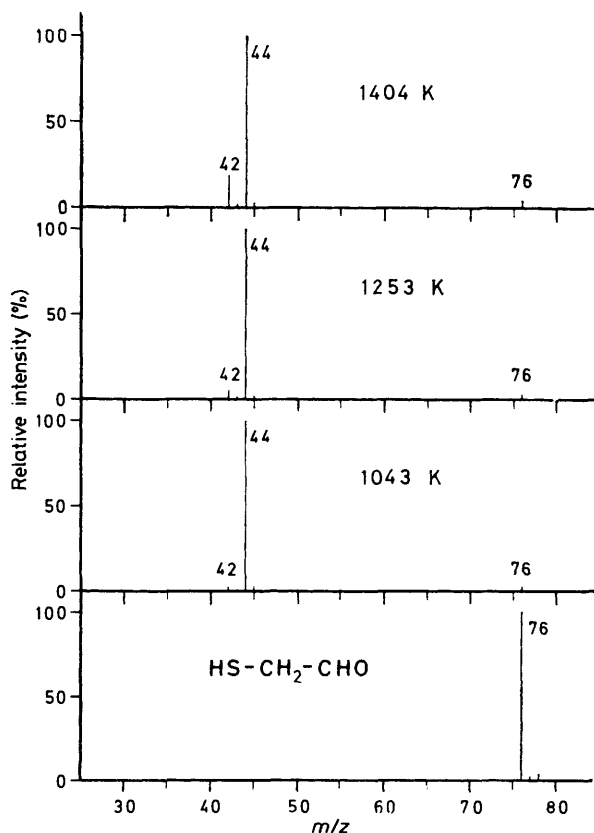
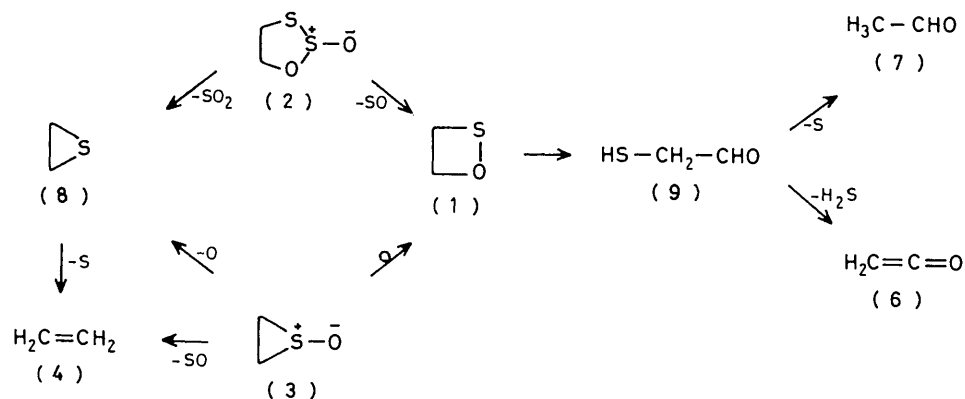


FIGURE 3 Field ionization mass spectra of mercaptoacetaldehyde before thermolysis and after gas-phase thermolysis at 1 043, 1 253, and 1 404 K



SCHEME

the case of (1) a similar decomposition pathway would be accompanied by a smaller energy gain. In addition, the rearrangement may be strongly facilitated in the monosulphur case, leading to (9), due to steric effects, the size of the sulphur atom apparently minimizing the strain in the transition state.

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REFERENCES

- ¹ For Part 6 see ref. 2b; for Part 5 see L. Carlsen, H. Egsgaard, and P. Pagsberg, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1256; for Part 4 see ref. 3.
- ² (a) G. H. Whitham and A. P. Davis, *J. Chem. Soc., Chem. Commun.*, 1981, 741; (b) L. Carlsen, H. Egsgaard, G. H. Whitham, and D. N. Harpp, *ibid.*, p. 742.
- ³ L. Carlsen, H. Egsgaard, and D. N. Harpp, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1166.
- ⁴ L. Carlsen, H. Egsgaard, and E. Schaumann, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1206, and previous papers in the series 'Oxathiirans.'
- ⁵ D. C. DeJongh, R. Y. Van Fossen, and A. Dekovich, *Tetrahedron Lett.*, 1970, 5045; D. C. DeJongh and R. Y. Van Fossen, *J. Org. Chem.*, 1972, **37**, 1129; D. C. DeJongh and M. L. Thomson, *ibid.*, p. 1135; C. Wentrup, *Tetrahedron Lett.*, 1973, 2919.
- ⁶ H. C. F. Su, C. Segebarth, and K. C. Tsou, *J. Org. Chem.*, 1961, **26**, 4993.
- ⁷ K. Kondo and A. Negishi, *Tetrahedron*, 1971, **27**, 4821.
- ⁸ L. Carlsen and H. Egsgaard, *Thermochim. Acta*, 1980, **38**, 47.
- ⁹ H. D. Beckey, 'Field Ionization Mass Spectrometry,' Pergamon, New York, 1971.
- ¹⁰ K. Levsen and H. D. Beckey, *Org. Mass Spectrom.*, 1974, **9**, 570.
- ¹¹ C. C. Van de Sande and F. W. McLafferty, *J. Am. Chem. Soc.*, 1975, **97**, 4613.
- ¹² J. G. Pritchard, *Org. Mass Spectrom.*, 1974, **8**, 103.
- ¹³ G. E. Harzell and J. N. Paige, *J. Am. Chem. Soc.*, 1966, **88**, 2616.
- ¹⁴ S. Saito, *Tetrahedron Lett.*, 1968, 4961.
- ¹⁵ L. Carlsen, H. Egsgaard, E. Schaumann, and J. Ehlers, *Chem. Ind. (London)*, 1979, 851.
- ¹⁶ S. W. Benson, *Chem. Rev.*, 1978, **78**, 23.
- ¹⁷ W. Carruthers, I. D. Ertwisle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind. (London)*, 1966, 342; D. B. Barnard-Smith and J. F. Ford, *Chem. Commun.*, 1965, 120.
- ¹⁸ M. Thiel, F. Asinger, and K. Schmiedel, *Liebigs Ann. Chem.*, 1958, **611**, 121.
- ¹⁹ K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J.-Y. Ding, *Can. J. Chem.*, 1975, **53**, 1103; W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, *J. Am. Chem. Soc.*, 1974, **96**, 7525 and references cited therein.