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Thermal Decomposition of 1,2-Oxathiolane in the Gas Phase[1)]

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The cyclic sulfenic ester 1,2-oxathiolane (**1**) decomposes thermally (400 – 450 K) exclusively to give acrolein (**3**) *via* 3-mercaptopropanal (**2**) by loss of hydrogen sulfide. Isotopic labelling experiments reveal the presence of a 1,2-oxathiolane-thietane 1-oxide equilibrium (**1** ⇄ **4**).

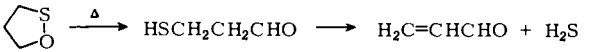
Thermischer Zerfall von 1,2-Oxathiolan in der Gasphase[1)]

Der cyclische Sulfensäureester 1,2-Oxathiolan (**1**) zersetzt sich thermisch (400 – 450 K) über 3-Mercaptopropanal (**2**) unter Verlust von H_2S ausschließlich zu Acrolein (**3**). Experimente mit isotopenmarkierten Verbindungen weisen auf ein 1,2-Oxathiolan-Thietan-1-oxid-Gleichgewicht (**1** ⇄ **4**).

In recent papers we reported the decomposition of the simple five-membered cyclic sulfenate 1,2-oxathiolane (**1**) in the gas phase under flash vacuum pyrolytic (FVP) conditions[1a-3)]. Acrolein (**3**) was found to be the major product[1a,2)]; however, a significant amount of allyl alcohol was supplementary observed[2,3)]. Formally, the products are formed by elimination of hydrogen sulfide and elemental sulfur, respectively. The present paper reports a study on the thermal decomposition of gaseous 1,2-oxathiolane[2)] in a static system in the temperature range 400 – 450 K (p(**1**) ≃ 0.1 Torr). The reactions were carried out in the thermostated gas-inlet system of a double focusing mass spectrometer, the progress of reactions being followed by field ionization (FI) and collision activation (CA) mass spectrometry[3,4,5)].

Results and Discussion

Thermolysis of the sulfenate **1** (M = 90) in the temperature range 400 – 450 K afforded, in contrast to the FVP studies, formation of acrolein (**3**) (M = 56) as the exclusive product (Fig. 1a).



1 **2** **3**

We have previously discussed the formation of **3** in terms of a primary rearrangement of **1** into 3-mercaptopropanal (**2**) (M = 90)[1a-3)] as sulfenates have been reported to decompose into a carbonyl compound and a mercaptane[6)], and since an identical decomposition pattern for **2** and **1** was observed[1,2)]. Also under the present conditions identical thermal behaviour of **1** and **2** was seen, *i. e.* **2** decomposes exclusively to acrolein (**3**). Thus, following the thermal decomposition of **1** by means of collisional activation (CA) mass spectrometry of the molecular ion m/z = 90, the intermediacy of

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2 in the thermal decomposition of **1** was clearly demonstrated by the appearence of a new set of signals in the CA mass spectrum as a function of time (Fig. 2). In Fig. 2b and c the CA mass spectra of the ion $m/z = 90$, present in the mass spectrum obtained after 35 and 50 min thermolysis, respectively, of **1** at 450 K are shown. Comparison with the CA mass spectra of the molecular ions of authentic 1,2-oxathiolane[2] (Fig. 2a) and 3-mercaptopropanal[7] (Fig. 2d) unambiguously lead to the assignment of the spectra in Fig. 2b and c as superpositions of the spectra in Fig. 2a and 2d, hence, demonstrating the intermediacy of **2**, the latter apparently being formed by intramolecular rearrangement of the sulfenate.

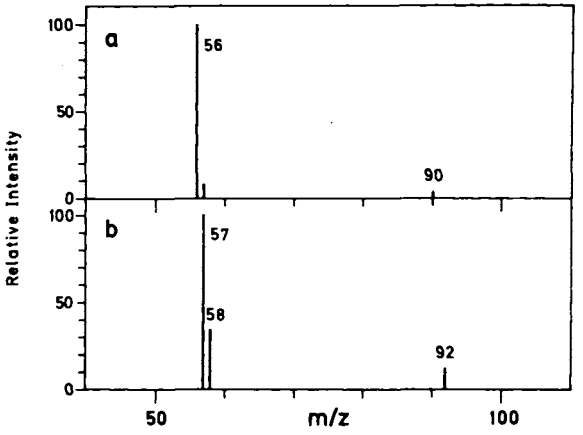
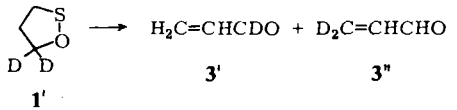


Fig. 1. Field Ionization Mass Spectra Obtained Following 25 min Thermolysis (425 K) of 1,2-Oxathiolane (**1**) (a) and [5,5-$^2H_2$]-1,2-Oxathiolane (**1'**) (b)

No data on the strength of the S – O single bonds in sulfenic esters have been reported. However, it seems reasonable to assume that the **1** → **2** rearrangement involves a S – O bond cleavage followed by transfer of one of the hydrogen atoms in the 5-position to the sulfur atom, **3** being consecutively generated by a 1,2-elimination of hydrogen sulfide. To obtain experimental verification on the actual mechanism we studied the thermal decomposition of the [5,5-$^2H_2$]-1,2-oxathiolane (**1'**). Thermolysis of **1'** (425 K) surprisingly gave rise to formation of two deuterium-labelled acroleins with molecular weights 57 and 58, corresponding to the presence of one and two deuterium atoms, respectively (Fig. 1b). The actual identity of the acroleins **3'** and **3''** was established by CAMS. In Fig. 4 the CA mass spectra of the field ionized molecular ions of the acroleins **3** ($m/z = 56$), **3'** ($m/z = 57$), and **3''** ($m/z = 58$), obtained by thermolysis of **1** and **1'**, respectively, are visualized. A predominant feature in the CA mass spectrum of **3** (Fig. 4c) appears to be the presence of an $[M - 1]^+$ ion, the hydrogen



1' **3'** **3''**

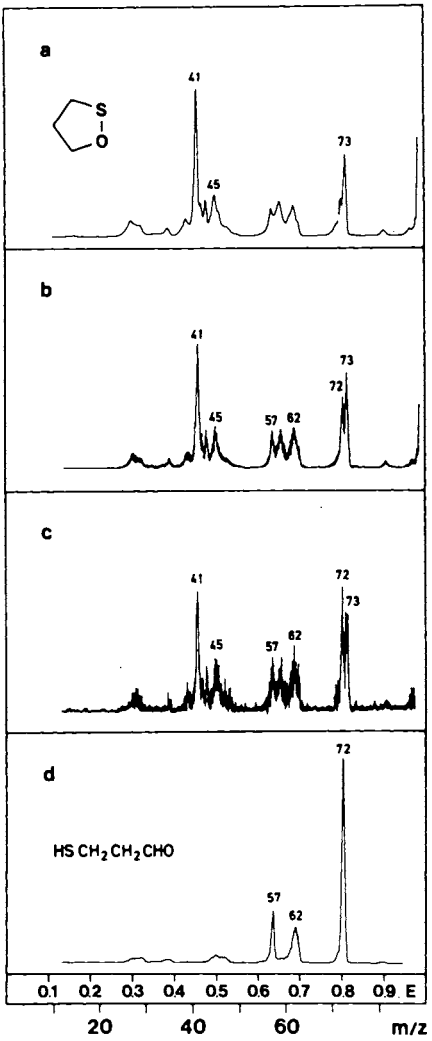


Fig. 2

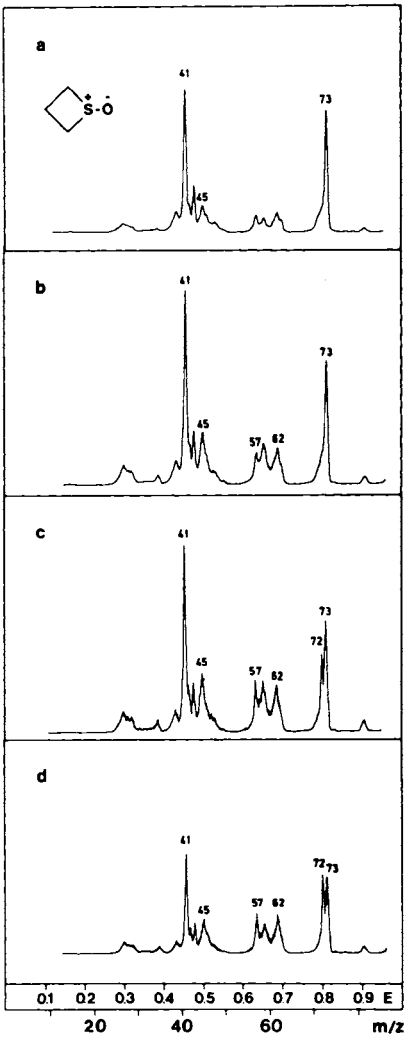


Fig. 3

Fig. 2 (left). Collision Activation Mass Spectra (CAMS) of the Electron Impact-Induced Molecular Ions of Authentic 1,2-Oxathiolane (**1**) (a) and 3-Mercaptopropanal (**2**) (d), and of the Ion m/z = 90 Obtained Following 35 (b) and 50 (c) min Thermolysis (450 K) of **1**, respectively

Fig. 3 (right). Collision Activation Mass Spectra (CAMS) of the Electron Impact-Induced Molecular Ions of Authentic Thietane 1-Oxide (**4**) (a) and of the Ion m/z = 90 Obtained Following 4 (b), 40 (c), and 80 (d) min Thermolysis (450 K) of **4**, respectively

being lost from the aldehyde group[8]. On this background the mono deuterium-labelled acrolein (**3'**) (Fig. 4b) immediately can be identified as [1-^{2}H]acrolein, since an $[M - 2]^+$ ion was detected. By analogy, it is obvious that the double labelled species **3''** does not exhibit deuterium labelling in the aldehyde function. A detailed study on

the CA fragmentations (Fig. 4, central sections) does not disclose the identity of **3''**, as both the [3,3-$^2H_2$]- and the [2,3-$^2H_2$] derivatives would give rise to the spectrum depicted in Fig. 4a. However, formation of [2,3-$^2H_2$]acrolein has to be a result of primary formation of 3-mercapto-[2,3-$^2H_2$]propanal, which by H_2S/HDS loss would lead to a mixture of [2,3-$^2H_2$]- and [3-^2H]acrolein, the latter, however, unequivocally being ruled out, as the only mono-labelled acrolein found (cf. Fig. 4b) exhibits the labelling in the aldehyde function (*vide supra*). Hence, we conclude that **3''** has to be assigned to [3,3-$^2H_2$]acrolein.

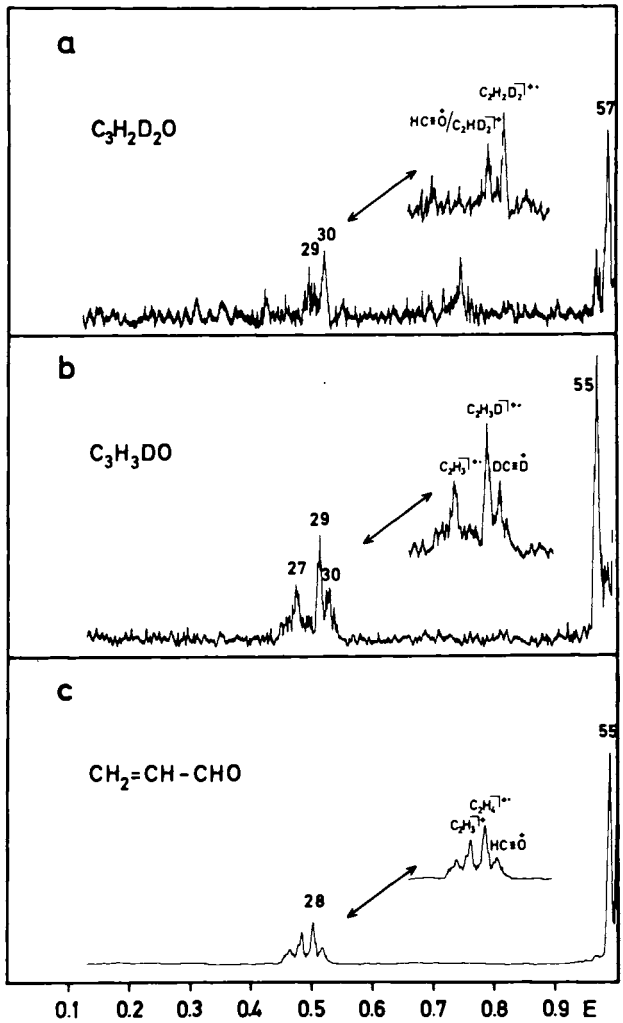


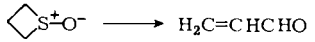
Fig. 4. Collision Activation Mass Spectra of the Field Ionized Molecular Ions of the Acroleins **3** (c), **3'** (b), and **3''** (a) Obtained Following Thermolysis of **1** and **1'**, respectively

Obviously, the apparent formation of the acroleins **3'** and **3''** from **1'** is a result of primary formation of the labelled 3-mercaptopropanals **2'** and **2''**, consecutively eliminating HDS and H_2S, respectively.

$$\underset{\mathbf{2'}}{DSCH_2CH_2CDO} \longrightarrow \underset{\mathbf{3'}}{H_2C{=}CHCDO} + HDS$$

$$\underset{\mathbf{2''}}{HSCD_2CH_2CHO} \longrightarrow \underset{\mathbf{3''}}{D_2C{=}CHCHO} + H_2S$$

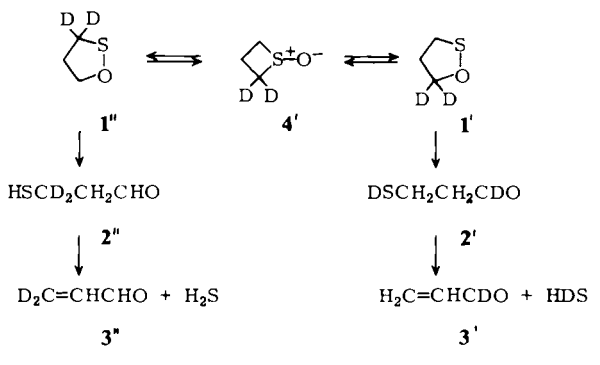
The formation of **3'** is in complete accord with the above proposed mechanism. On the other hand, the presence of **3''** among the reaction products is, by analogy, easily explained by decomposition of [3,3-$^2H_2$]-1,2-oxathiolane (**1''**), *i. e.* apart from the **1'** → **2'** → **3'** reaction, a **1'** ⇄ **1''** isomerization has to be taken into account. It has been reported that sulfenates may rearrange into sulfoxides[9], and in previous papers[1a,10] we reported on the thermally induced rearrangements of sulfoxides into sulfenates. Hence, it seems reasonable to formulate the **1'** ⇄ **1''** isomerization to proceed *via* the sulfoxide, [2,2-$^2H_2$]thietane 1-oxide (**4'**). Experimental verification was obtained by a study on the gas phase thermolysis of thietane 1-oxide (**4**) under conditions as described above. In Fig. 3 the CA mass spectra of $m/z = 90$ originating from **4** before thermolysis (a) and following thermolysis at 450 K for 4 (b), 40 (c), and 80 min (d), respectively, are depicted. Comparison of Fig. 3b and 2a strongly suggests the presence of considerable amounts of **1** in the reaction mixture responsible for the former spectrum, the significant ion being $m/z = 45$. Prolonged thermolysis (Fig. 3c and d) resulted in the characteristic change of $m/z = 73$ (loss of $^{\bullet}OH$) to $m/z = 72$ (loss of H_2O), the latter being accompanied by an increase in the relative intensity of $m/z = 57$. Both these fragments appear to be characteristic for the mercapto aldehyde **2** (cf. Fig. 2d). The eventual product in the thermal decomposition of **4** was exclusively found to be acrolein.



4 **3**

On the present background we are able to rationalize the thermal decomposition of the sulfenate **1** as illustrated in Scheme 1 by the thermolysis of **1'**.

Scheme 1



It should be noted that the here observed sulfenate-sulfoxide equilibrium to our knowledge is the first example of this type of reaction, which involves purely aliphatic species.

On the present knowledge no conclusions can be drawn on the actual pathway for the **1** → **2** rearrangement. However, we suggest that a 1,5-biradical is involved formed by homolytic cleavage of the S – O bond. Detailed studies, including kinetic measurements on this reaction, are left for separate investigations.

Experimental Part

3-(Phthalimidothio)-1-propanol and 3-(Phthalimidothio)-[1,1-$^2H_2$]-1-propanol were synthesized according to *Davis* and *Whitham*[11].

3-Mercapto-[1,1-$^2H_2$]-1-propanol: Under nitrogen 28 g (0.26 mol) of 3-mercaptopropanoic acid dissolved in 100 ml of dry THF was slowly added (ca. 2 h) to a slurry of 8.4 g (0.20 mol) of $LiAlD_4$ in 200 ml of dry THF. The resulting mixture was refluxed for 2 h. After cooling to 0°C D_2O (40 ml) was cautiously added (ca. 1 drop/5 s) to deactivate the complex. After completion of the deactivation the reaction mixture was filtered and the precipitate washed with 3 × 50 ml of THF. The combined THF-phase was dried (Na_2SO_4) and evaporated. The crude product (11.9 g) was purified by distillation: b.p. 86 – 87°C/14 Torr (lit.[12] 87°C at 14 mmHg), yield 5.7 g (23%).

A substantial amount of the corresponding 3-mercaptopropanal oligomer was obtained as by-product, owing to the rapid oligomerization of intermediary 3-mercaptopropanal in the reduction (cf. ref.[13]).

The *1,2-oxathiolanes* **1**, **1'** were prepared in the gas phase by smooth cracking (*in vacuo*) at about 80 – 100°C of the corresponding phthalimidothiopropanols. The gaseous sulfenates were collected directly in the thermostated gas-inlet system (2000 ml, $p \approx 10^{-1}$ Torr, T 400 – 450 K) of the mass spectrometer, which acted as reaction vessel in the thermolysis experiments.

Authentic *3-mercaptopropanal* (**2**) was prepared by smooth cracking *in vacuo* (≈ 100°C) of the corresponding oligomer, which was synthesized as described previously by *Schnabel* et al[13] (cf. also ref.[7]).

Mass Spectrometry: Varian MAT CH 5 D double focusing mass spectrometer with combined EI/FI/FD ion source. FI-spectra: 10 µm tungsten wire, activated in benzonitrile vapour, as emitter. In the MS/MS analyses the primary ions were selected at a resolution of ca. 500 and collisionally activated in the second field free region by means of a molecular He-gas beam. The CA mass spectra are obtained under identical conditions (*i. e.* energy resolution, collision gas pressure) and are uncorrected for contributions of unimolecular fragmentation processes. The application of FI and CA mass spectrometry as analytical procedure for gas phase reactions has been described in detail previously[3,4].

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[5] Field ionization gives in general rise to molecular ions only. The fragmentation pattern observed by CA induced decomposition closely resembles that observed by electron impact induced decompositions (cf. ref.[3]).

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[7] The identity of **2** was established by IR spectroscopy (*L. Carlsen, H. Egsgaard, F. S. Jørgensen*, and *F. M. Nicolaisen*, J. Chem. Soc., Perkin Trans. 2, in pkss). The possible presence of the isomeric species, 1-thietanol (*Givaudan, L., et Cie. S. A.* (inv.: *P. Dubs, H. Küntzel*, and *M. Pesaro*), Ger. Offen. 2, 314, 103 (18. Oct. 1973) [Chem. Abstr. **80**, 14833n (1974)]), can be excluded, at least in the actual temperature range, since calculation of the heat of formation of the two isomers, cf. *S. W. Benson*, Thermochemical Kinetics, 2nd ed., Wiley, New York 1976, revealed that 3-mercaptopropanal is the more stable isomer by ca. 15 kcal mol^{-1}.

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