

# Gas Phase Reactivity of Cation Radicals and Protonated Species from Isomeric C<sub>4</sub>H<sub>8</sub>S Thioethers

C. Paradisi\* and A. Visentini

Centro Studio Meccanismi Reazioni Organiche del CNR,  
Via Marzolo 1, 35131 Padova, Italy

P. Traldi\*

Area di Ricerca del CNR, Corso Stati Uniti 4,  
35100 Padova, Italy

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Four isomeric thioethers, 2,3-dimethylthiirane (**1**), 2-methylthietane (**2**), tetrahydrothiophene (**3**), and allyl methyl thioether (**4**), have been subjected to mass spectrometric analysis in the gas phase, under electron impact (EI) and chemical ionization (CI) conditions. The metastable molecular ions M<sup>+</sup> generated from **1-4** under EI (70 eV) conditions give distinct patterns of unimolecular fragmentation, thus indicating that isomer interconversion reactions are slower than dissociation (a possible exception, to some extent, is the case of [M<sub>2</sub>]<sup>+</sup> and [M<sub>3</sub>]<sup>+</sup>). The change of the relative intensities of some prominent peaks with increasing ion lifetime (decomposition within the ion source, the first, and the second field-free regions of the mass spectrometer) is pointed out. Metastable [MH]<sup>+</sup> ions, generated from **1-4** in chemical ionization experiments with CH<sub>4</sub>, all eliminate H<sub>2</sub> and H<sub>2</sub>S, although in different relative proportions. In addition to these processes protonated **4** also undergoes loss of C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, likely from a C-protonated structure.

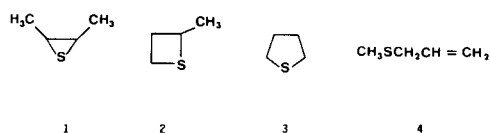
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## Introduction.

There is at present considerable interest in organosulfur ions in the gas phase, resulting both in fundamental studies, aimed at the determination of structures, reactivities and relevant thermochemical quantities, and in analytical applications. Several cyclic thioethers (CH<sub>2</sub>)<sub>n</sub>S (n = 2,3,4,...) have been examined under electron impact (EI) [1] and chemical ionization (CI) [2] conditions, and their characteristic fragmentation pathways have been described [1-4]. The compounds with n = 2-4 have also been investigated in a photoionization study from which the heats of formation of several organosulfur cations were derived [5]. In previous work with [C<sub>2</sub>H<sub>3</sub>S]<sup>+</sup> [6] and [C<sub>4</sub>H<sub>7</sub>S]<sup>+</sup> [7] ions we have observed that fast isomerization processes precede fragmentation of these closed-shell cationic species. In order to extend this investigation to odd electron species, we have examined the molecular ions, generated under EI conditions, of isomeric C<sub>4</sub>H<sub>8</sub>S thioethers of different ring-size. This report also describes the behavior of the thioethers conjugated acids [C<sub>4</sub>H<sub>9</sub>S]<sup>+</sup> obtained in chemical ionization experiments.

## Results and Discussion.

The compounds examined in this study are four isomeric C<sub>4</sub>H<sub>8</sub>S thioethers, 2,3-dimethyl thiirane (mixture of *cis* and *trans* isomers) (**1**), 2-methyl thietane (**2**), tetrahydrothiophene (**3**), and allyl methyl thioether (**4**):



The molecular ions of **1-4** decomposing in the ion source appear, in general, to maintain characteristic structural features. Thus, in accord with published data [8], the 70 eV EI mass spectra, partially reported in Table 1, consist mainly of the same peaks but differ substantially in the peak relative intensities. This is particularly true for compounds **1**, **4**, and **2-3**, the latter two being more closely similar. Compounds **1** and **4** are characterized by the presence of very abundant ions at m/z 59 [M-C<sub>2</sub>H<sub>5</sub>]<sup>+</sup> and 55 [M-HS]<sup>+</sup>, and m/z 73 [M-CH<sub>3</sub>]<sup>+</sup>, respectively. Noteworthy is the presence of the peak at m/z 73, in the mass spectrum of tetrahydrothiophene, which implies fragmentation of a molecular ion in a structural configuration different from that of the neutral precursor, likely an acyclic one.

Previous work with small sulfur-containing ions has demonstrated that interconversion among structurally distinct isomeric forms can readily take place prior to fragmentation [6,7]. We thought it of interest to study the behavior of the molecular ions of compounds **1-4** by analyzing their unimolecular dissociations (B/E and MIKE experiments, [9]) and their collisionally induced dissociations (CA experiments, [10]). In all of these experiments only those ions are sampled which survive decomposition within the ion source and which have, therefore, relatively low internal energies and long life-times. For these ions, isomerization reactions can compete with fragmentation processes [11]. A minor fraction of these ions possesses sufficient internal energy to undergo *unimolecular* decomposition prior to reaching the detector. The B/E = constant linked scans of M<sup>+</sup> produce a spectrum of the unimolecular fragmentations occurring in the first field free region (IFFR) of a double focussing mass spectrometer (time win-

Table 1

Data Relative to the Fragmentation of  $C_4H_9S^+$  Species from Precursors 1-4 in the Ion Source (I.S.) [a], in the I FFR (I), and in the II FFR (II) [b]

Ionic Species	m/z	Neutral Precursor											
		1		2		3		4					
		I.S.	I	II	I.S.	I	II	I.S.	I	II	I.S.	I	II
$M^+$	88	28	—	—	35	—	—	21	—	—	44	—	—
$[M-H]^+$	87	<1	5	1	1	6	1	6	3	3	3	1	1
$[M-2H]^+$	86	<1	6	1	<1	1	1	<1	5	5	<1	—	—
$[M-CH_3]^+$	73	4	22	2	5	32	46	2	14	21	41	72	68
$[M-H-CH_3]^+$	72	—	2	—	—	7	10	—	3	5	3	18	18
$[M-C_2H_4]^+$	60	12	27	17	34	25	25	43	20	19	2	6	8
$[M-C_2H_5]^+$	59	26	16	7	7	3	1	11	2	—	3	—	—
$[M-C_2H_6]^+$	58	2	2	3	2	—	—	5	—	—	3	—	—
$[M-HS]^+$	55	21	7	9	9	4	2	6	3	3	1	1	2
$[M-H_2S]^+$	54	6	13	60	5	22	15	5	50	44	—	2	3

[a] Selected ions. [b] Abundances relative to the sum of all fragments, including  $M^+$  in the I.S. column.

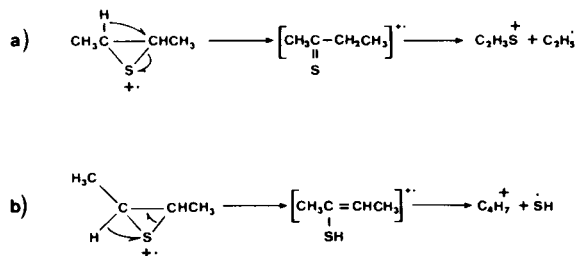
dow,  $10^{-6}$  seconds). The mass analyzed ion kinetic energy (MIKE) spectra originate from unimolecular fragmentations which take place in the second field free region of a double focussing mass spectrometer of reversed geometry (II FFR, time window,  $5 \times 10^{-6}$  seconds). Oftentimes, the comparisons of B/E and MIKE spectra can yield information on the kinetics of decomposition and on the occurrence of isomerization reactions.

Ion dissociation can be induced by means of collision with a neutral target [10]. In these experiments (CA) a much larger fraction of the ions escaping the ion source is sampled than in MIKE and B/E experiments. In the absence of collision gas the great majority of these ions would reach the detector without undergoing decomposition.

B/E and MIKE data for  $[M_1]^+ - [M_4]^+$  are reported in Table 1. It is evident that also the metastable  $M^+$  ions from the various precursors can be distinguished for their reactivity, with the possible exception of  $[M_2]^+$  and  $[M_3]^+$  which give, indeed, similar B/E and MIKE spectra. Let us consider the methyl loss from  $[M_3]^+$ . The relative abundance of the corresponding fragment ion (m/z 73) increases with the lifetime of the decomposing ion, from 2% to 14%, and to 21% for fragmentations occurring in the ion source, in the I FFR, and in the II FFR, respectively. This behavior is likely related to the kinetics for ring opening and isomerization of  $[M_3]^+$  to an ionic structure which can lose a methyl radical. We note that Franke and Schwarz [3] have shown that extensive reorganization of the carbon skeleton takes place in metastable  $[M_3]^+$  prior to  $C_2H_4$  elimination to form the thioacetaldehyde cation radical,  $[CH_3C(=S)H]^+$ .

Interestingly, while for  $[M_2]^+$  and  $[M_3]^+$  unimolecular loss of methyl is slightly more pronounced in the II FFR than in the I FFR, the opposite trend is found for  $[M_1]^+$ . Noteworthy is the predominant formation in the II FFR of the species  $[M-H_2S]^+$  which requires skeletal rearrangement and two H transfers. Also for the other unimolecular reactions of  $[M_1]^+$  clear differences are observed in the ion source, in the I FFR, and in the II FFR. In the II FFR, complex processes, such as the losses of  $C_2H_4$  and of  $H_2S$  prevail over relatively simpler ones, like the losses of  $C_2H_5$  and  $HS$ , respectively. Thus, it appears that ring-opening and molecular reorganization of metastable  $[M_1]^+$  have suitable rate coefficients to allow for the observation of distinct species in the I FFR and in the II FFR. Equations a) and b) in Scheme 1 show plausible mechanisms for the loss of  $C_2H_5$  and of  $HS$ , respectively. Elimination of  $C_2H_4$  and  $H_2S$  requires additional H-transfer steps.

Scheme 1



Most unimolecular fragmentations of  $[M_1]^+ - [M_3]^+$  are best explained as occurring from species of acyclic structure(s). The comparison of MIKE and B/E spectra of  $[M_1]^+ - [M_3]^+$  with those of  $[M_4]^+$  clearly indicates that the allyl-methyl thioether skeleton is not the ultimate pro-

duct of these ring-opening reactions.

The daughter spectra of [M<sub>1</sub>]<sup>+</sup>, [M<sub>2</sub>]<sup>+</sup> - [M<sub>3</sub>]<sup>+</sup>, and [M<sub>4</sub>]<sup>+</sup> obtained by collisional activation, are distinct and characteristic (Figure 1). This is not surprising in view of the fact that their unimolecular MIKE spectra are different, *i.e.* since ionic species with sufficient internal energy to undergo unimolecular decomposition (MIKE) do not structurally interconvert, it is not to be expected that species with lower energy will do so. As is generally the case [10], the CA spectra contain more peaks than the MIKE spectra, including some (minor) at low *m/z* values, like those at *m/z* 45 (HCS<sup>+</sup>) and *m/z* 27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup>), the result of extensive fragmentation, possibly due to multiple collisions. As for the major peaks, a correspondence is observed between the MIKE and the CA spectra for each of the examined ionic species.

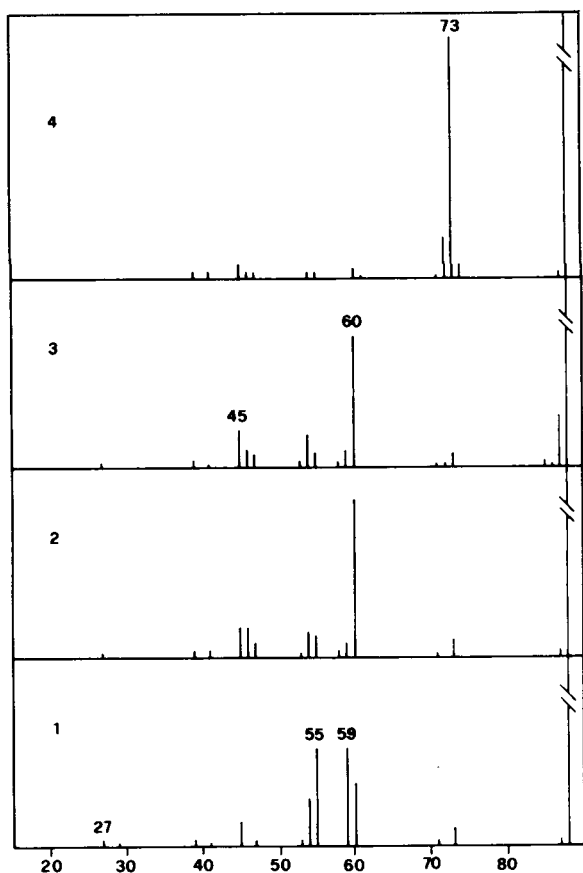


Figure 1. Daughter spectra of [M<sub>1</sub>]<sup>+</sup> - [M<sub>4</sub>]<sup>+</sup> (*m/z* 88) activated by 8 keV collisions with air.

The behavior of 1-4 has also been examined under CI conditions with CH<sub>4</sub> and NH<sub>3</sub> as reagent gases. In both cases protonation of all four compounds takes place readily. Thus, compounds 1-4 are more basic than NH<sub>3</sub> (PA = 853 kJ mole<sup>-1</sup>) [12]. The only available proton affinity data for C<sub>4</sub>H<sub>6</sub>S compounds, that for tetrahydrothiophene (PA = 856 kJ mole<sup>-1</sup>) [13], is in accord with these observations.

With a specific interest in the possible occurrence of acid catalyzed isomerization processes, we have examined the MIKE spectra of the four protonated [MH]<sup>+</sup> species. The results of these experiments, with CH<sub>4</sub> as reagent gas, are reported in Table 2. All [MH]<sup>+</sup> examined undergo unimolecular elimination of H<sub>2</sub> and H<sub>2</sub>S, although in somewhat different relative proportions. In addition to these processes, protonated methyl allyl thioether (4) undergoes also unimolecular elimination of C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>. These reactions are most likely explained as resulting from the C-protonated species, as shown in Scheme 2. Compound 4, indeed, contains two centers of likely comparable basicity, the sulfur atom and the C=C double bond (a rough indication that this is so comes from the comparison of PA data for tetrahydrothiophene, 856 kJ mole<sup>-1</sup> [13] and for cyclopentene, 827 kJ mole<sup>-1</sup> [12], respectively).

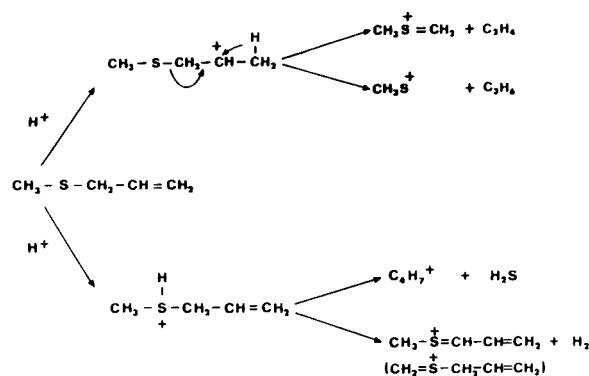
Table 2

Unimolecular Fragmentations in the II FFR of MH<sup>+</sup> Ions (C<sub>4</sub>H<sub>6</sub>S<sup>+</sup>, *m/z* 89) Produced from Compounds 1-4 in CI(CH<sub>4</sub>) Experiments [a]

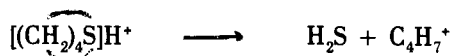
Precursor	Ionic Products, <i>m/z</i> (neutral lost)			
	87 (-H <sub>2</sub> )	61 (-C <sub>2</sub> H <sub>4</sub> )	55 (-H <sub>2</sub> S)	47 (-C <sub>3</sub> H <sub>6</sub> )
1	9	—	91	—
2	41	—	59	—
3	20	—	80	—
4	12	42	39	7

[a] Abundances relative to the sum of all fragments.

Scheme 2



The [MH]<sup>+</sup> species obtained from 1-4 in CI experiments with ammonia gave MIKE spectra in which no peaks due to fragment ions could be detected. This is due to the fact that with the weaker acid NH<sub>4</sub><sup>+</sup>, [MH]<sup>+</sup> ions are produced of lower internal energy, equal, at most, to the ΔH for the proton transfer reaction *i.e.* about 3 kJ mole<sup>-1</sup>. This excess energy is insufficient to overcome the barriers for fragmentation. The H<sub>2</sub>S elimination from protonated tetrahydrothiophene, for which thermochemical data is available, can be taken as an example.



The reaction is endothermic by 279.4 kJ mole<sup>-1</sup> [14], which represents the lowest possible activation barrier. The reaction is observed in CI(CH<sub>4</sub>) experiments which generate [MH]<sup>+</sup> ions with ca. 304 kJ mole<sup>-1</sup> excess energy [17], but not in CI(NH<sub>3</sub>) experiments in which the excess energy is only 3 kJ mole<sup>-1</sup>.

#### Conclusions.

In contrast with the behavior of metastable [C<sub>4</sub>H<sub>7</sub>S]<sup>+</sup> ions, which, generated from structurally different neutral precursors, undergo ready isomerization to a common structure(s) prior to fragmentation [7], the [C<sub>4</sub>H<sub>7</sub>S]<sup>+</sup> species examined in this study produce distinct spectra (with the possible exception of the molecular ions of **2** and **3**) as a result of unimolecular decomposition. Structural differences are confirmed by the results of collision experiments. [MH]<sup>+</sup> ions formed *via* protonation of the four thioethers **1-4** under CI conditions with CH<sub>4</sub> all undergo unimolecular H<sub>2</sub> and H<sub>2</sub>S losses, although in different relative proportions. In addition to these reactions, protonated allyl-methyl thioether undergoes unimolecular loss of C<sub>2</sub>H<sub>4</sub> and of C<sub>3</sub>H<sub>6</sub>. It is suggested that protonation of this substrate takes place both on S and on C, each leading to specific fragmentation reactions.

#### EXPERIMENTAL

Commercial samples of tetrahydrothiophene (**3**) and allyl methyl thioether (**4**) were distilled before use. 2,3-Dimethylthiirane (**1**) [18] and 2-methylthietane (**2**) [19] were prepared and purified according to published procedures.

All measurements were performed on a VG ZAB-2F instrument with the same source operated in the EI mode (70 eV, 200 μA) or in the CI mode (100 eV, 2 mA). The source temperature was 200° and the samples were introduced *via* septum inlet heated at 150°. In CI experiments the pressure in the ion source, as monitored by a Pirani head directly mounted on one insertion port of the source itself, was kept constant for all experiments at 0.5 Torr. Under these conditions the ratio M<sup>+</sup>/MH<sup>+</sup> for CH<sub>4</sub> and NH<sub>3</sub> was in the range of 0.3-0.5 [20]. The CA spectra were obtained by col-

lisions of 8 keV ions with air in the second field-free region. The pressure in the collision cell was such as to reduce the main beam intensity to 60% of its usual value.

#### REFERENCES AND NOTES

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