# Structure and Fragmentation Mechanism of $[C_3H_7S]^+$ Ions

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From a comparison of the metastable ion abundance ratios for loss of  $C_2H_4$  and  $H_2S$  from  $[C_3H_7S]^+$  ions in a series of alkyl thio ethers and thiols it was concluded that in most compounds these ions isomerize to a common structure prior to decomposition in the first field free region. The mechanism for  $C_2H_4$  loss from the  $[C_3H_7S]^+$  ion generated from  $CH_3SCH_2CH_3$  was investigated in detail using <sup>13</sup>C and <sup>2</sup>H labelling. A rearrangement with formation of a cyclic intermediate prior to the decomposition reaction is proposed. The fragmentation is preceded by extensive hydrogen scrambling. The carbon atoms of the expelled  $C_2H_4$  molecule are those of the  $CH_2=CH_3$  molety.

A knowledge of the structure of ions present in a mass spectrometer is of great importance for an understanding of the processes occurring in the instrument. Information about ion structures can be obtained by several methods, among which determination of metastable ion characteristics and labelling with isotopes are particularly important.<sup>1</sup> Ions from many classes of compounds have already been investigated and considerable knowledge of the structures and the fragmentation mechanisms of these ions has been obtained. Detailed studies have been made of the properties of  $[C_3H_7O]^+$ ions,<sup>2,3</sup> generally formed by fragmentation of aliphatic alcohols and ethers, and of  $[C_3H_8N]^+$  ions<sup>4</sup> observed in the mass spectra of amines. The metastable ion characteristics of  $[C_3H_7O]^+$  ions with nominal structure [CH<sub>3</sub>CH<sub>2</sub>O<sup>+</sup>=CH<sub>2</sub>], [CH<sub>2</sub>)<sub>2</sub>C=OH]. [CH<sub>3</sub>CH<sub>2</sub>CH=OH] and [CH<sub>3</sub>O<sup>+</sup>=CHCH<sub>3</sub>] were found to be distinctive,<sup>2</sup> although it was shown that  $[CH_3O^+=CHCH_3]$  isometrizes to  $[CH_3CH_2O^+=CH_2]$ prior to decomposition.<sup>5</sup> Also in collisional activation spectra, these structures were identified as stable ions.<sup>3</sup> Williams et al.<sup>4</sup> concluded that of five groups of structurally distinct  $[C_3H_8N]^+$  ions, viz.  $[CH_2^+ - NHCH_2CH_3]$  (*a*),  $[(CH_3)_2C^+ - NH_2]$ (b), $[CH_3CH_2CH^+-NH_2]$  (c),  $[CH_3CH^+-NHCH_3]$  (d) and  $[(CH_3)_2NCH_2^+](e)$ , the ions of types b and c and also of d and e decompose from identical structures and ions of type a constitute a third group. By means of <sup>2</sup>H and <sup>13</sup>Č labelling it was shown that in many ions hydrogen scrambling and carbon skeletal rearrangements occur prior to fragmentation.

Until now, few systematic studies have been made of small sulfur containing ions. In this paper we present some results obtained for  $[C_3H_7S]^+$  ions. Ions with general structure  $[C_nH_{2n+1}S]^+$  are commonly observed in the mass spectra of aliphatic thiols, sulfides and related compounds.<sup>6</sup> A comparison with the analogous  $[C_3H_7O]^+$  and  $[C_3H_8N]^+$  ions shows the effect of the heteroatom on isomerization and fragmentation reactions.

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# **RESULTS AND DISCUSSION**

## Metastable ion abundance ratios

The metastable ion abundance ratios for loss of  $C_2H_4$ and  $H_2S$  from the  $[C_3H_7S]^+$  ions in the series of compounds investigated are given in Table 1. Analogous to the stable ions identified for the corresponding oxygen and nitrogen containing ions the following stable  $[C_3H_7S]^+$  ions might be expected in these compounds:



It appears that  $[C_3H_7S]^+$  ions from the compounds 2-9, independent of their initial structure, show a metastable ion intensity ratio  $m_{C_2H_4}^*/m_{H_2S}^* = 0.59 \pm 0.10$ . If we employ the criterion of metastable ion abundance ratios as an indication of structural identity,<sup>8</sup> it appears likely that all these  $[C_3H_7S]^+$  ions decompose via a common intermediate. For ions generated from compound 1 the same fragmentations were observed but a somewhat different intensity ratio was measured, viz.  $m_{C_2H_4}^*/m_{H_2S}^* = 1.33$ . This difference does not necessarily indicate a different structure or mixture of

Table 1. Metastable ion intensity ratios for decomposition of  $[C_3H_7S]^+$  ions in the first field free region

	Neutral molecule	Decomposing ion	m <sub>C2H4</sub> /m <sub>H2S</sub>
1	CH <sub>3</sub> CH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub>	$[M - CH_3]^+$	1.33
2	CH <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$[M - CH_3]^+$	0.59
3	CH <sub>3</sub> SCH(CH <sub>3</sub> ) <sub>2</sub>	[M-CH <sub>3</sub> ] <sup>+</sup>	0.59
4	CH <sub>3</sub> SCH <sub>2</sub> CH <sub>3</sub>	[M-H] <sup>+</sup>	0.69
5	CH <sub>3</sub> SCH <sub>2</sub> CH <sub>2</sub> SCH <sub>3</sub>	$[M - CH_3S]^+$	0.54
6	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> SH	[MH]+	0.67
7	(CH <sub>3</sub> ) <sub>3</sub> CSH	$[M - CH_3]^+$	0.56
8	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )SH	[M-CH <sub>3</sub> ]+	0.64
9	(CH <sub>3</sub> ) <sub>2</sub> CHSH	[M-H]+	0.49

structures for the  $[C_3H_7S]^+$  ions of **1** as compared with those of **2–9**. As pointed out, small differences in the observed intensity ratios may reflect changes in internal energy distribution or indicate a slow isomerization reaction prior to decomposition rather than structural differences.<sup>2,5,9</sup>

On the other hand, it appears that also in labelling experiments the ions f behave differently from the ions

g upon loss of ethylene.  $[CD_2 = SCD_2CH_3](f_1)$  ions can be generated by loss of a methyl radical from  $[CH_3CD_2SCD_2CH_3]^{\dagger}$  [1a]. The measured intensities (normalized to a total of 100) for its metastable decompositions are:

$$[CD_2 \stackrel{+}{=} SCD_2 CH_3] \rightarrow C_2 H_2 D_2 + [CHD_2 S]^+ \qquad 80$$

$$\rightarrow C_2 H_3 D + [CD_3 S]^+ \qquad 10$$

$$\rightarrow C_2 D_3 H + [CH_2 DS]^+ \qquad 10$$

This product ratio is not random for any possible combination of H's and D's. The high percentage of  $C_2H_2D_2$  loss points to some fragmentation without a preceding scrambling process, supposing that the ethylene molecule is formed out of the original ethyl group. This can well be rationalized by assuming some decomposition of the unrearranged ion:

$$CD_2 = \overset{+}{S_{CD_2}} \xrightarrow{+} CD_2 \xrightarrow{+} CD_2 \xrightarrow{+} H + CH_2D_2$$
  
$$H - CH_2$$

This is in contrast with what is found for ions with the initial structure g (see below). Therefore the deviating metastable ion intensity ratio for compound **1** is most likely caused by decomposition(s) from a second  $[C_3H_7S]^+$  ion.

It may be concluded that  $[C_3H_7S]^+$  ions show a greater tendency towards rearrangement to a common structure than the comparable  $[C_3H_7O]^+$  and  $[C_3H_8N]^+$  ions. It is well known that ions of sulfur containing compounds in general readily rearrange in the mass spectrometer.<sup>10</sup>

# Labelling experiments for the loss of ethylene from $[CH_3S = CHCH_3]$

 $[C_3H_7S]^+$  ions mainly with the initial structure g, labelled with deuterium were generated from the specific-

ally labelled sulfides **3a** and **4a-4c** (Table 2). Hydrogen loss from compound **4** occurs principally from the  $\alpha$ -position of the ethyl group. The spectra of **4a** and **4c** show [M-H]/[M-D] ratios of 7.8 and 0.22, respectively. However, H/D exchange before the H/D loss may occur in the parent compounds, especially in the ethyl groups of **4b** and **4c**. Metastable decompositions of  $[M-D]^+$  ions of **4a** could not be detected. This indicates that for metastable ions the preference for hydrogen loss from the ethyl side is even greater than for normal ions.

The reaction studied here is the loss of ethylene from the labelled  $[C_3H_7S]^+$  ions in the first field free region. The observed label distribution for the thiomethoxy ions formed is given in Table 2. The intensities of the observed metastable transitions were normalized to a total of 100 for each type of ion.

From these results it is clear that H/D scrambling occurs before decomposition. The observed values can be compared with calculated intensity ratios assuming different degrees of scrambling. It appears that the observed values agree neither with complete scrambling of all hydrogen and deuterium atoms nor with scrambling of the atoms of the ethyl group only. Intensities as calculated for the case of complete scrambling of all hydrogen and deuterium atoms except one atom of the methyl group are given in Table 2. These values appear to be in good agreement with the observed intensities. A plausible interpretation is that before the scrambling process in the ion takes place, one of the hydrogen or deuterium atoms of the methyl group moves to a position where it is not involved in this process. Most probably this atom migrates to the sulfur atom of the ion.

In order to obtain more information about the mechanism of the scrambling reaction, the decomposition of a doubly labelled ion with structures  $[CD_3S = {}^{13}CH - CH_3]$  (g<sub>1</sub>) was also studied. It is formed by loss of a hydrogen atom from  $[CD_3S^{13}CH_2CH_3]^+$  (4d)<sup>†</sup>. When the ethylene is lost from this ion, the amount of H/D scrambling before fragmentation will, to a good approximation be the same as in IIa, so that also in g<sub>1</sub> complete scrambling of all hydrogen atoms and two deuterium atoms may be expected. The ratio of the various decomposition products can now be calculated for any fragmentation

<sup>†</sup> The incorporation of deuterium in this <sup>13</sup>C labelled sulfide was necessary for another study, in which the compound was also used as a precursor (to be published).

Table 2. Observed and calculated intensities of ions formed by loss of ethylene from  $[C_3H_7S]^+$  ions labelled with deuterium

	Neutral Molecule	ion investigated	[CH₃S] <sup>+</sup>	$[CH_2DS]^+$	[CHD <sub>2</sub> S] <sup>+</sup>	$[CD_3S]^+$	
3a	CD <sub>2</sub> SCH(CH <sub>2</sub> ) <sub>2</sub>	$[M - CH_3]^+$	1	33	59	6	obs
			0	40	53	7	calc
4a	CD <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub>	[M-H]+	1	36	56	7	obs
		• • • •	0	40	53	7	calc
4b	CH <sub>2</sub> SCD <sub>2</sub> CH <sub>2</sub>	[M-D]+	64	36	0	0	obs
			67	33	0	0	calc
4c	CD <sub>2</sub> SCD <sub>2</sub> CH <sub>2</sub>	$[M - D]^+$	0	19	62	19	obs
			0	20	60	20	calc

mode. The metastable ion intensities expected when the <sup>13</sup>C label is for 100% included in the expelled ethylene molecule are the same as observed for **4a** (cf. Table 2). The observed relative intensities for **4d** are:  $[CH_3S]^+$ , 1;  $[CH_2DS]^+$ , 35;  $[CHD_2S]^+$ , 57 and  $[CD_3S]^+$ , 7. As these values agree very well with those for **4a** (Table 2), it is concluded that the ethylene molecule formed upon fragmentation originates from the ethyl group.



A tentative mechanism in agreement with these observations is presented in Scheme 1. In analogy with what has been found for  $[C_2H_5S]^+$  ions,<sup>11</sup> a rearrangement with formation of a cyclic  $[C_3H_7S]^+$  ion (*j*) is suggested as a first step. In this ion one of the deuterium atoms originally located in the methyl group has moved to the sulfur atom and has so obtained a unique position. Scrambling of all other hydrogen and deuterium atoms may now occur in the propylene group. A fragmentation leading to loss of an ethylene molecule, preceded by a hydrogen shift, is a normal, well known  $\alpha$ -cleavage of the rearranged ion.

## **EXPERIMENTAL**

All measurements were carried out using an A.E.I. MS-902 mass spectrometer with a source temperature of 150 °C and an electron beam energy of 70 eV. Samples were introduced via an all-glass heated inlet system with a temperature of 120 °C. All compounds were thermally stable under the conditions of the experiments. The metastable ion intensities corresponding to fragmentation reactions in the first field free region were determined by means of the refocusing technique.<sup>7</sup> A number of measurements was carried out on an instrument equipped with a variable  $\beta$  slit.<sup>12</sup> All metastable intensities in this paper are an average of at least three measurements.

The unlabelled compounds were commercially available and distilled before use.

Ethanol- $\alpha$ , $\alpha$ -d<sub>2</sub> was prepared by reduction of acetyl chloride with LiAlD<sub>4</sub> (Merck A. G.; isotopic purity >98%).<sup>13</sup>

Ethyl tosylate- $\alpha, \alpha$ -d<sub>2</sub> was made from  $\alpha, \alpha$ -dideuteroethanol by the method of Tipson.<sup>14</sup>

Methyl iodide- $d_3$  was obtained by reaction of tetradeuteromethanol (Merck A. G.; isotopic purity >98%) with hydrogen iodide.<sup>15</sup>

Methyl mercaptan-d<sub>3</sub> was made from methyl iodided<sub>3</sub> by treatment with thiourea and subsequent decomposition of isothiouronium salt with base.<sup>16</sup> The mercaptan was distilled and converted into its sodium salt by reaction with sodium methanolate in methanol.

 $CH_3SCD_2CH_3$  (4b) was prepared by heating 1.83 g (14 mmol)  $CH_3CD_2OTs$  with 1.44 g (20 mmol) dry  $CH_3SNa$  in 3 ml DMSO for 5 h at 80 °C. The mixture was cooled and poured into 5 ml water of 0 °C. The upper layer was separated, dried and distilled twice. A fraction with boiling point 65–67 °C was used for the mass spectral measurements.

 $(CH_3CD_2)_2S$  (1a) was made by the same procedure from 1.40 g CH<sub>3</sub>CD<sub>2</sub>OTs and 0.84 g Na<sub>2</sub>S. Only the fraction with b.p. 89-91 °C was used.

 $CD_3SCH_2CH_3$  (4a) was synthesized by heating a mixture of 3.02 g C<sub>2</sub>H<sub>5</sub>SNa with 5 g CD<sub>3</sub>I in *n*-pentanol for 1.5 h. The mixture was fractionated several times and a sample with b.p. 64–66 °C was used for mass spectral measurements.

 $CD_3SCD_2CH_3$  (**4c**), b.p. 64-66 °C was prepared by the same procedure from 2.50 g  $CH_3CD_2OTs$  and 0.9 g  $CD_3SNa$ .

 $CD_3S^{13}CH_2CH_3$  (4d) was obtained by reaction at reflux temperature for 2.5 h of 0.50 g CH<sub>3</sub> <sup>13</sup>CH<sub>2</sub>I (Stohler Isotope Chemicals, isotopic purity: 86.5% <sup>13</sup>C as measured by mass spectrometry at low ionization energy) with 0.40 g CD<sub>3</sub>SNa in 2 ml water at pH = 8. After cooling the sulfide was separated from the water layer and dried on molecular sieves. It could be used without further purification.

The purity of all compounds was checked by gasliquid chromatography and mass spectrometry and was found to be at least 98%.

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