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A MASS SPECTRAL STUDY OF SOME SYMMETRIC AND UNSYMMETRIC SULFIDES, DISULFANES, AND TRISULFANES

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Summary

The low-resolution mass spectra of 13 trifluoromethyl and/or methyl sulfur-containing compounds ($CF_3S_nCF_3$, $CF_3S_nCH_3$, $CH_3S_nCH_3$, CF_3S_mCl, and CH_3S_mCl; $n = 1, 2, 3$; $m = 1, 2$) are reported and discussed. There is a considerable similarity between the fragmentation patterns of compounds with the same terminal groups. However, with a fluorinated and a non-fluorinated methyl group, the major fragmentation products produced are similar to those for the dimethyl compounds.

Introduction

In our work with polysulfanes, we have found it necessary to depend upon mass spectrometry for structural information about reaction products owing to the similarity of the respective NMR, UV and IR spectra. With the exception of dimethyldisulfane, which has been well characterized mass spectrometrically by Williams and co-workers [1], little information about the fragmentation of simple polysulfanes has been recorded in the available literature.

With most molecules that contain a trifluoromethyl entity, $[CF_3]^+$ is observed as the base peak at m/e 69. According to Majer [2], and based on our experience, this ion is one of the most common rearrangement ions in the spectra of carbon–fluorine compounds whether or not the CF_3 functional group is present.

In the following, we present and discuss the characteristics of the low-resolution fragmentation patterns of bis(trifluoromethyl) sulfide, methyl trifluoromethyl sulfide, dimethyl sulfide, bis(trifluoromethyl)disulfane, methyltrifluoromethyldisulfane, dimethyldisulfane, bis(trifluoromethyl)-trisulfane, dimethyltrisulfane, methanesulfenyl chloride, trifluoromethanesulfenyl chloride, methylchlorodisulfane and trifluoromethylchlorodisulfane at ionizing potentials of 20 and 70 eV. No peaks which could be attributed to metastable ions were observed.

The data from the spectra are presented in the tables given below, thus enabling a direct comparison between similar sulfur species at both ionizing potentials. All data are taken directly from the working spectra and are uncorrected for sulfur and chlorine isotope ratios. Data [3] already in the literature for alkyl and perfluoroalkyl sulfides and di- and tri-sulfanes give different relative abundances for respective *m/e* values, which most likely result from the use of different instruments and conditions. Values given in this work are given in terms of relative abundance (RA), with the most intense peak being taken as 100%.

Results

In contrast to polyfluoro- and perfluoro-paraffins and -olefins [4], where the molecular ion is relatively weak, the sulfanes studied in this work have fragmentation patterns which include a greater molecular ion abundance. A large variety of sulfur-containing species of high relative abundances were observed and are listed in Tables 1, 3, 4 and 5.

The molecular ions observed for the three alkyl and perfluoroalkyl sulfides are relatively intense at 20 eV (Table 1) and, in fact, the molecular ion is the base peak for CH_3SCH_3. At 70 eV, $[CF_3]^+$ (*m/e* 69) was found as the base peak for CF_3SCF_3 while $[CH_3S]^+$ (*m/e* 47) was the most abundant fragment for both dimethyl sulfide and methyl trifluoromethyl sulfide. A comparison of the relative abundance of $[CH_nS]^+$ with that of $[CF_nS]^+$ given in Table 2 shows that the ratio of the relative abundances at 70 eV is independent of the sulfide compound from which the fragment originates in the mass spectrometer. At 20 eV the relationship is less clear.

For the dialkyl di- and tri-sulfanes (Tables 3 and 4), the molecular ion is the base peak as reported [1, 3, 5] at 20 and 70 eV. The perfluoromethylsulfanes have trifluoromethyl as the most abundant ion with the exception of CF_3SSSCF_3, which has the parent ion (*m/e* 234) as the base peak at 20 eV.

The fragments with the greatest abundances in the alkyl samples for both 20 and 70 eV are $[CHS]^+$ (*m/e* 45), $[CH_2S]^+$ (*m/e* 46) and $[CH_3S]^+$ (*m/e* 47). At 70 eV, for dimethyldisulfane and dimethyltrisulfane, the $[CHS]^+$ fragment is second in intensity to the base peak. However, at 20 eV, $[CH_3SS]^+$ (*m/e* 79) is the second most abundant species. For the corresponding perfluoroalkylpolysulfanes, we find that the abundances of the similar perfluoro species are respectively lower. A change occurs for the perfluoropolysulfanes at 20 eV where we observe that $[CF_2SS]^+$ (*m/e* 114) for CF_3SSCF_3 and $[CF_3SS]^+$ (*m/e* 133) for CF_3SSSCF_3 are now the major species. For the trisulfanes, the $[CX_3SSS]^+$ (*m/e* [X = H, F] 111, 165) fragment is present but not to a greater extent than $[CX_3SS]^+$, except at 20 eV for bis(trifluoromethyl)trisulfane and methyltrifluoromethyltrisulfane.

The methyltrifluoromethyl di- and tri-sulfanes demonstrate an interesting relationship concerning predictable fragmentation patterns. There is a positive correspondence between the relative intensity of a particular

TABLE 1

Relative abundances for sulfides

	CF_3SCF_3[a]		CF_3SCH_3[a]				CH_3SCH_3[b]	
	20 eV	70 eV	20 eV		70 eV		20 eV	70 eV
			F[c]	H[d]	F	H		
$[CX]^+$		15.8			13.1	7.5		3.9
$[CX_2]^+$		7.2			8.3	16.1		6.0
$[CX_3]^+$	100.00	100.0	14.3	4.5	37.7	60.3		14.3
$[CXS]^+$	6.1	21.8	3.4	5.9	16.8	65.7	6.0	76.2
$[CX_2S]^+$	38.0	9.9	2.1	5.8	7.2	26.7	24.4	46.3
$[CX_3S]^+$		2.7	100.0			100.0	68.8	100.0
$[S]^+$		9.0			7.0			6.3
$[CS]^+$		3.6	7.3		13.3			11.6
$[M-X]^+$	4.0	2.5	5.7	3.9	14.4	4.0	20.6	21.2
$[M]^+$	55.4	7.1	59.9		26.8		100.0	52.7

[a] Ion source, 155 °C; gas inlet, 187 °C. ‘Ambient temperature. [c] X = F. [d] X = H.

TABLE 2

Comparison of relative abundances $RA_{[CF_nS]^+}/RA_{[CH_nS]^+}$[a] for sulfides

n	CF_3SCF_3/CH_3SCH_3	CF_3SCH_3
1	0.29	0.26
2	0.21	0.27
3	0.02	0

[a] RA = relative abundance.

fragment, such as $[CF_nS]^+$, in the unsymmetric polysulfane when compared with its relative abundance in the symmetric polysulfane at 70 eV. For example, $[CF_3]^+$ is a major fragment (RA = 100) in CF_3SSCF_3 and in CF_3SSCH_3 (RA = 50), while the abundance of $[CH_3]^+$ is low in both CF_3SSCH_3 and CH_3SSCH_3 (RA = 11.4 and 14.5, respectively). This positive correspondence of relative abundances is exhibited at 70 eV by $[CH_3SS]^+$ in dimethyldisulfane (RA = 69.3) and methyltrifluoromethyldisulfane (RA = 100) as well as in dimethyltrisulfane (RA = 82.2) and methyltrifluoromethyltrisulfane (RA = 91.5). The same positive correlation of relative abundances does not hold for $[CF_3SS]^+$ in CF_3SSSCF_3 and CF_3SSSCH_3. The unsymmetric compounds CH_3SCF_3, CH_3SSCF_3 and CH_3SSSCF_3 show that, given the option of possible fragmentation reactions, $[CH_3S]^+$ formation is preferred. Table 6 gives a direct comparison of the ratio of relative abundances of $[CF_nS]^+$ *versus* $[CH_nS]^+$ at 70 eV for di- and tri-sulfanes. These data confirm that the fragmentation products are independent of the particular

TABLE 3

Relative abundances for disulfanes

	CF_3SSCF_3[a]		CF_3SSCH_3[a]				CH_3SSCH_3[b]	
	20 eV	70 eV	20 eV		70 eV		20 eV	70 eV
			F[c]	H[d]	F	H		
$[CX]^+$		6.1			5.6			2.3
$[CX_2]^+$		4.6			4.1	3.2		4.6
$[CX_3]^+$	100.00	100.0	5.9		50.0	11.4		14.5
$[CXS]^+$		7.1		5.9	6.2	66.4	1.4	87.5
$[CX_2S]^+$	6.9	6.5	2.3	4.6	5.0	33.3	16.9	48.4
$[CX_3S]^+$	3.8	4.1		5.5	3.3	27.9	8.7	34.5
$[CXSS]^+$		6.3						2.2
$[CX_2SS]^+$	74.6	12.0		2.2		13.4		5.2
$[CX_3SS]^+$	1.7	12.9	2.3	70.3	7.3	100.0	30.1	69.3
$[S_2]^+$		7.1			8.0			6.4
$[CS]^+$ +	6.2	18.9 2.6	2.0		28.0			16.0
					1.3			
$[CSS]^+$			3.0		3.1			2.4
[M-S]+								1.7
[M-X]+		9.4			9.3			2.3
[M-SH]+							19.5	23.0
$[M]^+$	96.0	25.4	100.0		91.1		100.0	100.0

[a] **Ion** source, 155 °**C,** gas inlet, 187 °**C.** [b] **Ambient** temperature. [c] X = F. [d] X = H.

TABLE 4

Relative abundances for trisulfanes

	$CF_3S_3CF_3$[a]		$CF_3S_3CH_3$[a]				$CH_3S_3CH_3$[b]	
	20 eV	70 eV	20 eV		70 eV		20 eV	70 eV
			F[c]	H[d]	F	H		
$[CX]^+$		5.1			5.7			
$[CX_2]^+$		3.9						7.1
$[CX_3]^+$	34.8	100.0	5.5		56.5	10.6		12.6
$[CXS]^+$		7.3		11.2	7.8	91.5	10.0	95.5
$[CX_2S]^+$	5.5	5.8	4.8	5.5	7.8	39.1	4.7	38.4
$[CX_3S]^+$	1.5	6.5		19.6	8.0	53.8	17.3	60.7
$[CXSS]^+$	2.5							
$[CX_2SS]$+	2.6					**5.9**	**9.8**	13.2
$[CX_3SS]^+$	33.3	41.7	5.6	41.1	11.5	91.5	30.8	82.2
$[CXSSS]^+$							5.6	
$[CX_2SSS]$+	2.5							
$[CX_3SSS]^+$	38.1	11.4		48.8	6.7	38.9	14.2	24.0
$[S]^+$		9.8			14.1		3.8	19.6
$[S_2]^+$	19.3	49.6	6.1		65.0		3.8	36.8
$[CS]^+$	2.4	2.6			9.6			9.4
$[CSS]^+$	2.5		6.1		6.3		**3.9**	5.7
[M-S]+	3.0	2.2	6.4		5.6		15.6	16.8
[M-X]+		**2.7**[a]						
$[M]^+$	100.0	43.1	100.0		100.0		100.0	100.0

[a] **Ion** source, 155 °**C, gas** inlet, 187 °**C.** [b] **Ambient** temperature. [c] X = F. [d] X = H.

TABLE 5

Relative abundances for sulfenyl chlorides and chlorodisulfanes

	CF_3SCl^a		CH_3SCl^b		CF_3SSCl^a		CH_3SSCl^b	
	20 eV	70 eV	20 eV	70 eV	20 eV	70 eV	20 eV	70 eV
$[CX]^+$		16.3		4.7		7.4		2.5
$[CX_2]^+$		9.0		7.9		5.9		5.5
$[CX_3]^+$	100.0	100.0		11.8	55.6	100.0	2.1	11.4
$[CXS]^+$		12.1	17.5	73.9		8.3	20.1	89.6
$[CX_2S]^+$	5.8	15.5	11.6	27.3	11.2	6.9	12.2	38.5
$[CX_3S]^+$	18.3	17.5	100.0	100.0	6.9	9.1	44.0	75.5
$[CX_2SS]^+$							3.3	3.8
$[CX_3SS]^+$					54.4	38.0	100.0	100.0
$[S]^+$		21.4		8.2		19.3		16.8
$[S_2]^+$					100.0	89.2	12.0	51.1
$[SCl]^+$	7.3	20.3	3.9	8.3	5.6	15.1	2.0	8.6
$[SSCl]^+$					11.4	11.6	2.9	3.6
$[CSSCl]^+$							5.1	5.0
$[CS]^+$		3.9		8.1		4.1	2.0	12.0
$[CSS]^+$					9.9	4.4	5.6	3.5
$[M-S]^+$							32.2	
$[M-SH]^+$							12.6	
$[M-X]^+$	4.1	9.4	7.2	5.4		3.3		3.2
$[M]^+$	58.0	19.3	69.7	28.7	67.5	27.3	77.5	43.6

[a] X = F; ion source, 155 °C, gas inlet, 187 °C. [b] X = H; ambient temperature.

TABLE 6

Comparison of relative abundances $RA_{[CF_nS]^+}/RA_{[CH_nS]^+}$ for di- and tri-sulfanes

n	CF_3SSCH_3	$CF_3S_3CH_3$	CF_3SSCF_3/CH_3SSCH_3	$CF_3S_3CF_3/CH_3S_3CH_3$
1	0.09	0.08	0.08	0.07
2	0.15	0.20	0.14	0.15
3	0.12	0.15	0.14	0.11

functional group on the opposite end of the sulfur linkage, whether it be methyl or trifluoromethyl. Even though some $[CF_nS]^+$ species were not observed when the ionization potential was 20 eV, the data obtained exhibit the same general trend as found in that for 70 eV. When the same comparison is made for the $[CX_3SS]^+$ species at both 20 and 70 eV, the greater number of fragmentation products still generally occurs with the alkyl-containing species. It is interesting to note that the respective ratios representing $RA_{[CF_nS]^+}/RA_{[CH_nS]^+}$ for the unsymmetric di- and tri-sulfanes given in Table 6 do not exhibit any significant change. The mass spectra of CF_3SSSCH_3 at 20 and 70 eV are illustrated in Figure 1(a) and (b), respectively.

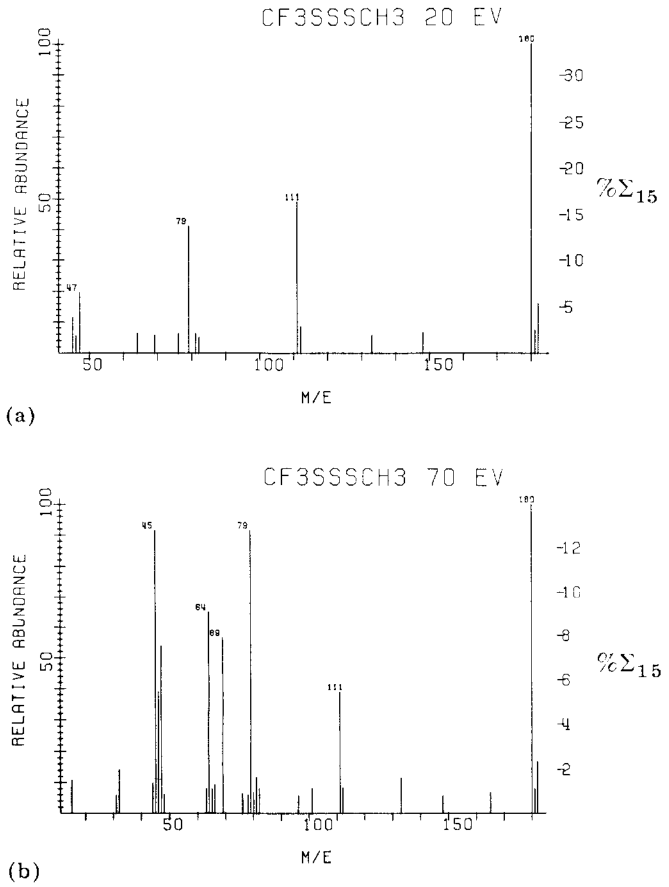

Fig. 1. Mass spectra of CF_3SSSCH_3 at (a) 20 eV and (b) 70 eV.

The sulfenyl chlorides and chlorodisulfanes generally follow the trend set by the spectra discussed earlier. At 20 eV and 70 eV, $[CF_3]^+$ is the base peak for CF_3SCl while $[CH_3S]^+$ is the most abundant fragment for CH_3SCl. However, for trifluoromethylchlorodisulfane with $[CF_3]^+$ as the base peak at 70 eV, $[S_2]^+$ (*m/e* 64) is the base fragment at 20 eV. Instead of $[CH_3S]^+$ or the parent ion as the most abundant fragment for CH_3SSCl at 20 and 70 eV, we observed $[CH_3SS]^+$ (*m/e* 79) with RA = 100. The mass spectra of CF_3SSCl at 20 and 70 eV are given in Figure 2(a) and (b), respectively.

Discussion

Many of the observations reported above can be correlated with the presence of sulfur atoms and their concomitant ability to accommodate the resultant positive charge. This phenomenon accounts for the large molecular ion abundance for the sulfanes.

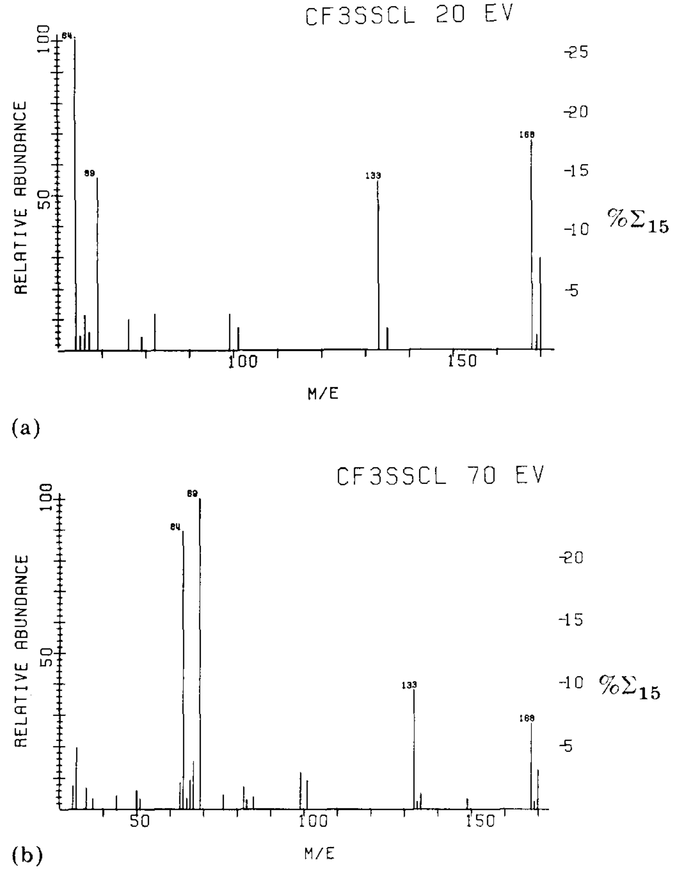

Fig. 2. Mass spectra of CF_3SSCl at (a) 20 eV and (b) 70 eV.

Levy and Stahl [5] have stated that α-bond cleavage is an important process in the mass-spectral fragmentation of symmetric sulfides of high molecular weight. The main fragmentation pattern in totally fluorinated sulfides, disulfanes and trisulfanes is observed to involve the formation of $[CF_3]^+$ *via* a similar mechanism. Substitution of both of the methyl groups with trifluoromethyl groups in the polysulfanes results in a decrease in the relative abundances of the species $[CXS]^+$, $[CX_2S]^+$, $[CX_3S]^+$ and $[CX_3SS]^+$ because of a destabilizing effect of the fluorine atoms attached to the carbon atoms on positive ion formation. The decrease in the relative abundance of the $[CF_3]^+$ moiety observed for $CF_3S_nCH_3$ as compared with $CF_3S_nCF_3$ is a function of the stabilizing effect of the sulfur atoms (bonded to the CH_3) on positive ion formation which inhibits the formation of large amounts of the trifluoromethyl fragment.

Whilst our data do not allow detailed fragmentation pathways to be proposed, similarities exist between our results for sulfanes and those of Kaae and Senning [6] for bis(trichloromethyl)-disulfane and -trisulfane, e.g., spectra at 70 eV give $[CCl_3]^+$ as the parent ion for both CCl_3SSCCl_3 and $CCl_3SSSCCl_3$, which is comparable with $[CF_3]^+$ for CF_3SSCF_3 and CF_3SSSCF_3. The fragmentation mechanisms suggested by these authors for the electron-impact processes involving these symmetric trichlorosulfanes appear to be reasonable for the symmetric trifluorosulfanes studied in our work. Such proposed pathways for CF_3SSCF_3 are shown in Figure 3.

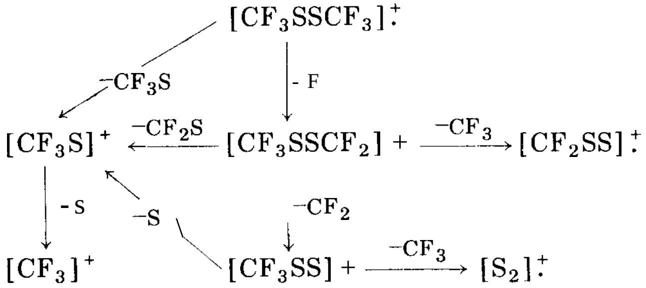

Fig. 3. The main fragmentation pathways proposed for CF_3SSCF_3

All spectra of sulfanes which have a CH_3 moiety contain fragment ions corresponding to $[CH_3SH]^+$ and $[CH_3SH_2]^+$ in varying abundances, which indicates a process involving a complex re-organization of the molecular ion. High-resolution techniques would be needed to distinguish the relative amounts of $[CH_3{}^{34}S]^+$ and $[CH_3{}^{32}SH_2]^+$ in the spectra. It is interesting to note that in the unsymmetric compounds, no ions are seen corresponding to $[CF_3SH]^+$, $[CF_3SH_2]^+$ or $[CF_3{}^{34}S]^+$ which suggests that a mechanism different from that proposed by Williams and co-workers [1] for CH_3SSCH_3 must be operative. No fragments which may be assigned as $[CX_3S_nY]^+$ ($n = 2, 3$; $Y = H$ or F) were detected in the low-resolution spectra. Possible pathways for the fragmentation of unsymmetric disulfides are given in Figure 4.

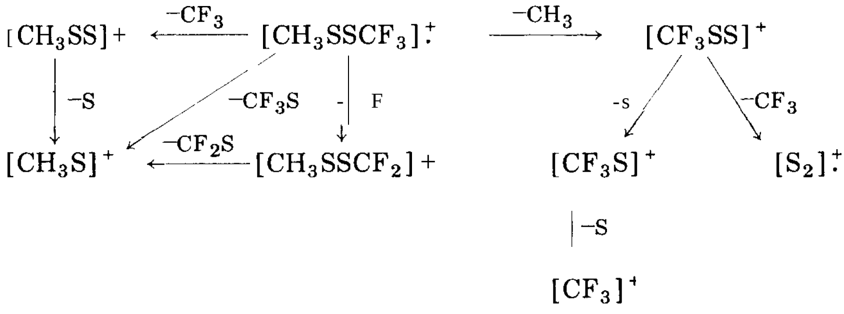

Fig. 4. The main fragmentation pathways proposed for CH_3SSCF_3.

The relative abundances given in Tables 3, 4 and 5 for the disulfanes, trisulfanes and chlorodisulfanes confirm that the $[CX_3SS]^+$ species are the most stable of the sulfur-containing fragments produced at 70 eV, with

$[CX_3S]^+$ being more stable than $[CX_3SSS]^+$ except in bis(trifluoromethyl)-trisulfane. At 20 eV, however, a similar order of stability cannot be clearly established. The data also indicate that a similar process leading to the formation of $[CX_3S_n]^+$ ($n = 1, 2, 3$) must be occurring for each sulfane.

With the sulfanes, the important positive ion formation processes are predominantly those which involve severing of the sulfur–sulfur bond and sulfur–carbon bond as demonstrated in Figures 3 and 4. The relative abundances of ions for the symmetric sulfides, disulfanes and trisulfanes demonstrate that the spectra of the unsymmetric sulfur compounds may be predicted by comparing the relative abundances in the 70 eV spectra of the symmetric compounds as shown in Tables 2 and 6.

Comparison of the mass-spectral fragmentation patterns of the analogous oxygen compounds with those in this work would be very interesting. Unfortunately, little of the data needed for such a comparison are available in the literature. This is an area which needs further study.

Experimental

Mass spectra were recorded using a Hitachi Perkin–Elmer RMU-6E mass spectrometer operating at ionizing potentials of 20 and 70 eV. The gas inlet system was used for sample introduction in each case. The ion source and the gas inlet system were maintained at temperatures of 155 °C and 187 °C, respectively, for all samples except dimethyl sulfide, dimethyltrisulfane, methanesulfenyl chloride and methylchlorodisulfane when instrument conditions were maintained at ambient temperature to reduce thermal re-arrangement and decomposition [7, 8]. An ion acceleration voltage of 1800 V was used in all cases with an ionizing current of 80 μA. The maximum allowed sample pressure in the mass spectrometer was 8×10^{-7} Torr. All spectra were recorded over the *m/e* range 6 to 300.

Trifluoromethanesulfenyl chloride [9], methyl trifluoromethyl sulfide [10], trifluoromethylchlorodisulfane, methyltrifluoromethyltrisulfane and bis(trifluoromethyl)trisulfane [11] were prepared according to methods given in the literature. Commercially available dimethyl sulfide (Aldrich), bis(trifluoromethyl)disulfane (P.C.R.) and dimethyldisulfane (Crown Zellerbach) were used after purification. Dimethyldisulfane and chlorine gas were reacted at −20 °C for 1 h to produce CH_3SCl while H_2S was used with methanesulfenyl chloride to make dimethyltrisulfane. Methyltrifluoromethyldisulfane resulted from the reaction of methanethiol and CF_3SCl. Methylchlorodisulfane was obtained from the interaction of methanethiol and sulfur dichloride. All samples were purified by gas chromatography or low-temperature vacuum-distillation techniques until no changes were noted in their mass spectra. However, dimethyltrisulfane decomposed in the ballast container of the mass spectrometer above ambient temperatures while CH_3SSCl rearranged rapidly at room temperature making it impossible to obtain a pure sample.

Acknowledgements

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