employing a weighted least-squares method. Reference CA spectra used for this were the averages of those from several precursors for **a** and **b**, and of spectra from seven separate protonations of ethylene sulfide (four different days) for **d**. The latter spectra were corrected for isotopic contributions from $C_2H_4S^+$ and $C_2H_3S^+$ ions according to their relative CA cross sections. The CA spectrum of **d** fits best a computer-synthesized spectrum of a mixture of 12% **a** and 88% **b**, but the abundances of these peaks differ from those of the **d** spectrum by an average of 1.7 standard deviations (two peaks differ by more than three times the standard deviation). For the calculated quantitative analysis of assumed isomeric mixtures (last column Table I), the average of the standard deviations was between 0.4 and 1.2 (mean 0.8). The reference spectra of **a**, **b**, and **d** did not change at low electron energy within a comparable experimental error.

The ionizing efficiency measurements for the $C_2H_5S^+$ and $C_2H_2D_3S^+$ ions from $C_2H_5SCD_3$ were the composite values of four separate determinations, but were still subject to substantial errors. The signal/noise ratio for the *m/e* 61 peak at 11 eV was ~3/1, and the accuracy of the electron energy values was ±~1 eV because the fragment and molecular ions showed substantially different slopes and the fragment ion curve showed substantial tailing.

Samples. $C_2H_5SCD_3$ was prepared from CD_3I and C_2H_5SH[3b] and purified by gas chromatography. C_2H_5SD was prepared from C_2H_5SH by exchange with D_2O in the inlet system. All of the compounds were obtained from commercial sources and checked for purity by mass spectrometry.

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(15) Note, however, that Keyes and Harrison find $\Delta H_f(CH_2SH^+) = 219$ kcal/mol and $\Delta H_f(CH_3S^+) = 214$ kcal/mol, relative stabilities which are in reverse order to our conclusions for CH_3CHSH^+ vs. $CH_3CH_2S^+$.
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Structure and Formation of Stable $C_3H_7S^+$ Ions[1]

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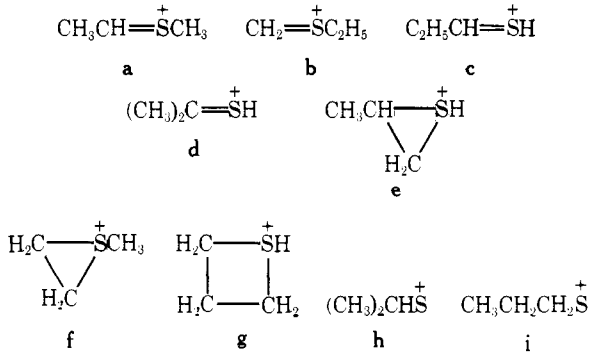
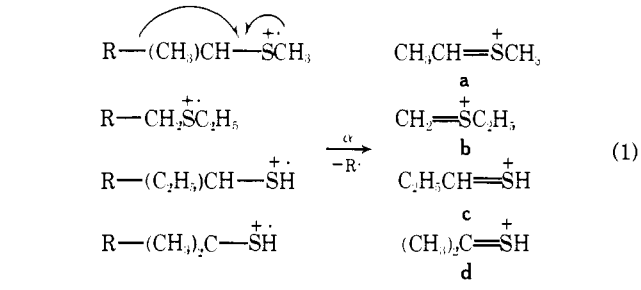
Abstract: Seven gaseous $C_3H_7S^+$ isomers are shown to be stable for $\geq 10^{-5}$ s and identifiable from their collisional activation (CA) mass spectra: $CH_3CH{=}\overline{SCH_3}^+$ (**a**), $CH_2{=}SC_2H_5^+$ (**b**), $C_2H_5CH{=}SH^+$ (**c**), $(CH_3)_2C{=}SH^+$ (**d**), $CH_3\overline{CHCH_2SH}^+$ (**e**), $\overline{CH_2CH_2SCH_3}$ (**f**), and $\overline{CH_2CH_2CH_2SH}^+$ (**g**). Ions formed as $(CH_3)_2CHS^+$ rearrange in $<10^{-5}$ s to **d** and **a** (~5:1), and those formed as $CH_3CH_2CH_2S^+$ to **c**; isomers **e** and **f** appear to undergo partial isomerization to **c** and to **a**, respectively. Identification using CA of these $C_3H_7S^+$ isomers has given detailed information on competing fragmentation mechanisms of alkyl thiol and sulfide cations. Seven major pathways are identified, several of which can be competitive in producing $C_3H_7S^+$ from a single compound. These mechanisms involve α-cleavage, β-cleavage, and C–S bond cleavage; the first two can be accompanied by hydrogen rearrangement through a saturated or unsaturated ring transition state. In general, the factors found to favor particular mechanisms are consistent with conclusions from previous studies.

In the previous study[1] the structures of $C_2H_5S^+$ ions with lifetimes $>10^{-5}$ s were investigated using collisional activation (CA) spectra.[3] Three ion structures, $CH_3S{=}CH_2^+$, $CH_3CH{=}SH^+$, and $\overline{CH_2CH_2SH}^+$, were found to be stable within these lifetime requirements. The stability of the cyclic ion was found to be comparable to that of these linear isomers, and to be formed with facility through a β-cleavage displacement mechanism,[4] supporting earlier postulations.[5,6] In comparing these ions to their $C_2H_5O^+$ analogs, this suggests that resonance stabilization is also important in the linear isomers $CH_3S{=}CH_2^+$ and $CH_3CH{=}SH^+$, and there is less ring strain energy in $\overline{CH_2CH_2SH}^+$ than in its oxygen analog. Carbon–sulfur cleavage of C_2H_5S–R to yield $CH_3CH_2S^+$ is also relatively more facile than in the oxygen analogs,[4,5,7] but this product ion is relatively unstable, isomerizing to $CH_3CH{=}SH^+$ in 10^{-5} s; apparently a loose activated complex for the C_2H_5S–$R^+\cdot$ cleavage favors this reaction for higher energy ions. It appeared to be of particular interest to extend these studies to the $C_3H_7S^+$ homologs as a much wider variety of structures such as **a**–**i** are possible.[8] The ions **a**, **b**, and **f** have been studied by ion cyclotron resonance spectroscopy,[6a,b] and their ion–molecule reactivities support linear structures for **a** and **b** and a cyclic structure for **f**. In a CA study of $C_3H_7O^+$ ions only the linear oxonium analogs of **a**–**d** were identified;[9] however, this could be due to relatively small differences in the CA spectra of pairs of cyclic and linear ions (vide infra). Pre-



vious investigations[4,5] have shown that a much wider variety of fragmentation pathways are possible (reactions 1-7) in the mass spectra of aliphatic thiols and sulfides in comparison to



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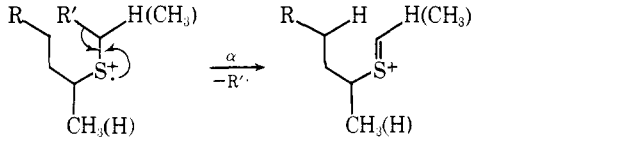

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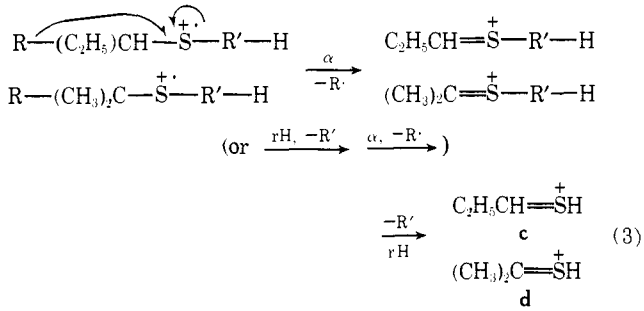

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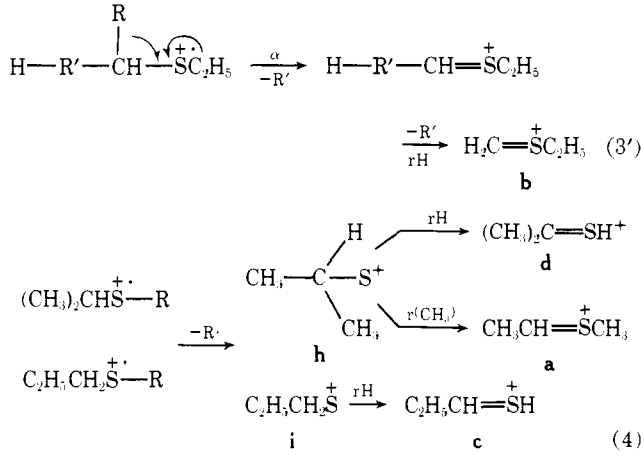
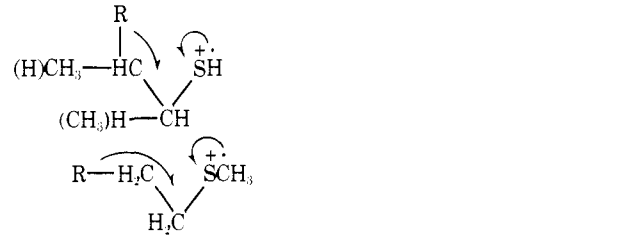


(4)

those of their oxygen analogs, making detailed elucidation of mechanisms more difficult using conventional techniques.

Results and Discussion

Reference Ions. CA spectra of $C_3H_7S^+$ ions prepared from a variety of precursors are shown in Table I. Inspection of such spectra utilizing a computer error minimization program shows that there are seven distinguishable and characteristic patterns. By analogy to previous studies,[4,5] such as those of $C_2H_5S^+$,[1] $C_2H_5O^+$,[3a,c] $C_3H_7O^+$,[9] $C_2H_6N^+$,[3b] and $C_3H_8N^+$ ions, the ubiquitous α-cleavage reaction[1] should form stable ions; α-methylalkyl methyl sulfides should yield **a**, α-unsubstituted alkyl ethyl sulfides should yield **b**, α-ethylalkyl thiols should yield **c**, and α,α-dimethylalkyl thiols should yield **d**. It has been assumed that the first six precursors listed (Table I) yield such $C_3H_7S^+$ ions of high isomeric purity; CA spectra of these ions formed using low electron energies were the same within experimental error, and, as will be shown below, no reactions



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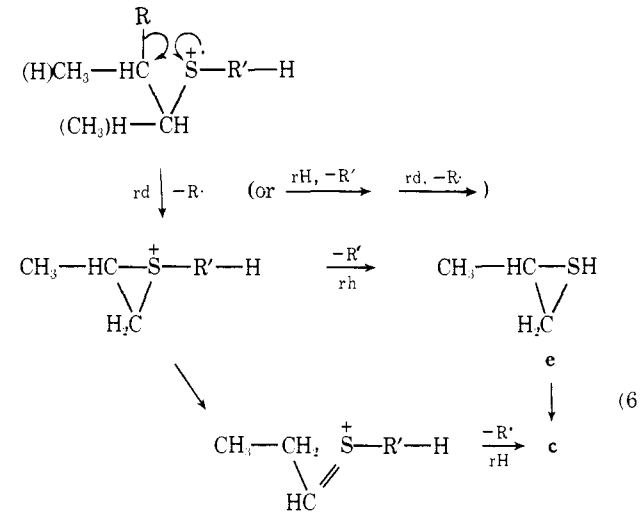

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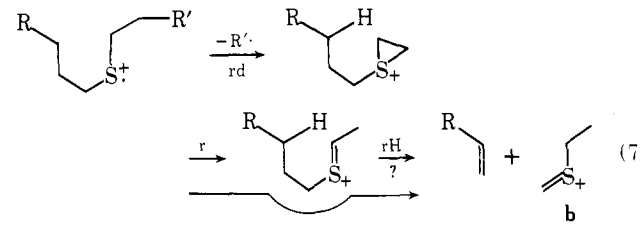

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Table I. Collisional Activation Spectra of $C_3H_7S^+$ Ions

Compound	Major reactions	$[C_3H_7S^+]$, normal MS, %	*m/e* of daughter ion[a]																	Ion structure[b]	
			27	29	33	39	41	45	46	47	49	57	58	59	60	61	69	71	73	74	Best	Possible alternative
$CH_3CH_2(CH_3)CHSCH_3$	1	100	5.7	0.9	0.5	2.0	(31)	23	6.6	(37)	7.2	5.2	14	22	9.4	0.4	0.5	0.8	1.6	(8)	a	
$(CH_3CH_2)_2S$	1	100	9.7	12	0.3	1.6	(33)	31	23	(104)	0.8	2.8	6.5	7.4	1.9	1.0	0.6	0.8	1.1	(2)	b	
$CH_3(CH_2)_2SCH_2CH_3$	1	100	10	13	0.4	1.6	(26)	31	22	(110)	0.9	2.7	5.6	7.1	1.8	0.8	0.4	0.7	1.2	(2)	b	
$CH_3(CH_2)_3SCH_2CH_3$	1	100	11	12	0.4	1.6	(22)	30	23	(84)	0.7	3.0	5.9	7.3	1.8	1.0	0.4	0.7	1.0	(2)	b	
$(CH_3CH_2)_2CHSH$	1	30	5.3	2.0	1.1	20	(108)	24	5.1	(81)	0.6	5.5	12	10	2.8	0.6	2.7	4.7	4.7	(16)	c	
$(CH_3)_3CSH$	1	25	2.5	0.2	1.6	21	(89)	9.2	1.3	(28)	0.2	7.7	16	34	1.4	0.1	2.2	2.4	0.6	(4)	d	
CH_3CHCH_2SH[c]	CI		6.5	0.7	2.2	23	(100)	23	5.7	(79)	0.2	5.2	11	10	1.6	1.1	2.4	3.5	4.0	(19)	e	
$CH_2CH_2CH_2SH$[c]	CI		7.0	0.5	1.8	18	(79)	29	21	(114)	0.1	2.8	5.6	4.0	0.7	0.6	2.4	3.7	3.6	(18)	g	
$CH_3(CH_2)_4SCH_3$	5	15	6.5	2.1	0.7	1.9	(41)	23	11	(49)	8.0	4.6	12	18	7.8	1.4	0.5	0.6	1.9	(6)	f[d]	
$CH_3(CH_2)_3SCH_3$	5	20	5.7	1.2	0.6	1.6	(32)	22	8.5	(38)	8.0	5.1	13	21	9.4	1.0	0.4	0.7	1.6	(8)	a, 70; f	a, 95; b
15 eV[e]			7.1	1.0	0.6	1.8	(15)	24	8.8	(21)	7.1	6.2	12	19	9.0	0.8	0.4	0.6	1.4	(8)	a, 50; f	a, 95; b
$CH_3CH_2SCH_3$	1,5	4	7.1	3.1	0.9	2.2	(39)	25	9.5	(56)	5.5	5.4	10	20	6.6	0.8	0.5	1.1	2.2	(5)	a, 55; b, 20; f	a, 75; b
19 eV[e]			8.1	4.3	0.9	1.4	(12)	28	11	(27)	4.6	5.5	12	15	6.9	0.6	0.4	0.9	1.3	(21)	a, 55; b, 30; f	a, 65; b
$CH_3CH_2(CH_3)CHSH$	1,5	5	5.2	1.0	1.8	21	(143)	20	5.0	(102)	0.6	5.4	12	14	2.5	0.4	2.3	3.6	4.4	(11)	c, 50; d, 15; e	c, 85; d
14 eV[e]			4.9	1.2	1.9	23	(121)	22	4.7	(90)	0.6	4.7	12	12	2.4	0.2	2.8	4.1	3.9	(13)	c, 60; d, 10; e	c, 90; d
$(CH_3)_2CHSH$	1,5	1	3.1	0.5	1.6	22	(84)	11	2.9	(51)	0.6	6.7	13	27	2.2	0.2	2.8	3.2	2.9	(44)	c, 30; d	a, 5; d, 70; e
16 eV[e]			2.4	0.5	1.3	19	(52)	12	2.4	(32)	0.5	7.4	15	29	4.0	0.3	2.1	3.1	2.4	(60)	c, 25; d	a, 10; d, 75; e
$CH_3CH_2(CH_3)CHSCH_2CH_3$	2,3,3'	8	8.7	9.5	0.8	5.4	(46)	28	17	(89)	1.6	3.4	7.8	10	2.9	0.8	0.9	1.2	2.1	(5)	a, 15; b, 65; c, 10; e	a, 10; b 70; c
12 eV[e]			9.9	8.9	0.6	2.5	(15)	28	18	(46)	2.4	3.6	8.5	10	4.5	0.5	0.6	0.7	1.0	(6)	a, 25; b, 70; e	a, 25; b, 70; c
$CH_3(CH_2)_3SCH(CH_3)_2$	2,4	70	8.1	8.7	0.7	5.8	(17)	25	20	(30)	0.5	3.7	7.8	14	2.6	1.0	0.8	1.1	1.0	(8)	a, 5; b, 75; d	
16 eV[e]			5.9	5.0	0.9	9.0	(18)	21	13	(25)	0.4	4.9	9.7	21	3.8	1.1	1.3	1.5	0.9	(10)	a, 10; b, 50; d	
$(CH_3CH_2(CH_3)CH)_2S$	3	10	4.8	1.6	1.6	19	(113)	23	5.3	(93)	0.5	5.3	12	10	3.1	0.5	3.1	4.7	6.0	(17)	c	
$(CH_3CH_2CH_2)_2S$	3,4,7	15	5.8	4.2	1.2	13	(80)	24	12	(84)	1.0	4.6	9.8	11	3.4	0.7	2.0	3.2	4.7	(14)	b, 30; c	
16 eV[e]			7.5	4.4	1.1	12	(52)	26	13	(59)	0.9	3.9	9.6	11	2.6	0.9	1.8	2.6	3.7	(22)	b, 40; c	
$((CH_3)_2CH)_2S$	4	8	2.9	0.4	1.2	18	(78)	11	2.4	(35)	0.7	6.0	16	32	4.4	<0.1	2.3	2.5	1.2	(9)	a, 15; d	
16 eV[e]			2.0	0.1	1.2	19	(63)	10	1.2	(20)	1.0	5.7	16	35	3.8	<0.1	2.6	1.5	0.3	(10)	a, 10; d	
$(CH_3)_2CHSCH_2CH_3$	4,7	10	4.6	3.2	1.3	15	(81)	15	6.9	(58)	1.1	5.8	13	27	3.2	0.2	1.6	2.2	1.0	(7)	a, 15; b, 20; d	
19 eV[e]			3.9	2.1	1.3	13	(33)	13	4.8	(19)	1.7	6.5	12	31	5.7	0.4	1.6	2.1	0.9	(15)	a, 25; b, 10; d	
$CH_3(CH_2)_2SCH_3$	4,5	10	6.5	2.6	0.8	4.8	(34)	25	9.8	(44)	5.7	5.1	12	18	6.5	0.5	0.7	1.1	1.8	(61)	a, 45; b, 15; c, 15; f	a, 65; b, 20; c
17 eV[e]			7.2	2.8	1.0	4.5	(19)	24	9.0	(30)	5.3	5.9	12	17	7.3	0.7	0.7	1.1	1.6	(77)	a, 45; b, 15; c, 15; f	a, 70; b, 20, c

$(CH_3)_2CHCH_2SH$	5	3	4.9	0.6	1.5	20	(138)	21	5.2	(97)	1.6	5.6	13	13	3.4	0.7	2.1	3.3	4.2	(10)	a, 15; c, 35; d, 5; e	a, 10; c, 80; d
19 eV[e]		6.1	0.9	2.0	19	20	(102)	20	5.3	(84)	2.7	5.6	9.6	12	3.3	1.0	3.0	4.3	5.1	(11)	a, 15; c, 40; e	a, 10; c, 85; d
$((CH_3)_2CHCH_2)_2S$	6	3	5.1	1.0	1.1	14	(79)	22	6.7	(67)	2.8	4.3	13	16	5.8	0.6	1.7	3.2	4.7	(15)	a, 40; c	
18 eV[e]			5.7	1.3	1.5	11	(61)	21	5.0	(44)	4.0	6.8	11	17	7.1	0.3	1.9	2.1	4.5	(21)	a, 50; c	
$(CH_3(CH_2)_3)_2S$	7	2	8.1	8.5	0.5	3.0	(24)	28	19	(57)	2.3	3.5	7.6	10	4.7	1.3	0.5	1.0	1.7	(7)	a, 25; b, 70; c	
11 eV[e]			8.7	8.4	0.8	1.8	(9)	27	19	(38)	1.9	3.4	8.2	12	5.2	0.8	0.8	0.6	1.0	(8)	a, 30; b, 70	
$(CH_3)_2CHCH_2SCH_3$	?	8	5.0	0.9	0.5	2.2	(23)	21	6.6	(28)	7.5	5.0	14	22	11	0.5	0.5	0.8	2.7	(10)	a	

[a] Abundances relative to the total ion abundance = 100 excluding small and poorly resolved peaks (total abundance ⩽23%), and peaks from metastable ion decompositions at *m/e* 41, 47, and 74. [b] Mixtures were analyzed using a weighted least-squares method. Accuracy of compositions ~5% absolute for mixtures of **a**, **b**, **c**, and **d**. Values for the proportion of **a**:**f** and of c:e are of low accuracy (see ref 10 and 11); if the calculation indicated the presence of either e or **f**, a "possible alternative" composition was calculated, assuming that the true abundances differed from those measured on average by 2.0 standard deviations. [c] Produced by ion source protonation with methanol at high pressure and corrected for isotopic contributions from $C_3H_6S^+$ and $C_3H_5S^+$ ions. [d] Probably not the spectrum of pure **f** ions; see text. [e] Ionizing electron energy; in other cases 70 eV was used.

yielding other $C_3H_7S^+$ isomers should be expected from these precursors.

For reference spectra the cyclic ions **e** and **g** were generated directly by protonation of propylene sulfide[10] and tetramethylene sulfide, respectively; again reasonable isomeric homogeneity was assumed because of the insensitivity of the spectra to electron energy. The *S*-methyl cyclic ion **f**, which also appears to be stable,[6a,b] should be formed from α-unsubstituted alkyl methyl sulfides by the β-cleavage displacement mechanism (eq 5). Of the compounds studied here *n*-pentyl methyl sulfide formed the $C_3H_7S^+$ ions giving the most unique CA spectrum, which did not change at low electron energy, so this should represent the $C_3H_7S^+$ ions with the highest proportion of the **f** isomer,[11] although these probably are not completely homogeneous isomerically (vide infra). It was found[1] that the CA spectrum of protonated ethylene sulfide closely resembles that of its ring-opened isomer $CH_3CH{=}SH^+$; similarly, the CA spectrum of **e** resembles that of **c**, and **f** that of **a**. These differences are outside experimental error, but their small magnitude makes analysis of isomeric $C_3H_7S^+$ mixtures for the pairs **c** and **e**, and especially **a** and **f**, of relatively low accuracy.[10,11]

The $C_3H_7S^+$ decomposition reactions producing the peaks observed in the seven distinguishable CA spectra are consistent with the isomeric structural assignments. A large peak at *m/e* 39 ($C_3H_3^+$) is found only for those isomers containing three contiguous carbon atoms, **c**, **d**, **e**, and **g**. The *S*-methyl structures **a** and **f** give uniquely significant peaks at *m/e* 49, possibly $CH_3SH_2^+$, and have the largest peaks corresponding to the loss of methyl (*m/e* 60). The *S*-ethyl ion **b** has the largest peaks corresponding to $C_2H_5^+$ and loss of C_2H_5 (*m/e* 29 and 46). The CHS^+ and CH_2S^+ CA peaks are smallest for **d**, the only isomer for which formation of such ions should involve the loss of separate carbon atoms attached to the same carbon atom. On the other hand, **d** ions give the largest peak for the loss of CH_4, which presumably incorporates one of the methyl groups and the sulfhydryl hydrogen atom. The largest loss of CH_2 comes from the three-membered ring ions **e** and **f**, as found for the analogous protonated ethylene oxide[3c] and sulfide[1] ions, although the loss of CH_2 in the CA spectrum of **b**, the only isomer containing a vinyl group, is nearly as great. The only isomer which does not contain a methyl group is **g**; it has the least abundant CA peaks for the losses of CH_{3-6}. The isomer **g** also gives the largest peak corresponding to the loss of C_2H_4, but this is a less reliable structural indication because the abundance of this peak is affected by ion internal energy.

Fragmentation Mechanisms. Although seven different $C_3H_7S^+$ isomers are thus identifiable by CA, the variety of anticipated pathways for their formation (eq 1-7) means that often there is more than one possible mechanism for the formation of an identified isomer. Only one of the pathways leads to **f** and two to **e**, the cyclic isomers; however, three can form **d**, four **a**, and five **b** and **c**. (None of the compounds examined gave $C_3H_7S^+$ spectra consistent with that of the protonated thiacyclobutane **g**.) In the following discussion there will be shown in parentheses the approximate percentage (with reference to the base peak of the normal mass spectrum) of ions having the particular isomeric structure, and the other pathways that could possibly lead to the formation of that isomer; unless indicated otherwise, it will be shown in other discussion that these alternative pathways are less probable.

The α-cleavage reaction 1 predicts that **a** ions should be produced from *sec*-butyl methyl sulfide (100%) and ethyl methyl sulfide (2%, also eq 5) consistent with the CA spectral evidence. Similarly, diethyl (100%), propyl ethyl (100%, also eq 3′ and 7), butyl ethyl (100%, also eq 3′ and 7) and methyl ethyl (0.8%, also eq 5) sulfides yield **b** ions; α-ethylpropylthiol (30%) and *sec*-butylthiol (3%, also eq 5) yield **c** ions; and *tert*-butylthiol (25%) and isopropylthiol (0.7%, also eq 4) yield

d ions. As has been well established for other α-cleavage reactions, these data show that this pathway is favored for the α-cleavage involving the loss of the largest alkyl radical or loss from the most substituted carbon atom.[4] For most, but not all, compounds in which $C_2H_5S^+$ or $C_3H_7S^+$ is the largest peak in the normal mass spectrum, this peak is formed mainly by α-cleavage.

Formation of **a** or **b** ions by α-cleavage followed by hydrogen rearrangement through an unsaturated ring transition state[4,5] (eq 2) is possible for only two of the compounds studied here. Isomer **a** is formed from ethyl *sec*-butyl sulfide (1.2%) and **b** from isopropyl *n*-butyl sulfide (50%). It is especially encouraging that in the latter case the CA spectrum indicated that 75% of the $C_3H_7S^+$ ions have structure **b**, the same value found by Sample and Djerassi[5b] in their classic study utilizing isotopic labeling. Following their reasoning, formation of **a** from ethyl *sec*-butyl sulfide is less favorable because both the methyl lost in the α-cleavage and the hydrogen rearranged involve cleavage of bonds to less substituted carbon atoms.

For only one compound, di-*sec*-butyl sulfide, does reaction 3 appear to provide a strongly favored pathway for the formation of $C_3H_7S^+$ ions, yielding isomer **c** (10%, also eq 6). The yield of this product is substantially reduced in ethyl *sec*-butyl sulfide (0.8%, also eq 6), for which the less favorable rearrangement of a primary hydrogen is required. These results indicate that reaction 3 should yield only a small proportion of the **c** ions formed from di-*n*-propyl sulfide (10%, also eq 4), as the α-cleavage step involves hydrogen loss. No appreciable amount (<2%) of **c** is observed for ethyl *n*-propyl sulfide, for which formation requires the unfavorable loss of an α-hydrogen atom and rearrangement of a primary hydrogen atom. The only compounds studied here which could produce **d** by reaction 3 are the isopropyl sulfides; the α-cleavage step would be unfavorable, involving hydrogen loss, so that reaction 4 is the more likely pathway for **d** formation (vide infra). Consistent with this, deuterium labeling shows that none of this α-H is lost in the formation of $C_3H_7S^+$ from isopropyl *n*-butyl sulfide.[5b]

Equation 3′ is a possible variant of this reaction in which α-cleavage is followed by alkene loss with H-rearrangement at the original α carbon, not the sulfur atom.[4] Of the molecules studied only ethyl *sec*-butyl sulfide appears to yield $C_3H_7S^+$ ions (isomer **b**) by this pathway (5%). Note that reaction 3′, which involves loss of the same α-CH_3 as eq 3, but rearrangement of a α-H instead of a β'-H, apparently is favored over reaction 3 for this precursor; it would be surprising if this is due to the relative stabilities of **b** and **c**, as $CH_2{=}SCH_3^+$ appears to be less stable than $CH_3CH{=}SH^+$.[1] Ions **b** could conceivably be produced by reaction 3′ from $RCH_2SC_2H_5$ where $R \geq C_2H_5$, but here α-cleavage (eq 1) appears to be much more probable. An appreciable amount of **b** also arises from isopropyl ethyl sulfide (2%); a more complex mechanism is necessary to explain this result.

Direct C–S bond cleavage to yield ions **h** and **i** (eq 4) is expected from previous studies.[1,4,5] However, the absence of characteristic CA spectra (vide supra) indicates that these ions isomerize in the 10^{-5} s before collision. It was observed previously that all of the $C_2H_5S^+$ ions formed by loss of R from C_2H_5SR have the structure $CH_3CH{=}SH^+$, presumably formed at higher energies by migration of an α-hydrogen atom.[1] Although the analogous migration of the α-methyl in $CH_3CH_2S^+$ to yield $CH_2{=}SCH_3^+$ was not observed, apparently migration of the secondary α-CH_3 of $(CH_3)_2CHS^+$ (**h**) occurs in competition with α-H migration to yield $CH_3CH{=}S^+CH_3$ (**a**) as well as $(CH_3)_2C{=}S^+H$ (**d**) (eq 4), with [**a**]:[**d**] ~ 1:5. This is observed for the isopropyl sulfides ethyl (**a**, 1.5%; **d**, 7%), isopropyl (**a**, 1.2%; **d**, 7%), and *n*-butyl (**a**, 3.5%; **d**, 14%). In contrast, the related $(CH_3)_2CHCH_2^+$ ions isomerize in the gas phase to a 2.6:1 mixture of $CH_3CHCH_2CH_3^+$ and $(CH_3)_2CCH_3^+$.[12] The negligible formation of **a** ions from isopropylthiol reflects the less favorable dissociation energy of the S–H bond.

For the isomerization of **i**, migration of the primary α-ethyl group to yield **b** should be much less favorable than migration of the α-H to yield **c**, based on the isomerization behavior of **h** and $CH_3CH_2S^+$. The CA data for di-*n*-propyl sulfide (**b**, 4.5%, also eq 7; **c**, 10%, also eq 3) give some, although not compelling, support for this. For this precursor it was rationalized above that eq 3 would not be an important pathway for formation of **c**, while for the formation of the smaller amount of **b** it will be argued (vide infra) that eq 7, not 4, is the more probable pathway indicating that for the products of reaction 4, [**b**] $\ll$ [**c**]. For both the methyl (**b**, 1.5%; **c**, 1.5%) and ethyl (**c**, <2%) *n*-propyl sulfides the amount of **i** formed appears to be low, in the latter case any **b** or **c** ions formed by reaction 4 being obscured by the dominant α-cleavage formation (eq 1) of the **b** isomer. At low energies it is also possible that C–S cleavage is aided by displacement involving an α-H to give **c** or **d**, or an α-CH_3 to give **a**, as postulated for the low energy formation of $CH_3CH{=}SH^+$ from $CH_3CH_2SCD_3$.[1]

Displacement with β-cleavage (eq 5) leads to the cyclic ion **e** for α- or β-methyl thiols and **f** for methyl *n*-alkyl sulfides, which then tend to rearrange to **c** and **a**, respectively. Formation of **c** and **e** from isobutyl- (**c**, 1%; **e**, 1.3%) and *sec*-butyl- (**c**, 2.5%, of which most could be formed by eq 1; **e**, 2%) thiol, and of **c** and/or **e** ions (0.3%) from isopropylthiol, in this manner is indicated. Although the close resemblance of the spectra of **c** and **e** make the ratio of their abundance difficult to determine accurately, a substantial proportion of **c** ions must be produced from isobutylthiol, and reaction 5 appears to offer a reasonable explanation. This ready isomerization **e** $\rightarrow$ **c** is consistent with the similarity in the CA degradations of **c** and **e**. It is possible that the small amount of **d** observed from *sec*-(0.8%) and isobutyl-(0.2%) thiol arises from the isomerization **e** $\rightarrow$ **d**, but this should be less favorable than **e** $\rightarrow$ **c**. Similar rationalizations could be applied to the formation of **f** and **a** by reaction 5 from the n-$C_nH_{2n+1}SCH_3$ compounds (n = 2: **a**, 2%, mainly by eq 1; **f**, 1%; n = 3: **a**, 4.5%; **f**, 2.5%; n = 4: **a**, 14%; **f**, 6%; n = 5: **a**, <15%; **f**, 15% − [**a**]). For most of these compounds the extent of subsequent rearrangement **f** $\rightarrow$ **a** also is substantial, but cannot be quantified because of the similarity in the CA spectra of these isomers and the doubtful purity of the **f** ions from *n*-pentyl methyl sulfide used as a standard.

The isotopic labeling studies of Sample and Djerassi[5b] indicated that 27% of the $C_3H_7S^+$ ions from *n*-butyl and *n*-amyl isopropyl sulfide are formed by reaction 6. Assuming the ready isomerization **e** $\rightarrow$ **c** indicated above, reaction 6 also appears to be the only reasonable explanation for the formation of **c** ions from diisobutyl sulfide (2%). Initial formation of **e** from this compound would appear to be favored, as it involves β-displacement of a secondary methyl and rearrangement of a tertiary hydrogen atom. The amount of **e** observed is much smaller than **c**; this could be due to ring opening of the intermediate cyclic ion (eq 6) as well as of **e**. For di-*sec*-butyl sulfide reaction 6 should be less favorable (both of the bonds cleaved in forming **e** are on less substituted carbons than for diisobutyl sulfide), suggesting that its **c** ions (10%) arise largely from reaction 3. Similarly, the indicated **e** ions (0.8%), as well as **c** ions (0.8%), from ethyl *sec*-butyl sulfide could be due (Table I, "possible alternative") largely to **c** ions resulting from reaction 3.

The final possible combination of reactions involves β-cleavage, perhaps isomerization, and rearrangement through an unsaturated ring transition state, as represented by eq 7. This can explain the predominant **b** fraction of the $C_3H_7S^+$ ions formed by di-*n*-butyl sulfide (1.4%) with β-displacement of an ethyl radical and rearrangement of a secondary hydrogen

atom. A larger amount (although a smaller fraction of the $C_3H_7S^+$ ions) is formed as **b** for di-*n*-propyl sulfide (5%, eq 4 is unlikely, vide supra), despite the fact that this involves the loss of methyl and rearrangement of a primary hydrogen atom; the lower formation of **b** from di-*n*-butyl sulfide could result from competition by the dominant formation of $C_2H_5S^+$ by reaction 2. The **b** ions formed from propyl and butyl ethyl sulfides should arise only in small part by eq 7, α-cleavage appearing to be the much more probable pathway. Our data do not distinguish between the alternative rearrangement of hydrogen to the ring methylene, or to the unsaturated carbon of the isomerized intermediate ion; the ready ring opening of **e** and **f** indicated above would favor the latter explanation.

Additional Reaction Pathways. The formation of **a** ions from methyl isobutyl (8%), di-*n*-butyl (0.5%), and diisobutyl sulfide (1.2%) ions does not appear to arise from a combination of reactions 1-7. Isomerization of an *n*- or isobutyl to a *sec*-butyl skeleton (before or after H loss) could give **a** by reactions such as 1 or 2; isotopic labeling should help to establish more definitive mechanisms.

Conclusions

As found for the formation of $C_2H_5S^+$ ions, the α-cleavage reactions appear to provide the most important pathways for the formation of $C_3H_7S^+$ ions, both by direct cleavage (eq 1) and by a combination of α-cleavage and rearrangement reactions (eq 2 and 3). Displacement rearrangement with β-cleavage (eq 5) is also of importance; for *n*-alkyl methyl sulfides this reaction gives $C_3H_7^+$ abundances which are 15-20% of those of the α-cleavage product, $C_2H_5S^+$; for *n*-alkyl thiols the ratio is substantially higher (~50%).[5,6] As found for α-cleavage, the even-electron ions formed by β-cleavage can undergo further rearrangement through either saturated (eq 6) or unsaturated (eq 7) ring transition states.[4] For reactions involving C-S bond cleavage, the previous study[1] indicated for CH_3CH_2SH that losses of H from α-C, β-C, and S are in the ratio 44:38:18, and for $CH_3CH_2SCH_3$ that losses of CH_3 from α-C and from S are in the ratio 75:25. The low importance of C-S cleavage (eq 4) relative to either α- or β-cleavage is confirmed in this study; for $C_2H_5CH_2SC_2H_5$ the loss of ethyl is nearly all from the α-C, while for $CH_3CH_2CH_2SCH_3$ the losses of CH_3 are 15% from S to produce **c** and ~70% from β-C to produce **a** and **f**.

As observed for the monovalent sulfur ion $CH_3CH_2S^+$,[1] the isomers $(CH_3)_2CHS^+$ and $CH_3CH_2CH_2S^+$ are unstable, isomerizing to **d** and **a** ([**d**]:[**a**] ~ 5:1) and to **c**, respectively. Despite the uncertainty in measuring the spectra of the cyclic ions **e** and **f**, they appear to have a substantially higher tendency than found for the unsubstituted protonated ethylene sulfide[1] to undergo ring openings yielding the open-chain isomers.[13] The unsubstituted $\overline{CH_2CH_2SH}^+$ and its ring-opened product $CH_3CH{=}SH^+$ appear to have nearly equivalent stabilities;[1] possibly the additional methyl group stabilizes the cyclic ions **e** and **f** less than it does their ring-opened products **c** and **a**.

The mass spectra of aliphatic thiols and sulfides exhibit a much wider variety of decomposition pathways than do the spectra of their oxygenated analogs; however, the detailed information on the isomeric products supplied by the CA spectra shows that the reactions observed in general correlate well with established mechanisms.[4,5]

Experimental Section

The measurements were carried out as described previously.[1,14] Samples were obtained from commercial sources, checked by mass spectrometry, and purified by gas chromatography where necessary. Although the CA spectra of the $C_3H_7S^+$ ions from *sec*-butyl and isobutyl methyl sulfide are nearly identical, the normal mass spectra of these compounds are not, exhibiting base peaks at *m/e* 75 and 61, respectively.

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References and Notes

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(11) Using combinations of the CA spectra of ions **a**-**e** and **g**, the CA spectrum of $C_3H_7S^+$ ions from methyl *n*-pentyl sulfide can be fit best by the mixture 85% **a**:15% **b**. However, abundance of these spectra differ on average by 1.9 SD (see ref 10). Further, a very recent publication [K. Levsen, H. Heimbach, C. C. Van de Sande, and J. Monstrey, *Tetrahedron*, **33**, 1785 (1977)] elegantly establishes the cyclic nature of ion f by showing that $C_3H_5D_2S^+$ ions from $FC_6H_4OCH_2CD_2SCH_3$ and $FC_6H_4OCD_2CH_2SCH_3$ give identical CA spectra.
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