bond. See also ref 63b.

(63) (a) R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951); (b) R. E. Rundle in "Survey of Progress in Chemistry", Vol. 1, A. F. Scott, Ed., Academic Press, New York, N.Y., 1963, p 81.

(64) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(65) J. Jortner, S. A. Rice, and E. G. Wilson, *J. Chem. Phys.*, **38**, 2302 (1963).

(66) M. A. Ratner and J. R. Sabin, *J. Am. Chem. Soc.*, **93**, 3542 (1971).

(67) R. S. Mulliken and B. Liu, *J. Am. Chem. Soc.*, **93**, 6738 (1971).

(68) F. Keil and W. Kutzelnigg, *J. Am. Chem. Soc.*, **97**, 3623 (1975).

(69) In the analogous PH_5 system, the axial H–P–H system contributes significantly to both the 3a′ and 4a′ CMO's (see Figure 1 in ref 70). The nonbonding orbital in the present analysis would correspond most closely to the linear combination of these CMO's which purges the contributions from the equatorial hydrogens.

(70) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94**, 3035 (1972).

(71) (a) Reference 70 notes that the nodal structure of 4a′ in the analogous system PH_5 precludes appreciable contributions from s-type functions on P. (b) Also for PH_5, a 4-31G calculation finds the coefficients of the "inner" and "outer" 3s functions on P to be just −0.0139 and 0.0302, respectively (J. M. Howell, private communication to T.A.H.).

(72) Note that the contributions from other valence OAO's should not be greatly diminished, since a change in population for a hybrid OAO strongly involved in bonding (hence having a population of ~1 electron) changes its contribution to the valency only to second order; cf. eq 7.

(73) (a) I. H. Hillier and V. R. Saunders, *Int. J. Quantum Chem.*, **4**, 203 (1970); (b) *Trans. Faraday Soc.*, **66**, 1544, 2401 (1970).

(74) (a) M. F. Guest, I. H. Hillier, and V. R. Saunders, *J. Chem. Soc., Faraday Trans. 2*, **68**, 114, 867 (1972); (b) M. F. Guest and I. H. Hillier, *Int. J. Quantum Chem.*, **6**, 967 (1972).

(75) While the results cited do not represent an exhaustive compilation, no attempt has been made to exclude data which did not support our thesis. Since this area continues to be of great theoretical interest, no doubt additional calculations and comparisons will be forthcoming.

(76) D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **48**, 4968 (1968). Footnote 10 discusses the possible exaggeration of d-orbital participation when small basis sets are used.

(77) S. Rothenberg, R. H. Young, and H. F. Schaefer III, *J. Am. Chem. Soc.*, **92**, 3243 (1970).

(78) F. P. Boer and W. N. Lipscomb, *J. Chem. Phys.*, **50**, 989 (1969).

(79) J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.*, **64**, 5142 (1976).

(80) D. L. Wilhite and L. Spialter, *J. Am. Chem. Soc.*, **95**, 2100 (1973).

(81) G. M. Schwenzer and H. F. Schaefer III, *J. Am. Chem. Soc.*, **97**, 1393 (1975).

(82) S. Rothenberg and H. F. Schaefer III, *J. Chem. Phys.*, **53**, 3014 (1970).

(83) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **21**, 368 (1971).

(84) For PF_5, especially, the large stabilization energy may partly reflect the better suitability for hybridization with s and p functions of the contracted d orbitals associated with relatively positive central atoms; cf. ref 16b,c.

(85) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory", Wiley, New York, N.Y., 1970, pp. 174, 175.

Structure and Formation of Gaseous $C_2H_5S^+$ Ions[1]

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Abstract: Characterization of $C_2H_5S^+$ ions in the gas phase using their collisional activation (CA) spectra shows that only $CH_3SCH_2^+$ (**a**), CH_3CHSH^+ (**b**), and $\overline{CH_2CH_2S}H^+$ (**d**) are stable. Contrary to previous evidence, $CH_3CH_2S^+$ (**c**) is less stable, isomerizing to **b** in $<10^{-5}$ s, and no evidence for the formation of $HSCH_2CH_2^+$ (**e**) or $CH_2{=}CHSH_2^+$ (**f**) could be found. The cyclic ion **d** is relatively more stable than its $C_2H_5O^+$ analogue, this isomer accounting for most of the $C_2H_5S^+$ ions formed in the mass spectra of *n*-alkyl thiols. For decompositions of $C_2H_5SR^{+\cdot}$ ions, C–S bond cleavage is facile in comparison to C–O scission in ethyl ethers, despite the relatively low stability of the initial product **c**; apparently the looseness of the activated complex is an important factor in making this reaction competitive. A variety of mechanisms for the formation of such ions (eq 1–6) were tested, and the isomeric products in general agree with the predicted structures.

Of the possible isomeric ions of the formula $C_2H_5S^+$, **a–f** (Table I), several have been postulated as products of unimolecular ion decompositions in the mass spectra of thiols and thioethers[3-6] and of ion–molecule reactions.[7,8] In an effort to obtain more conclusive data, we have examined $C_2H_5S^+$ isomers from a variety of sources using collisional activation (CA) mass spectra; such data have proven to be uniquely useful for structural characterization of gaseous organic ions of lifetimes $\geq 10^{-5}$ s, as CA spectra are insensitive to ion internal energy.[9] This report constitutes an extension of previous CA studies of analogous even-electron $C_2H_5O^+$ and $C_2H_6N^+$ isomers,[10] probing the effect of replacing a first-row heteroatom by a second-row analog.

The major fragmentation pathways proposed previously for the mass spectra of thiols and thioethers are shown in Scheme I; formation of isomers **a–c**, and **d** or **e**, is consistent with isotopic labeling and correlative evidence.[3-6] No studies postulating the formation of isomer **f** were found.

Isomers **c** and **d** have attracted particular interest; the abundances of peaks corresponding to the formation of these ions by reactions 4 and 5 are remarkable in comparison to the mass spectra of the corresponding oxygen-containing compounds.[3-5] The mass spectrum of CH_3CD_2SH shows $[(M - D)^+]/[(M - H)^+] = 45{:}55$, which was interpreted to indicate that **c** formation (eq 4) is equivalent to that of **b** (eq 1),[6] in sharp contrast to the behavior of oxygenated compounds.[11] Appearance potential studies find the heat of formation (ΔH_f) of $C_2H_5S^+$ ions thought to have structures **a, b,** and **c** to be experimentally indistinguishable,[5,6] and higher than the estimated value of **d**;[7] in contrast, the values for the oxygenated analogs show substanital differences (Table I). The ΔH_f value of $(C_2H_5S)^+$ derived from C_2H_5SH of 203 kcal/mol[6] (210 for $C_2HD_4S^+$ from C_2D_5SH)[5] presents a special dilemma, as this should represent a minimum value for ions **b, c,** and **d** (eq 1, 4, and 5, respectively) if these are formed without reverse activation energy. The apparent equivalence in stability of **c** to that of **a** and **b,** in contrast to their oxygen analogs, has been attributed by Keyes and Harrison[5] to the much *less* effective resonance stabilization of **a** and **b,** lowering their stabilities to be comparable to that of **c.** However, SCF molecular orbital calculations[12] for $HOCH_2^+$ and $HSCH_2^+$ indicate that sulfur forms a *stronger* π bond to the adjacent cationic center than does oxygen. It has also been suggested that the formation of **c** is more competitive relative to that of its oxygen analog owing to the greater ability of sulfur to stabilize the positive charge on itself in ion **c.** [3c]It should be noted that no direct experimental evidence for the existence of the $CH_3CH_2S^+$ isomer **c** appears to have been reported.

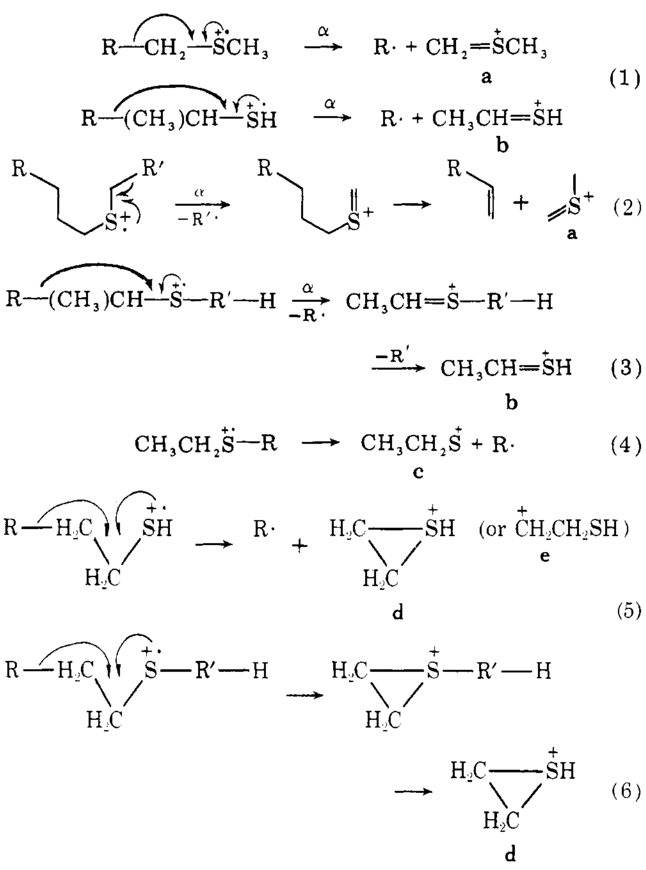
The cyclic ion **d** has also eluded direct experimental characterization.[13] Formation of **d** by eq 5 has been proposed to account for the much larger relative abundance of $(C_2H_5S)^+$ ions in the spectra of *n*-alkyl thiols than that of $(C_2H_5O)^+$ in

Table I. $C_2H_5S^+$ Ions

Ion	ΔH_f, kcal/mol	ΔH_f of the analogous oxygen ion
a $CH_2{=}S^+CH_3$	205,[5] 203[a]	158[8]
b $CH_3CH{=}S^+H$	197,[5] 203[b]	143[8]
c $CH_3CH_2S^+$	202,[5] 203[b]	~195[c,5]
d $CH_2CH_2SH^+$	192[c,7]	169[8]
e $^+CH_2CH_2SH$	(210)[d]	
f $CH_2{=}CHS^+H_2$		

[a] Mean value from four precursors.[6] [b] Value using C_2H_5SH as the precursor, so that ions formed were presumed to be isomers **b** and/or **c.**[6] [c] Estimated value. [d] Value derived from C_2D_5SH; structure **e** suggested as possible explanation for large discrepancy in comparison to value found for **b.**[5]

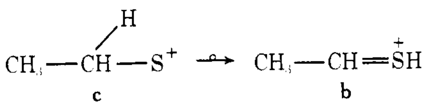
Scheme I



the corresponding alcohol spectra.[3,4] It has also been postulated that **d** is formed by loss of water from protonated β-mercaptoethanol,[7] and from the ion-molecule reaction of H_2S and protonated ethylene oxide.[8] It is pointed out that the cyclic ion **d** should be favored energetically over protonated ethylene oxide, there being considerably less ring strain energy with the second-row atom.[7,8]

Results and Discussion

Reference Ions. The CA spectra of $C_2H_5S^+$ ions prepared from a variety of percursors are shown in Table II. Unless noted otherwise, spectra taken at low ionizing electron voltages were the same within experimental error, indicating that the $C_2H_5S^+$ isomeric composition is independent of energy. Inspection of such spectra utilizing a computer error minimization program shows that only three characteristic patterns are distinguishable. The α-cleavage reaction (eq 1) is probably the best documented of the pathways shown, and leads to the assignment of structures **a** and **b** to the $C_2H_5S^+$ ions produced from methyl alkyl sulfides (without α substituents) and α-methylalkyl thiols, respectively. However, the CA spectrum of $C_2H_5S^+$ ions from $C_2H_5SCD_3$, which presumably are formed as **c** by reaction 4, is identical within experimental error with the spectrum from **b.** Although the CA spectrum of **b** is also similar to that from the protonation of ethylene sulfide (**d**), in this case the differences are statistically significant and reproducible in measurements on different days. As justified further below, a rapid isomerization involving H-atom transfer (eq 7) is indicated; note that methyl transfer to yield **a** is not competitive.

 (7)

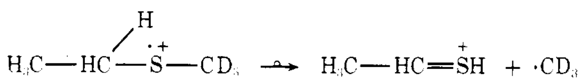
$$\underset{\textbf{c}}{CH_3{-}\overset{\overset{H}{/}}{C}H{-}S^+} \longrightarrow \underset{\textbf{b}}{CH_3{-}CH{=}\overset{+}{S}H} \qquad (7)$$

The spectrum of **d** cannot be matched to that of any combination of **a** and **b**, but does fit the CA spectra of $C_2H_5S^+$ ions from all *n*-alkyl thiols examined (eq 5, vide infra). We conclude that the protonation of ethylene sulfide does yield stable ions of isomer **d**; the spectrum measured could arise in part from **b** formed by isomerization, but its lack of dependence on electron energy indicates that this is minor. The isomerization of **d** to **e** should be insignificant based on their predicted stabilities;[3,4] further evidence of this will be given below. Thus the CA spectra indicate that the isomerizations of **a**, **b**, and **d** involve substantial activation energies and provide no evidence for the formation of **c**, **e**, or **f** ions of lifetimes $\geq 10^{-5}$ s from the variety of precursors studied.

The $C_2H_5S^+$ decomposition reactions producing the peaks observed in the three distinguishable CA spectra support their assignment to isomers **a**, **b** (not **c**), and **d** (although equally consistent with **e**). The spectrum assigned to **a**, which does not have adjacent carbon atoms, shows $C_2H_{1-4}{}^+$ ions (*m/e* 25-28) of much lower abundance than those of **b** and **d.** The ratio $[C_2H_5S^+ - CH_2]/[C_2H_5S^+ - CH_3]$ is smaller for **a** (0.15) and **b** (0.2) than for **d** (0.5), consistent with the CH_3 groups in **a** and **b** and the type of CH_2 group in **d**; a similar CA behavior was noted for the linear vs. cyclic isomers of $C_2H_4O^{+\cdot}$.[10a] and $C_2H_5O^+$.[10b] The CA spectrum of **c** should show substantial differences vs. that of **b,** such as the presence of $C_2H_5{}^+$ and/or S^+ peaks; these are not significant in the spectrum of $C_2H_5S^+$ from $C_2H_5SCD_3$.

Heats of Formation of $CH_2{=}SCH_3{}^+$ (a) and $CH_3CH{=}SH^+$ (b). The similarities of the ΔH_f values of **a**, **b**, and **c** found by Keyes and Harrison raised doubts as to whether these ions actually have the indicated structures.[5] For isomers **a** and **b**, the CA data fully support these structure assignments; further, indirect evidence will be given below that **b** is somewhat more stable than **a**, qualitatively consistent with the measured difference of 8 kcal/mol in their ΔH_f values. Note the corresponding ~15 kcal/mol difference for the $C_2H_5O^+$ isomeric analogs.[8]

Heat of Formation of $CH_3CH_2S^+$ (c). The ready isomerization **c** → **b** indicated by the CA data is surprising because of the near equivalence of the heat of formation values reported for **b** and **c.**[5,6] Measurements on $C_2H_5SCD_3$ gave appearance potentials of 10.75 eV for $C_2H_5S^+$ ions and 10.84 eV for $C_2H_2D_3S^+$ ions, presumed to be **c** and **a**, respectively;[5] the CA spectrum (Table II) shows the former to have the structure **b.** Further, only 25% of the $C_2H_5S^+$ ions from $C_2H_5SCH_3$ have structure **b**, the remaining being **a**; this would not be expected if the loose complex reaction (eq 4) forming **c** had a lower activation energy than the α-cleavage reaction (eq 1) forming **a.** Alternatively, the lowest energy reaction could be an anchimeric assisted rearrangement leading directly to **b** (eq 8;

 (8)

$$H_3C{-}\overset{\overset{H}{/}}{H}C{-}\overset{\cdot+}{S}{-}CD_3 \longrightarrow H_3C{-}HC{=}\overset{+}{S}H + \cdot CD_3 \qquad (8)$$

Table II. Collisional Activation Spectra of $C_2H_5S^+$ Ions

		m/e of daughter ion[a]																	
Compound	Reaction	25	26	27	28	32	33	34	35	44	45	46	47	56	57	58	59	60	Ion structure[b]
$CH_3S(CH_2)_3CH_3$[c]	1	0.2	0.8	6.2	0.2	0.6	0.7	0.8	(18)	4.2	36	17	2.5	0.9	6.1	12	11	(4.0)	**a**
$CH_3SCH_2CH(CH_3)_2$	1	0.2	0.7	6.1	0.1	0.6	0.7	0.7	(18)	4.2	37	17	2.5	0.9	6.1	12	11	(3.7)	**a**
CH_3SCH_2Cl	1	0.1	0.7	5.6	0.1	0.6	0.7	0.6	(13)	4.5	38	18	2.9	0.8	5.5	11	10	(5.2)	**a**
$((CH_3)_2CHCH_2)_2S$	2	0.2	1.1	5.7	0.4	0.6	0.6	0.7	(7.6)	3.9	35	16	3.0	1.2	5.9	13	13	(9.6)	**a**
$(CH_3CH_2CH_2)_2S$[d]	2	0.2	0.8	5.8	0.4	0.7	0.8	0.7	(8.0)	4.0	35	16	2.7	1.1	6.7	12	13	(9.3)	**a**[e]
CH_3SSCH_3	−SH	0.2	0.7	6.1	0.2	0.8	0.8	0.7	(13)	4.2	38	17	2.4	0.9	5.5	12	11	(3.2)	**a**
$(CH_3)_2CHSH$	1	0.5	3.4	11	0.8	1.2	2.2	1.8	(27)	2.7	18	2.9	0.6	1.8	12	22	20	(8.1)	**b**
$CH_3CH_2(CH_3)CHSH$	1	0.6	3.8	12	1.3	1.4	2.6	1.9	(19)	2.5	17	2.5	0.5	1.8	12	22	19	(8.8)	**b**
$((CH_3)_2CH)_2S$	3	0.6	3.4	11	1.8	1.3	2.5	1.7	(8.1)	2.2	16	2.1	0.5	1.6	11	23	22	(14)	**b**
$(CH_3CH_2(CH_3)CH)_2S$	3	0.7	4.2	12	2.0	1.5	3.1	2.2	(10)	2.2	16	1.9	0.5	1.5	10	22	19	(11)	**b**
$(CH_3)_2CHS(CH_2)_3CH_3$	3	0.7	3.1	9.3	1.7	1.4	2.2	1.8	(14)	2.4	18	3.2	1.0	1.8	11	21	22	(17)	**b**[e]
$(CH_3CH_2)_2S$	3, 4	0.5	3.1	11	1.0	1.1	2.1	1.9	(23)	2.4	18	3.3	0.6	1.7	11	23	20	(11)	**b**
$CH_3CH_2SCH(CH_3)_2$	3, 4	0.6	2.9	11	1.0	1.1	2.3	2.0	(21)	2.4	17	2.6	0.6	1.5	11	23	21	(12)	**b**
$CH_3CH_2SCH(CH_3)CH_2CH_3$	3, 4	0.5	3.0	10	1.0	1.3	2.2	2.0	(19)	2.3	18	2.8	0.6	2.0	12	23	21	(11)	**b**
$CH_3CH_2SCH_3$	1, 4	0.2	1.5	7.7	0.4	0.9	1.0	1.1	(21)	3.9	32	14	2.0	1.2	7.2	14	13	(5.0)	**a** (85%), **b**
13 eV[f]	1, 4	0.2	0.9	6.3	0.3	1.0	1.3	0.8	(12)	4.5	32	14	2.3	1.1	7.5	15	13	(5.5)	**a** (80%), **b**
$CH_3CH_2S(CH_2)_2CH_3$	2, 4	0.6	2.8	9.8	1.0	1.2	1.8	1.8	(22)	3.2	21	6.2	1.2	1.6	9.9	19	19	(14)	**a** (25%), **b**[e]
12 eV[f]	2, 4	0.7	3.0	9.4	1.3	1.6	2.4	1.4	(7.3)	4.8	23	8.4	1.3	1.5	7.9	17	17	(14)	**a** (40%), **b**[e]
$CH_3CH_2S(CH_2)_3CH_3$	2, 4	0.3	1.8	8.2	0.6	1.0	1.6	1.7	(20)	3.6	26	10	1.8	1.3	8.4	18	17	(11)	**a** (50%), **b**[e]
17 eV[f]	2, 4	<0.2	1.4	7.2	0.7	1.3	1.1	0.8	(7.5)	4.5	30	11	2.2	1.7	8.1	16	14	(13)	**a** (65%), **b**[e]
$\overline{CH_2CH_2S}H$[g]	CI	0.9	3.4	12	1.5	1.7	2.7	2.5	(22)	2.9	20	3.7	1.7	1.7	10	18	18	(—)	**d**
$CH_3(CH_2)_3SH$	5	0.8	3.3	12	0.8	1.4	2.3	2.6	(30)	3.0	20	3.7	1.5	1.9	11	18	18	(7.8)	**b** (15%), **d**
12 eV[f]	5	0.9	3.7	13	1.2	1.4	1.6	1.7	(22)	2.4	21	3.8	1.7	1.3	10	18	19	(7.1)	**b** (15%), **d**
$CH_3(CH_2)_4SH$	5	0.7	3.3	12	0.9	1.7	2.3	2.4	(30)	2.8	20	3.9	1.3	1.6	11	18	19	(12)	**b** (15%), **d**
$CH_3(CH_2)_6SH$	5	0.8	3.4	11	1.0	1.3	2.2	2.1	(28)	2.7	20	4.1	1.6	1.6	9.8	18	20	(12)	**b** (15%), **d**
CH_3CH_2SH	1, 4, 5	0.9	3.5	12	0.9	1.4	2.3	2.2	(32)	2.7	17	3.4	0.8	2.0	11	20	20	(14)	**b** (60%), **d**
14 eV[f]	1, 4, 5	1.2	4.5	12	1.4	2.8	3.0	2.2	(15)	3.8	18	2.7	0.4	2.2	11	19	17	(13)	**b** (50%), **d**
$CH_3S(CH_2)_2CH_3$[h]	1	0.3	1.1	6.8	0.2	1.3	0.9	0.6	(13)	5.6	39	17	2.2	0.9	5.3	10	8.4	(3.0)	**a**
$(CH_3)_2CHSH$[h]	1	1.1	5.5	13	1.2	2.3	3.0	2.2	(19)	3.1	17	2.3	0.4	1.8	11	19	17	(5.0)	**b**
$CH_3CH_2SCH_3$[h,i]	1, 4	0.5	2.2	8.8	0.4	1.7	1.5	1.1	(15)	5.8	33	13	1.8	1.3	6.9	12	10	(3.5)	**a** (75%), **b**
$CH_3CH_2SCD_3$[h,j]	4, 7	1.2	5.2	14	1.5	2.2	3.5	2.3		3.3	17	2.3	0.5	1.7	11	19	18		**b**

[a] Abundances relative to the total ion abundance = 100 excluding small peaks at *m/e* 14, 15, and 29, and those from metastable ion decompositions at *m/e* 35 and 60. [b] Mixtures were analyzed using a weighted least-squares method. Accuracy of compositions 5% absolute for mixtures of **a** and **b** and for mixtures of **a** and **d,** 30% absolute for mixtures of **b** and **d.** [c] The spectra of *n*-propyl and *n*-pentyl methyl sulfide are identical within experimental error. [d] The spectrum of di-*n*-butyl sulfide is identical within experimental error. [e] Some **d** cannot be excluded, so that reaction 6 is an additional possible pathway for $C_2H_5S^+$ formation. [f] Ionizing electron energy; in other cases 70 eV was used. [g] Produced from ethylene sulfide and water at high pressure. Data are an average of several spectra and are corrected for isotopic contributions from $C_2H_4S^+$ and $C_2H_3S^+$ ions. [h] Data measured several months later under somewhat different experimental conditions. [i] Ionizing electron energy 20 eV. [j] Corrected for unlabeled ethyl methyl sulfide and for $C_2HD_2S^+$ formed from $C_2H_2D_3S^{+}\cdot$.

note the similarity to eq 7); this is consistent with the CA evidence and the indicated lower ΔH_f value of **b** compared to **a.**[5] The bulk of $C_2H_5S^+$ ions could still be formed as **c** from higher energy molecular ions through simple cleavage (eq 4); because reaction 4 involves less double bond formation than the competing reaction 1, it presumably has a looser activated complex, and so could still be competitive at higher energies despite a higher activation energy requirement. To test this alternative explanation, we remeasured $[C_2H_5S^+]/[C_2H_2D_3S^+]$ from $C_2H_5SCD_3$ as a function of electron energy. This ratio was ≤ 0.35 at all energies, and dropped relatively rapidly ($0.35 \rightarrow 0.2$) from ~15 to ~12 eV, observations consistent with a *higher* heat of formation for **c** than **a**;[14] in contrast, when the electron energy was lowered below there was no further change in this ratio within experimental error (the ratio actually appeared to rise slightly), consistent with the formation of **b** by eq 8 and with Harrison's[5] measurements. However, there were substantial experimental uncertainties in our ratio determinations.

Another conflicting indication of the high tendency for **c** formation is the report[6] that the mass spectrum of CH_3CD_2SH yields $(M - D)^+$ (**b,** eq 1) and $(M - H)^+$ (presumed[6] to be **c,** eq 4) in the ratio 45:55. However, we find for the mass spectrum of C_2H_5SD that $[(M - H)]/[(M - D)^+] = 82{:}18$, so that losses of the H atoms from the α- and β-carbon atoms in CH_3CH_2SH (eq 1 and 5) are approximately equivalent, and much *larger* than H loss from S (eq 4). Because eq 4 should have a looser activated complex than eq 1 (vide supra), 5, or 8, this should indicate that H loss from S has the highest activation energy of the H losses from C_2H_5SH. We thus conclude that $\Delta H_f(\mathbf{c})$ is substanitally greater than 205 kcal/mol,[15] which is consistent with the facile isomerization of **c** to **b,** and there is no need to invoke any unusual degree of ionic stabilization by sulfur in $CH_3CH_2S^+$. In the mass spectra of C_2H_5S–R compounds the higher abundance of $(C_2H_5S)^+$ ions, relative to that of $(C_2H_5O)^+$ from C_2H_5O–R, thus does not show that ions such as **a** and **b** which are formed in competing reactions are necessarily less well stabilized by resonance than their oxygen-containing counterparts. The main characteristic of the $CH_3CH_2S^+$ ion favoring its formation appears to be that the charge stabilization, although limited, does not produce double bond character, with concomitant loss of free rotors, in the activated complex to the degree found for even α-cleavage reactions (eq 1), making eq 4 competitive with such lower activation energy reactions for higher energy molecular ions.

Fragmentation Pathways. There do not appear to be any reasonable alternatives to the assumption that the ubiquitous α-cleavage reaction (eq 1) gives the stable isomers **a** and **b.** These CA spectral assignments are also consistent with the products expected for the general reactions which involve α-cleavage followed by rearrangement through unsaturated (eq 2) and saturated (eq 3) ring transition states.[3,4] Sulfides in which neither alkyl group has α-substituents and one has at least a three-carbon chain, here illustrated by di-*n*-propyl, di-*n*-butyl, and diisobutyl sulfide, give predominantly the **a** isomer, as predicted by eq 2. Sulfides with an α-methylalkyl and an alkyl larger than methyl can yield the **b** isomer (eq 3), as shown by the data from diisopropyl, di-*sec*-butyl, and isopropyl *n*-butyl sulfide; **b** could also be formed in these compounds by the reverse of these steps, initial rearrangement loss of the olefin R′ to form $R\text{-}(CH_3)CH\text{-}SH^{+\cdot}$ followed by α-cleavage (eq 1).[4b] The $C_2H_5S^+$ ion formed from CH_3SSCH_3 by the rearrangement elimination of SH has the **a** structure as predicted.[16]

The *n*-alkyl thiols $C_nH_{2n+1}SH$, where $n = 4$, 5, and 7, yield $C_2H_5S^+$ ions whose CA spectra indicate that these are mainly the **d** isomer, consistent with primary formation through displacement rearrangement (eq 5).[3,4] Formation of **d** from C_2H_5SH should involve the loss of the β-hydrogen atom (eq 5); the abundances of $(M - H)^+$ and $(M - D)^+$ in the spectra of CH_3CD_2SH[6] and C_2H_5SD (vide supra) are in approximate agreement with the ~40% **d** indicated by the CA spectrum. Reaction 5 should involve a tighter activated complex than reactions 1 or 4, consistent with the ~50% **d** (a value with a large experimental uncertainty) formed from C_2H_5SH with 14-eV ionizing electrons. Based on the appearance potential studies of C_2H_5SH, this suggests that $\Delta H_f(\mathbf{d}) \leq 203$ kcal/mol[6] (or 210 kcal/mol using the value[5] for $C_2HD_4S^+$ from C_2D_5SH, which could be high due to an isotope effect); this cannot be used as evidence that $\Delta H_f(\mathbf{d}) < \Delta H_f(\mathbf{b})$ unless it can be established that there is no reverse activation energy for the formation of **b** from C_2H_5SH. Thus the high tendency to form **d** in the mass spectra of *n*-alkyl thiols, in comparison to the formation of protonated ethylene oxide in alcohols,[10b] derives from the relative stability of the cyclic ion **d**; this supports the previous postulation of the lower ring strain energy which should result from sulfur incorporation.[7,8]

Some of the compounds studied could yield $C_2H_5S^+$ ions from more than one of the mechanisms outlined above. The ethyl α-methylalkyl sulfides yield only the **b** isomer, but this could occur through both reactions 3 and 4. The ethyl alkyl sulfides in which the alkyl group does not contain an α-methyl can produce **a** by reaction 2 as well as **b** by reaction 4. In contrast to the 3:1 dominance in methyl ethyl sulfide of **a** formation by reaction 1 over **b** by 4, **a** yields are 25, 50, and 40% for the *n*-propyl, *n*-butyl, and isobutyl, respectively, ethyl sulfides; these values increase with decreasing energy of the ionizing electrons. In line with the previous discussion concerning the looseness of the activated complex for eq 4, here in competition with a rearrangement (eq 2) the reaction producing the less stable **c** ions is actually favored.

Formation of **d** has also been postulated by a two-step process (eq 6) for sulfides $RSCH_2CH_2R'$, where R is larger than methyl; isotopic labeling indicated that 27% of the $C_2H_5S^+$ ions are formed by reaction 6 for *n*-butyl and *n*-amyl isopropyl sulfide, but none for *n*-amyl isoamyl sulfide.[3b] Our CA results are consistent with this conclusion for *n*-butyl isopropyl sulfide, but show that at most 10% **d** is formed in competition with eq 2 for di-*n*-propyl and di-*n*-butyl sulfide. For the mass spectra of compounds in which eq 6 is in competition with reactions forming **b** the yield of **d** is not large; the quantity cannot be determined because of the similarities in the CA spectra of **b** and **d.**

Relative Stabilities of the $C_2H_5S^+$ Isomers. These studies thus indicate that the stabilities of $CH_3CH{=}SH^+$ (**b**) and the cyclic ion **d** are comparable, and that $CH_3S{=}CH_2^+$ (**a**) could be slightly less stable than **b.** Isomer **c** containing monovalent sulfur is clearly less stable than **b,** indicating that π bonding to the heteroatom is indeed important in the stabilization of ions **a** and **b;** this is also supported by the observation that the formation of **a** by reaction 1 involves a tighter activated complex than the formation of **c** by reaction 4. Formation **c** by reaction 4 can be dominant when the competing formation of a more stable ion involves a reaction with an even tighter activated complex, such as reaction 2 forming **a** in ethyl *n*-propyl sulfide; thus $CH_3CH_2S^+$ (**c**) appears to be significantly more stable than $HSCH_2CH_2^+$ (**e**) (for whose formation no CA evidence could be found), suggesting that there is appreciable charge stabilization by the monovalent sulfur.[3b] Preliminary STO-3G calculations by Dr. J. D. Dill qualitatively support these conclusions in finding much higher ΔH_f values for **c** and **f** than for **a, b,** or **d.** Isomer **a** is indicated as less stable than **b** but more than **d;** calculations employing full geometry optimization are planned, as this refinement could be especially important in determining an accurate value for $\Delta H_f(\mathbf{d})$.

Experimental Section

Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer of reversed geometry.[17] A 100-μA ionizing electron beam of 70 eV energy (lower where noted) and an accelerating potential of 7.8 kV were used; sample reservoir and ion source temperature was 150°. The magnetic field is set to select the $C_2H_5S^+$ precursor ions; ionic products of their metastable decompositions (the MI spectrum) occurring in the field-free drift region between the magnetic and electrostatic (ESA) analyzers are measured by scanning the ESA potential repeatedly under computer control. The pressure in a special collision chamber near the β-focal point[17b] is increased with helium until the precursor ion intensity is reduced to 25% of its original value, and CA product abundances are determined in a second ESA scan. The resulting CA spectra are the computer-averaged composites of at least 16 scans.

Comparisons of CA spectra for isomeric identification and mixture analysis were made using a computer error minimization program 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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References and Notes

(1) Collisional Activation and Metastable Ion Characteristics. 50. Part 49: T. Wachs and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **23**, 243 (1977).

(2) On leave from the Delft University of Technology, the Netherlands.

(3) (a) E. J. Levy and W. A. Stahl, *Anal. Chem.*, **33**, 707 (1961); (b) S. Sample and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 1937 (1966); (c) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967, pp 276–283.

(4) (a) C. Lifshitz and Z. V. Zaretskii in "The Chemistry of the Thiol Group", S. Patai, Ed., Wiley, New York, N.Y., 1974, pp 325–353; (b) F. W. McLafferty, "Interpretation of Mass Spectra", 2nd ed, Benjamin Addison-Wesley, Reading, Mass., 1973, pp 56–62, 152–155.

(5) B. G. Keyes and A. G. Harrison, *J. Am. Chem. Soc.*, **90**, 5671 (1968).

(6) D. Amos, R. G. Gillis, J. L. Occolowitz, and J. F. Pisani, *Org. Mass Spectrom.*, **2**, 209 (1969).

(7) J. K. Kim, M. C. Findlay, W. G. Henderson, and M. C. Caserio, *J. Am. Chem. Soc.*, **95**, 2184 (1973).

(8) R. H. Staley, R. R. Corderman, M. S. Foster, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1260 (1974).

(9) (a) F. W. McLafferty, P. F. Bente, III, R. Kornfeld, S.-C. Tsai, and I. Howe, *J. Am. Chem. Soc.*, **95**, 2120 (1973); (b) F. W. McLafferty, R. Kornfeld, W. F. Haddon, K. Levsen, I. Sakai, P. F. Bente, III, S.-C. Tsai, and H. D. R. Schuddemage, *ibid.*, **95**, 3886 (1973).

(10) (a) C. C. Van de Sande and F. W. McLafferty, *J. Am. Chem. Soc.*, **97**, 4613 (1975); (b) B. van de Graaf, P. P. Dymerski, and F. W. McLafferty. *J. Chem. Soc., Chem. Commun.*, 978 (1975); (c) K. Levson and F. W. McLafferty, *J. Am. Chem. Soc.*, **96**, 139 (1974).

(11) G. R. Phillips, M. E. Russell, and B. H. Solka, *Org. Mass Spectrom.*, **10**, 819 (1975).

(12) F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, *Can. J. Chem.*, **53**, 1144 (1975).

(13) CA evidence for **d** is reported in a preliminary communication.[10b]

(14) The ratio [*m/e* 61]/[*m/e* 64] is a maximum at an ionizing energy of ~15 eV, this ratio dropping to 0.25 at 70 eV. This decrease could be due to the increased tendency for secondary decompositions such as $CH_3CH_2S^+ \rightarrow CH_3CH_2^+ + S$ (there is a corresponding increase in $[C_2H_5^+]$) for **c** ions formed with higher internal energies. Thus this is also at least consistent with the postulated lower stability for **c** than for **a**.

(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. $CH_3CH_2S^+$.

(16) J. H. Bowie, S.-O. Lawesson, J. O. Madsen, C. Nolde, G. Schroll, and D. H. Williams, *J. Chem. Soc. B*, 946 (1966).

(17) (a) T. Wachs, P. F. Bente, III, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 333 (1972); (b) T. Wachs, C. C. Van de Sande, P. F. Bente, III, P. P. Dymerski, and F. W. McLafferty, *ibid.*, **23**, 21 (1977).

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: $CH_3CH{=}SCH_3^+$ (**a**), $CH_2{=}SC_2H_5^+$ (**b**), $C_2H_5CH{=}SH^+$ (**c**), $(CH_3)_2C{=}SH^+$ (**d**), $CH_3\overline{CHCH_2S}H^+$ (**e**), $\overline{CH_2CH_2S}CH_3$ (**f**), and $\overline{CH_2CH_2CH_2S}H^+$ (**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 $\overline{CH_2CH_2S}H^+$, 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 $\overline{CH_2CH_2S}H^+$ 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-