(13) Nitzsche, L. E.; Davidson, E. R. *J. Chem. Phys.* **1978**, *68*, 3103. Nitzsche, L. E.; Davidson, E. R. *J. Am. Chem. Soc.* **1978**, *100*, 7201.
(14) See, for example, Morse, P. M.; Feshbach, H. "Methods of Theoretical Physics"; McGraw-Hill: New York, 1953; p 1153.
(15) Hylleraas, E. A.; Undheim, B. *Z. Phys.* **1930**, *65*, 759. McDonald, J. K. L. *Phys. Rev.* **1933**, *43*, 830.
(16) Sharma, C. S.; Coulson, C. A. *Proc. Phys. Soc., London* **1962**, *80*, 81.
(17) Cohen, M.; Dalgarno, A. *Rev. Mod. Phys.* **1963**, *35*, 506.
(18) Trefftz, E.; Schlüter, A.; Deltmar, K.-H.; Jörgens, K. *Z. Astrophys.* **1957**, *44*, 1.
(19) Davidson, E. R. *J. Chem. Phys.* **1964**, *41*, 656. **1965**, *42*, 4199.
(20) Stenkamp, L. Z.; Davidson, E. R. *Theor. Chim. Acta* **1977**, *44*, 405.

Collisional Activation and Theoretical Studies of Gaseous CSH_3^+ Ions[1,2]

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Abstract: Collisional activation mass spectra of m/z 47 ions from a variety of sulfur-containing compounds demonstrate that both the protonated thioformaldehyde, $H_2C{=}SH^+$ (a), and thiomethoxy, $H_3C{-}S^+$ (b), ion structures are stable (lifetimes $>10^{-5}$ s). Formation of a occurs by α cleavage from thiols, as well as by low-energy anchimeric cleavage from methyl sulfides and by rearrangement of b at higher energies from methyl sulfides. The more stable isomer is indicated by CA to be a, in contrast to previously published thermochemical data. Ab initio calculations indicate that b is a triplet ion; empirical corrections allowing for neglect of correlation are necessary to give heat of formation values of a and b (205 and 215 kcal/mol, respectively) consistent with the experimental results. The activation energy for the rearrangement b → a is substantial (~40 kcal/mol).

Introduction

A problem of long-standing interest in organic chemistry has been the difference in behavior between oxygen and sulfur. Based on solution-phase studies it has generally been accepted that oxygen is the more effective at stabilizing adjacent carbocation centers, while sulfur more effectively stabilizes carbanions and radicals or radical-like photoexcited states.[3] The major reasons for this trend, it has been argued, are the superior π-donating ability of oxygen vs. the π-accepting ability of sulfur, the latter attributed to $d\pi$-$p\pi$ overlap.[3,4] These conclusions have recently been questioned on the basis of theoretical studies,[5,6] which indicate sulfur to be as effective as oxygen in stabilizing cations,[5] and show that interactions involving d functions on sulfur are energetically less important than the greater polarizability associated with its larger, more diffuse orbitals.[6] A recent paper by Caserio and co-workers reviews these arguments.[7]

A number of gas-phase studies involving sulfur-containing positive ions have provided additional information,[7-16] but results have not led to a consistent interpretation. The fragmentation of $HOCH_2CH_2SH^{+\cdot}$ yields a higher abundance of $H_2C{=}SH^+$ (a) than of $H_2C{=}OH^+$,[8] supporting the theoretical conclusion[5a] that a is better stabilized by π interaction. Similarly, recent ion cyclotron resonance studies[7] show that gas-phase formation from $CH_3YCH_2Cl^{+\cdot}$ of $CH_3SCH_2^+$ is preferred over that of $CH_3OCH_2^+$. Further support is provided by the observation that gaseous thioalkoxide ($R_2CH{-}S^+$) isomers of $C_2H_5S^+$ and $C_3H_7S^+$ ions rearrange rapidly to the more stable protonated thiocarbonyl structures $R_2C{=}SH^+$.[9] On the other hand, appearance potential studies of CSH_3^+ [11-16] indicate the $H_3C{-}S^+$ (b) structure to be as[11] or more[12] stable than a, in strong contrast to the situation regarding the oxygen analogues, in which there is little doubt that the $H_2C{=}OH^+$ structure is significantly more stable than other isomers.[17,18]

Combined experimental and theoretical investigations of CSH_3^+ and COH_3^+ are reported in this and the accompanying paper,[18] respectively. Collisional activation (CA) mass spectrometry[19] is used to distinguish between a and b formed under various conditions and ab initio molecular orbital theory to obtain detailed geometries and energies for these and related ions. The results indicate that the most stable form of CSH_3^+ is a, ~10 kcal/mol more stable than the triplet b.

Experimental Section

CA measurements of m/z 47 were made as described previously[9,19] on a computerized double-focusing mass spectrometer of reversed geometry using 7.8-kV accelerating potential and 150 °C ion source temperature. Each spectrum (Table I) is the computer-averaged composite of at least 16 scans. Additional peaks present but not used were m/z 45 and 46, also formed by metastable ion decomposition; m/z 44, a large peak (~five times greater than m/z 33) whose abundance is independent of the mode of formation; m/e 34, which originates in part from $^{34}SCH^+$; and m/z 23.5 (CSH_3^{2+}, weak, very sharp, and of poor reproducibility). Standard deviations, estimated from several separate runs on methyl sulfide, are the larger of ±7% relative or ±0.5% absolute (greater for low-energy ionization). Mixture analysis was based on the m/z 15:14 ratio. CH_3SD was prepared from CH_3SH by exchange with D_2O in the inlet system; the m/z 49:48 from low electron-energy ionization indicated ~92% isotopic purity. Other samples were obtained commercially.

Molecular orbital calculations were carried out using the GAUSSIAN 70 series of computer programs.[20] The minimal STO-3G basis set[21] was used for full geometry optimization of each structure, followed by single calculations with the 4-31G basis[22] at STO-3G geometries. In some cases further optimization was carried out with the 4-31G basis. Calculations of open-shell species employed the UHF procedure of Pople and Nesbet.[23] General discussions of the methodology are given by Pople;[24] for an evaluation of the accuracy of STO-3G and 4-31G calculated properties involving second-row elements (Na-Cl) see Collins et al.[25]

Experimental Results and Discussion

Collisional Activation Spectra. In the CA spectra of m/z 47 ions from a variety of precursors (Table I) two patterns are evident. The spectrum assigned to protonated thioformaldehyde, $H_2C{=}SH^+$ (a), is that found for the thiols RCH_2SH which should give a by R loss via α cleavage;[9] spectra identical within experimental error are found for R = H, CH_3, n-C_3H_7,

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Table I. Collisional Activation Spectra of CSH_3^+ Ions

compd	*m/z* of daughter ion 12	13	14	15	32	33	ion structure[a]
CH_3SH	1.4	3.1	9.0	1.1	35	50	a
12 eV[b]	1.8	4.7	9.2	1.2	36	48	a
CH_3CH_2SH	1.4	2.7	9.3	0.6	35	51	a
16 eV	3.1	4.1	11.5	1.4	34	46	a
$CH_3CH_2CH_2CH_2SH$	1.9	3.6	10.2	0.7	34	50	a
$HOCH_2CH_2SH$	2.1	3.4	9.1	0.9	37	48	a
17 eV	2.0	3.9	10.7	0.4	35	48	a
CH_3SCH_3	2.1	3.3	8.6	0.9	36	49	a
12 eV	2.4	4.0	11.3	1.4	34	47	a
$C_2H_5SCH_3$	2.6	4.1	9.2	1.9	40	41	a (95%), b
i-$C_3H_7SCH_3$	2.3	4.0	9.4	4.5	39	41	a (80%), b
n-$C_3H_7SCH_3$	2.5	4.1	10.0	2.6	39	42	a (90%), b
20 eV	2.5	5.4	14.3	0.9	35	42	a
$CH_2CHCH_2SCH_3$	1.8	4.6	9.4	2.8	35	46	a (90%), b
$C_2H_5SC_2H_5$	2.0	3.8	10.5	0.8	34	49	a
CH_3SSCH_3	1.8	3.4	8.5	6.2	39	41	a (65%), b
12 eV	2.0	3.3	10.3	2.1	37	45	a (95%), b
CH_3SOCH_3[c]	1.9	3.8	7.8	3.2	39	40	a (80%), b
$CH_3SOCH_2SCH_3$	1.6	2.4	7.9	5.1	38	45	a (70%), b
14 eV	3.1	3.3	13.9	1.6	32	46	a
CH_3SD (-H)[d,e]	1.7	2.0	5.4	6.6	30	26	a
14 eV[d]	1.2	1.7	4.8	9.7	26	32	a
CD_3SH (-H)[d]	1.4	0.0	3.5	0.0	29	0.0	a
13 eV[d]	2.2	0.0	3.9	0.0	36	0.0	a
CD_3SH (-D)[d]	2.0	0.1	3.0	4.8	36	20	a
13 eV[d]	2.0	0.1	3.2	6.7	32	19	a

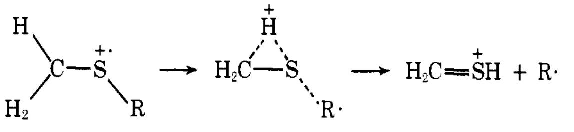
	m/z of daughter ion 16	17	18	34[f]	35[f]	36[f]
CH_3SD (-H)	0.9			27	5.2	
14 eV	0.8			23	4.4	
CD_3SH (-H)	13.1	0.0	1.0	52	0.0	6.9
13 eV	11.7	0.0	1.8	44	0.0	5.0
CD_3SH (-D)	6.6	0.6	0.0	26	3.8	1.6
13 eV	6.1	1.2	0.0	29	3.6	1.7

[a] a = $H_2C{=}SH^+$, b = $H_3C{-}S^+$. Mixtures analyzed by *m/z* 15/14 ratio, estimated error ±15%, assuming that CH_3SSCH_3 gives 50% b at 17.5 eV (see text). [b] Ionizing energy 70 eV unless specified. [c] Dimethyl sulfoxide; corrected for isotopic contributions from H_2CS^+ and HCS^+ to CSH_3^+. [d] Remainder of spectrum at bottom of table. [e] Contains ~8% CH_3SH^+. [f] Possible contributions from $S(H,D)_2^+$ at this mass. SH_2^+ abundance in CA spectrum of CSH_3^+ from CH_3SH is 5.3 units, so these CA spectra are normalized to a total of 105 abundance units.

and $HOCH_2$ at high and low ionizing energies. The spectrum of a is also obtained from ethyl sulfide, presumably[9] through α cleavage and rearrangement loss of ethylene.

The CSH_3^+ ions from dimethyl disulfide yield a different CA spectrum which is consistent with the presence of the thiomethoxide ion structure. Cleavage of the CS bond of CH_3-S^+ ions should produce CH_3^+ (*m/z* 15) and S^+ (*m/z* 32), whose abundances are increased in this CA spectrum compared to that of a; generation of these fragments from $H_2C{=}SH^+$ requires rearrangement. However, changing the ionizing electron energy changes this CA spectrum; at 12 eV it resembles closely that of ion a, and the spectra at other energies are consistent with a mixture of the two ion structures (Figure 1). Because the highest proportion of b is observed at 18 eV, none of these CA spectra should represent that of pure b; the compositions of Table I were calculated arbitrarily assuming the 18-eV spectrum to represent equal amounts of a and b.[26] Except for CH_3SCH_3, significant amounts of b are produced at 70 eV from other CH_3SR compounds;[28] the proportion of b appears to be higher for those compounds in which the S-R bond is weaker. Again, low ionizing energies lead to higher proportions of a.

Indirect $CH_2{=}SH^+$ Formation at Low Energies. The fact that a is favored over b upon lowering the ionizing energy for CH_3SR compounds suggests the presence of a low-energy, tight-complex reaction leading directly to protonated thioformaldehyde (eq 1). Evidence that the formation of higher homologues of a involves such a displacement process has been presented previously.[9] Because the entropy of this process is unfavorable, its dominance at threshold energies indicates that ion a must be somewhat more stable than b, assuming that the reverse activation energy is small.


(1)

Indirect $CH_2{=}SH^+$ Formation at High Energies. The decrease in the relative abundance of b formed from CH_3SSCH_3 at ionizing energies >18 eV, as well as the substantial amounts of a present in other 70-eV methyl sulfide spectra, indicates that another process leading to a is important at higher energies. Rearrangement of the molecular ion prior to fragmentation seems unlikely,[9] as its tight complex transition state should be poorly competitive at high energies. A more plausible scheme is that b ions formed with sufficiently high internal energies rearrange to the more stable a ions on the $\sim 10^{-5}$-s time scale of the CA experiment; the fact that higher homologues of b could not be detected was explained[9] on the basis of the high tendency for rearrangement analogous to b → a. The Figure 1 data are consistent with a substantial activation energy barrier (possibly 40 kcal)[26] for rearrangement b → a.

Table II. Theoretical Energies and Geometries of Sulfur-Containing Species

compd	symmetry	state	total energy, hartrees STO-3G	total energy, hartrees 4-31G	geometry[a]
SH^+	$C_{\infty v}$	$^3\Sigma^-$	−393.488 37	−397.281 24[b]	SH = 1.380
SH_2	C_{2v}	$^1A_1$	−394.311 63	−398.202 99[c]	SH = 1.329, HSH = 92.5
SH_3^+	C_{3v}	$^1A_1$	−394.666 72	−398.458 91[d]	SH = 1.354, HSH = 96.6
HCS^+	$C_{\infty v}$	$^1\Sigma^+$	−430.860 10	−435.080 78	CS = 1.468, CH = 1.100
$H_2C{=}SH^+$	C_s (planar)	$^1A'$	−432.056 39 (0.0 kcal/mol)[f]	−436.272 73 (0.0)	CS = 1.630, SH = 1.351, CH_1 = 1.110,[e] CH_2 = 1.100, CSH = 98.3, SCH_1 = 124.2, SCH_2 = 119.0
$H_3C{-}S^+$	C_{3v}	$^3A_1$	−432.103 79 (−29.7)[f]	−436.301 45 (−18.0)[f]	CS = 1.826, CH = 1.092, SCH = 108.1
$H_3C{-}S^+$	C_s	$^1A'$	−432.008 47 (30.1)	−436.218 06 (34.3)	CS = 1.790, CH_1 = 1.103, CH_2 = 1.091, SCH_1 = 102.8, $SC(H)_{23}$ = 132.1, H_2CH_3 = 113.2
$H_2{\cdots}HCS^+$	C_{2v}	$^1A_1$	−431.978 05 (49.2)	−436.208 36 (40.4)	CS = 1.469, CH_1 = 1.100, H_2H_3 = 0.714, $H_1{\cdots}(H)_{23}$ = 2.589
$H_3CS\cdot$	C_s	$^2A'$	−432.299 96	−436.596 83	CS = 1.794, CH_1 = 1.087, CH_2 = 1.087, SCH_1 = 109.2, $SC(H)_{23}$ = 129.9, H_2CH_3 = 108.0
CH_3SH	C_s (staggered)	$^1A'$	−432.896 00	−437.179 90	CS = 1.797, SH = 1.331, CH_1 = 1.085, CH_2 = 1.087, CSH = 95.1, SCH_1 = 109.9, $SC(H)_{23}$ = 129.3, H_2CH_3 = 108.0

[a] Optimized at STO-3G. Bond lengths in ångstroms, angles in degress. Except where noted otherwise, H_2 and H_3 are symmetry equivalent and $(H)_{23}$ refers to the midpoint of a line from H_2–H_3. [b] Optimization at 4-31G gives SH = 1.379, $E = -397.281\ 24$ hartrees. [c] Optimization at 4-31G gives SH = 1.354, HSH = 95.5, $E = -398.203\ 95$ hartrees (also found in ref 25). [d] Optimization at 4-31G gives SH = 1.354, HSH = 100.2, $E = -398.459\ 92$ hartrees. [e] H_1 syn, H_2 anti to SH. [f] Ion energy referred to $H_2C{=}SH^+$ as zero; for triplet $CH_3{-}S^+$ a better value of +8.4 kcal/mol is derived empirically (see text).

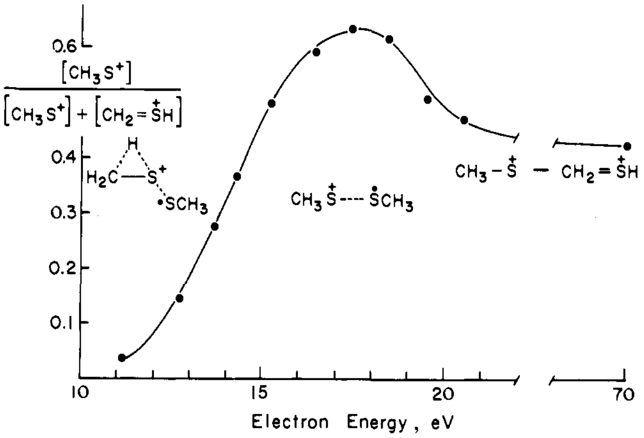


Figure 1. The relative abundance of thiomethoxy ions in the CSH_3^+ ions formed from dimethyl disulfide as a function of ionizing electron energy.

Thus the lowered [b]/[a] from dimethyl disulfide (Figure 1) found at both low and high ionizing energies is explicable in terms of molecular ion isomerization accompanying decomposition (eq 1) and fragment ion isomerization (b → a), respectively. From methyl sulfide no significant fraction of b is formed at any ionizing energy; an additional factor in this case may be the low probability of forming molecular ions with appropriate internal energies. The photoelectron spectrum of CH_3SCH_3[29] indicates that a very small proportion of molecular ions will be formed with internal energies of 0.5–2.5 eV.[30] Photoelectron spectra of larger methyl alkyl sulfides and dimethyl disulfide[31] show much smaller gaps between the first and second bands.

CD_3SH and CH_3SD. The loss of H from $CD_3SH^{+\cdot}$ has a lower appearance potential (AP) than the loss of D; our findings qualitatively confirm the reported[12] values of 11.76 and 12.01 eV, respectively. This observation was previously interpreted as indicating a lower heat of formation for $CD_3{-}S^+$ than $CD_2{=}SH^+$.[12] However, the CA spectra show that only a is formed at both high and low ionizing energies; the $[C(H,D)_3^+]/[C(H,D)_2^+]$ values in the CA spectra of both ions (and for CSH_2D^+ from CH_3SD) are those expected for a. Thus methanethiol also appears to undergo displacement rearrangement (eq 1) at low energies to give a by loss of the thiol hydrogen atom. For CD_3SH the observed[12] difference in AP(−H) vs. AP(−D) could be due to a kinetic isotope effect favoring loss of H. At high energies a is the dominant isomer formed; in the case of CSD_3^+ ions from CD_3SH this suggests again that most ions formed directly as b have sufficient internal energy to isomerize to a in 10^{-5} s. Consistent with this, Harrison has recently found that the metastable ion decomposition behavior for both CSD_3^+ and $CSHD_2^+$ from CD_3SH is identical with that expected for a.[32]

The CA spectrum of $CD_2{=}SH^+$ indicates that substantial H-D scrambling occurs prior to the CA fragmentation. Hydrogen scrambling in higher energy a ions could involve b, H-bridged structures, and/or the carbene-substituted sulfonium ion, $:CHSH_2^+$, all of which are indicated by MINDO/3 to be energetically accessible below the fragmentation threshold for a.[33]

Thermochemical Studies. The above data indicate that previous appearance potential studies of CSH_3^+ ions measured a, not b, ions.[34] The ionic heats of formation (ΔH_f) for a derived[16] from these measurements vary from 210[13] to 222[11] kcal/mol;[11-16] Harrison's extensive studies[12] showed minimum values ~214 kcal/mol. Obviously, substantial experimental errors are associated with most of these values; by analogy to studies on $CH_2{=}OH^+$,[36] the value of $\Delta H_f(CH_2{=}SH^+)$ is less than 213 kcal/mol, possibly by a significant amount.

Theoretical Results and Discussion

Results of ab initio calculations on a, b, and related systems are given in Table II; it is necessary to calibrate these against literature values before interpreting the results.

SH^+. In other theoretical studies[41-43] of SH^+ an optimized bond length of 1.352 Å was obtained[43] with a near-Hartree-Fock spd basis. This and the experimental value of 1.350 Å[44] for neutral SH indicate that our values of 1.380 and 1.379 Å are too large, evidently owing to the exclusion of d functions; similar trends are found in other second-row monohydrides.[25] Combining IP(SH) = 10.40 eV[45] and ΔH_f(SH) = 35 kcal/mol[40] leads to $\Delta H_f(SH^+)$ = 275 kcal/mol. This compares favorably with the theoretical value for the triplet, which lies below $^1\Delta$ by 1.16 eV.[42]

SH_2. The STO-3G geometry of SH_2 determined here and elsewhere[25] is in excellent agreement with experiment (r = 1.336, HSH = 92.2).[46] The 4-31G[25] and a near-Hartree-Fock[43] geometry are less accurate; earlier theoretical studies have been critically reviewed.[47]

SH_3^+. In contrast to OH_3^+, which is nearly planar,[48] SH_3^+ is strongly bent and has a substantial inversion barrier (30–35 kcal/mol).[43,49–51] Our STO-3G geometry is not identical with another (r = 1.345, HSH = 96.0)[49] but agrees with the best available Hartree–Fock result (r = 1.360, HSH = 98.7).[43] Upon 4-31G optimization the indicated structure becomes slightly less pyramidal, a trend found also for H_3O^+ and NH_3.[52]

HCS^+. The STO-3G geometry of HCS^+ is in good agreement with a MINDO/3 determination (CH = 1.092, CS = 1.470),[33] both indicating a triple CS bond. Appearance potential (AP) studies[16] give widely varying estimates of $\Delta H_f(HCS^+) \sim 300 \pm 30$ kcal/mol. MINDO/3 gives 245 kcal/mol[33] but this may be low; for HCO^+, MINDO/3 gives 185 vs. 195 kcal/mol experimentally.[16] At 4-31G, $HCS^+ + H_2$ is calculated to lie 41 kcal/mol above $H_2C{=}SH^+$; from ΔH_f(a) < 213 (vide supra), $\Delta H_f(HCS^+)$ < 254 kcal/mol.

$H_2C{=}SH^+$. From semiempirical[33,53] and ab initio[5,54] studies a is found to be planar with a relatively small CSH angle (98.3° at STO-3G, 100.9° at 4-31G,[5] 109.2° at MINDO/3[33]) and a CS bond (1.65 Å,[5,54] 1.61,[33] 1.63 Å at STO-3G) order of two. Population analysis indicates a significant degree of π bonding between C and S and a rotational barrier about the CS bond higher than that estimated for $H_2C{=}OH^+$.[5] These considerations suggest that the structure $H_2C{=}SH^+$ is preferable to $H_2C^+{-}SH$, in contrast to conclusions from AP studies.[37]

$H_3C{-}S^+$. In b there are formally four nonbonding valence electrons on sulfur to be distributed among three orbitals. According to Hund's rule the most stable configuration should be a triplet, in agreement with the calculated results. Jahn–Teller distortion in the singlet leads to C_s symmetry; the CS bond is shorter than that in the triplet, the CH bond in the plane of symmetry is lengthened, and the associated SCH angle is smaller, indicating hyperconjugative interaction between a CH bond and the coplanar, formally vacant, p orbital on sulfur. A MINDO/3 study[33] of CSH_3^+ ions did not examine triplet states or the $H_3C{-}S^+$ structure, but two H-bridged geometries were found to be minima on the singlet surface. One of these (C_s symmetry) was examined here at STO-3G and found to collapse to the $^1A'$ structure of Table II. MINDO/3 is known to favor bridged ion structures to a greater extent than STO-3G.[55] Contrary to the CA results, both STO-3G and 4-31G indicate b to be more stable than a; empirical corrections to these values will be discussed below.

$H_2 \cdots HCS^+$. Based on a suggestion by Schleyer et al. concerning the COH_3^+ system,[56] a complex of C_{2v} symmetry between H_2 and HCS^+ was examined. H_2 and HCS^+ are found to retain their individual geometries in a weakly bound state with a distance of 2.589 Å between the HCS^+ hydrogen and the midpoint of H_2. At STO-3G or 4-31G this complex is bound by less than 1 kcal/mol relative to separated species. A local potential minimum was also found for the C_{2v} configuration $H_2 \cdots SCH^+$, but after partial optimization the indicated energy of this complex was higher than that of $H_2 \cdots HCS^+$.

$H_3CS\cdot$. The thiomethoxy radical is found to be only slightly distorted relative to C_{3v} symmetry, having nearly tetrahedral bond angles at carbon like the triplet b ion. The calculated CS bond distance in the radical (1.794 Å) is closer to that of the singlet (1.790 Å) than the triplet (1.826 Å). Thus it is difficult to predict from Franck–Condon factors which state will be obtained upon ionization. STO-3G may underestimate these values; ab initio studies with larger basis sets find[54] CS distances of 1.881 Å for the radical and 1.852 Å for the ion (electronic state not specified).

From an energetic viewpoint, ionization to the triplet is clearly favored, with a calculated (4-31G, adiabatic) ionization potential of 8.04 vs. 10.31 eV for the singlet (although neglect of correlation energy may make the singlet value too large by ~1 eV). Ab initio calculations[5b] including d functions on sulfur, but without complete geometry optimization, indicate $H_3CS\cdot$ to be 49 kcal/mol more stable than its $\cdot CH_2SH$ isomer; a theoretical reinvestigation of this rather large value would be of interest.

CH_3SH. The STO-3G basis underestimates the CS distance in methanethiol by 0.021 Å compared to the experimental 1.818 Å;[57] a previous calculation[25] at STO-3G gave 1.804 Å with a slightly higher total energy. Other theoretical approaches give values over a wide range: 1.742 Å by MINDO/3,[51] 1.857 Å with a large spd basis,[6c] 1.881 Å at 4-31G,[25] and 1.790 Å with a minimal basis augmented with d functions.[25] Evidently the potential surface for CS stretching in H_3CSH is quite flat, as also suggested by molecular mechanics investigations.[58] This is a result of the polarizability of sulfur,[5–7] and reflects the weakness of CS bonding; the bond energy of CS in CH_3SH is 67 kcal/mol compared to 82 kcal/mol for that of CC in CH_3CH_3.[59]

Relative Energies of CSH_3^+ Isomers. Triplet H_3CS^+ is calculated to lie below $H_2C{=}SH^+$ by 18 kcal/mol at 4-31G (30 at STO-3G). However, it is well known that Hartree–Fock theory does not correctly reproduce singlet–triplet differences, since the correlation energy for states of higher multiplicity is lower than for closed-shell species. Two methods are used here to estimate this deficiency. The first assumes that the correction is the same as that for CH_2, for which recent calculations[60] find the triplet to be more stable than the singlet by 11 kcal/mol; at 4-31G the difference is calculated[61] to be 37 kcal/mol, in error by 26 kcal/mol. Adding this correction to our 4-31G triplet H_3CS^+ energy indicates that the energy of b lies 8 kcal/mol above that of a, consistent with the CA results. This method of estimating singlet–triplet differences has been applied to other systems with reasonable results.[62]

In the second correction procedure, the *relative* heats of formation for a and b are estimated by comparing each with a series of related ions by means of hypothetical reactions (Table III) for which the theoretical reaction energy is combined with known ΔH_f values for three of the species to estimate the value of the fourth. Such comparisons generally result in a cancellation of errors and reproduce experimental trends fairly well,[62–65] especially when isodesmic[63] reactions are employed.

Protonated thioformaldehyde (a) may be viewed as a substituted methyl cation. Thus isodesmic cation stabilization reactions[65] comparing a with the methyl cation (reaction 1) and substituted derivatives (reactions 2–4) may be employed. The large positive reaction energy for reaction 1 indicates sulfur to be strongly stabilizing α to a carbonium ion center, more so than a methyl substituent (reaction 2), much less than amino (reaction 3), and somewhat less than hydroxy (reaction 4). (The latter conclusion is in conflict with experimental observations,[5–8] indicating that the absolute ΔH_f value is high.)

The hydrogenation reactions 5 and 6 and the exchange reaction 7 are not isodesmic, and thus perhaps less reliable, as suggested by the more widely different heats of formation derived from them. Averaging the predicted $\Delta H_f°$ values from

Table III. Theoretical Heats of Formation for CSH_3^+

no.	reaction	reaction energy[a]	$\Delta H_f°(CSH_3^+)$[b]
1	$CH_2{=}SH^+ + CH_4 = CH_3SH + CH_3^+$	38.5	235
2	$+ CH_3CH_3 = CH_3SH + CH_2CH_3^+$	8.6	225
3	$+ CH_3NH_2 = CH_3SH + CH_2NH_2^+$	−54.8	233
4	$+ CH_3OH = CH_3SH + CH_2OH^+$	−9.3	217
5	$+ H_2 = CH_3^+ + SH_2$	15.7	240
6	$+ 2H_2 = CH_4 + SH_3^+$	−45.7	215
7	$+ H_2O = H_2S + CH_2OH^+$	−1.2	219
			av 226 ± 10
8	$CH_3{-}S^{+\,c} + H_2 = SH^{+\,d} + CH_4$	4.4	253
9	$+ CH_4 = SH^+ + CH_3CH_3$	27.7	245
10	$+ H_2S = SH^+ + CH_3SH$	27.2	247
11	$+ CH_3^+ = SH^+ + CH_2CH_3^+$	−2.2	235
12	$+ HOOH = HOO^{+\,e} + CH_3SH$	76.5	212
			av 238 ± 16

[a] kcal/mol, calculated using 4-31G energies from Table II or W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1975), for nonsulfur compounds. [b] kcal/mol, calculated by combining theoretical reaction energy with experimental heats of formation from references such as ref 16, 39, and 40. [c] $^3A_1$ state (reactions 8–12). [d] $^3\Sigma^-$ state (reactions 8–11). [e] $^3A''$ state.

all seven reactions provides the theoretical estimate of $\Delta H_f°(H_2C{=}SH^+) = 226 \pm 10$ kcal/mol. Like 4-31G-derived estimates for certain other ionic species,[62] this value is clearly too high.

To describe triplet H_3CS^+, reactions with the known triplet ions SH^+ and HO_2^+ were used to enhance error cancellation. Reaction 10 is isodesmic, and reaction 12 is nearly so, the two sides differing only by a bond to hydrogen. Reaction 11 indicates the stabilizing effect of methyl substitution on SH^+ to be about the same as on CH_3^+, which is larger than its effect on the neutral molecules H_2 (reaction 8), CH_4 (reaction 9), and SH_2 (reaction 10). Reaction 12 demonstrates the energetic unfavorability of HO_2^+ relative to CH_3S^+, a point not readily generalized. The average heat of formation for triplet CH_3S^+ from these reactions is 238 ± 16 kcal/mol.

These estimates are too high, but the predicted a − b difference, 12 kcal/mol, is in the right direction and in fair agreement with the value of 8 kcal/mol derived above. However, it is evident that calculations employing larger basis sets and correlation estimates are required in order to deal further with this problem.

A comparison to the oxygenated ions is also helpful. Based on the observations[5-8] that sulfur is slightly more effective than oxygen at stabilizing adjacent carbocation centers in gas-phase species, reaction 4 of Table III should be endothermic; ΔH_f (a) = 205 kcal/mol yields an experimental reaction energy of +3 kcal/mol favoring the sulfur ion. Based on the calculated difference of ΔH_f(a) and ΔH_f(b), and the maximum value of ΔH_f(a)[36] and the minimum value of ΔH_f(b)[34] cited above, we estimate ΔH_f(a) ~ 205 and ΔH_f(b) ~ 215 kcal/mol.

Although we have not carried out detailed calculations addressing the question of the barrier to b → a rearrangement, some comments can be made. Consider a hypothetical three-step rearrangement process: (1) spin pairing in b to give singlet H_3CS^+; (2) 1,2-hydrogen shift through a bridged transition state to nonplanar H_2C^+-SH; (3) 90° rotation about the CS bond leading to the product, a. According to the empirically corrected 4-31G results, step 1 requires an activation energy (E_a) of 26 kcal/mol. For step 2, a single STO-3G calculation at a reasonable geometry indicates $E_a \sim 30$ kcal/mol. For step 3, the calculations of Wolfe[5] indicate that rotated H_2C^+-SH lies only 2 kcal/mol higher than singlet H_3CS^+, so that the overall E_a is ~56 kcal/mol. The actual value for a synchronous process is likely to be somewhat lower; a value of 1.5–2 eV would appear to be consistent with Figure 1.[26]

RCH_2–S^+ Energies. In contrast to the appreciable stability found for b, in the homologous $C_2SH_5^+$ and $C_3SH_7^+$ systems[9] the thioalkoxy ions $R_1R_2CH{-}S^+$ corresponding to b rearrange without detectable activation to the protonated thioketone ions $R_1R_2C{=}\overset{+}{S}H$ corresponding to a. This is not unexpected, as stabilization of a by methyl substitution adjacent to C^+ should be greater than stabilization of b, in which the interaction between S^+ and CH_3 is small. An ab initio calculation of the isodesmic comparison

$$CH_3{-}S^+(^3A_1) + CH_3CH{=}\overset{+}{S}H \rightarrow CH_3CH_2{-}S^+(^3A') + CH_2{=}SH^+$$

yields a reaction energy of +12.5 kcal/mol at STO-3G,[66] consistent with the failure to observe $CH_3CH_2{-}S^+$.[9]

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References and Notes

(1) Collisional Activation and Metastable Ion Characteristics. **65**. Part 64: M. S. Kim, R. C. Dunbar, and F. W. McLafferty, *J. Am. Chem. Soc.*, **100**, 4600 (1978).
(2) A preliminary communication of this work has appeared: J. D. Dill and F. W. McLafferty, *J. Am. Chem. Soc.*, **100**, 2907–2908 (1978).
(3) C. C. Price and S. Oae, "Sulfur Bonding", Ronald Press, New York, 1962.
(4) Y. Yano and S. Oae, *Mech. React. Org. Sulfur Compd.*, **4**, 167 (1969), and references cited therein; K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969); D. L. Coffen, *Rec. Chem. Prog.*, **30**, 275 (1969); M. Orchin and H. H. Jaffe, "The Importance of Antibonding Orbitals", Houghton Mifflin, Boston, 1967; E. C. Kooyman in "Organosulfur Chemistry", M. J. Janssen, Ed., Wiley-Interscience, New York, 1967; D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965.
(5) (a) F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolf, *Can. J. Chem.*, **53**, 1144 (1975); (b) F. Bernardi, I. G. Csizmadia, H. B. Schlegel, M. Tiecco, M. Whangbo, and S. Wolfe, *Gazz. Chim. Ital.*, **104**, 1101 (1974).
(6) N. D. Epiotis, R. L. Yates, F. Bernardi, and S. Wolfe, *J. Am. Chem. Soc.*, **98**, 5435 (1976); F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M. Whangbo, and S. Wolfe, *ibid.*, **97**, 2209 (1975); W. T. Borden, E. R. Davidson, N. H. Andersen, A. D. Denniston, and N. D. Epiotis, *ibid.*, **100**, 1604 (1978); J.-M. Lehn and G. Wipff, *ibid.*, **98**, 7498 (1976); V. B. Koutecky and J. I. Musher, *Theor. Chim. Acta*, **33**, 227 (1974); A. Streitwieser, Jr., and S. P. Ewing, *J. Am. Chem. Soc.*, **97**, 190 (1975); A. Streitwieser, Jr. and J. E. Williams, Jr., *ibid.*, **97**, 191 (1975); D. T. Clark in "Organic Compounds of Sulfur, Selenium, and Tellurium", Vol. 1, The Chemical Society, London, 1970.
(7) J. K. Pau, M. B. Ruggera, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, **100**, 4242 (1978).
(8) A. G. Harrison, C. D. Finney, and J. A. Sherk, *Org. Mass Spectrom.*, **5**, 1313 (1971).
(9) B. van de Graaf and F. W. McLafferty, *J. Am. Chem. Soc.*, **99**, 6806, 6810 (1977).
(10) W. J. Broer and W. D. Weringa, *Org. Mass Spectrom.*, **12**, 326 (1977).
(11) D. Amos, R. G. Gillis, J. F. Pisani, and J. L. Occolowitz, *Org. Mass Spectrom.*, **2**, 209 (1969).
(12) B. G. Keyes and A. G. Harrison, *J. Am. Chem. Soc.*, **90**, 5671 (1968).
(13) R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 2490

(1965).

(14) T. F. Palmer and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 4661 (1962).

(15) B. G. Hobrock and R. W. Kiser, *J. Chem. Phys.*, **66**, 1551, 1648 (1962); **67**, 648 (1963).

(16) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1,* **6** (1977).

(17) R. D. Bowen and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 378 (1977).

(18) J. D. Dill, C. L. Fischer, and F. W. McLafferty, *J. Am. Chem. Soc.*, following paper in this issue.

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

(20) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, GAUSSIAN 70, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(21) First row (Li–F): W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). Second row (Na–Ar): W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1970).

(22) First row (C–F): R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971). Second row (P–Cl): W. J. Hehre and W. A. Lathan, *ibid.*, **56**, 5255 (1972) (although more properly termed 44-31G, 4-31G will be used here).

(23) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

(24) J. A. Pople in "Applications of Electronic Structure Theory", H. F. Schaefer, III, Ed., Plenum Press, New York, 1977.

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

(26) The Figure 1 data are surprisingly similar to those found for benzyl and tropylium ions produced from toluene[27] which show a maximum of 52% benzyl at ~16 eV electron ionization; this is shown to be consistent with an activation energy of ~1.7 eV for $benzyl^+ \rightarrow tropylium^+$.

(27) F. W. McLafferty and F. M. Bockhoff, *J. Am. Chem. Soc.*, **101**, 1783 (1979).

(28) The dimethyl sulfoxide data are consistent with its reported rearrangement to $CH_3S\text{-}OCH_3^{+\cdot}$ on ionization.[11]

(29) D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *J. Phys. Chem.*, **76**, 1030 (1972); S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **68**, 281 (1972).

(30) F. W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, *J. Am. Chem. Soc.*, **92**, 6867 (1970).

(31) G. Distefano, A. Ricci, F. P. Colonna, D. Pietropaolo, and S. Pignataro, *J. Organomet. Chem.*, **78**, 93 (1974); R. J. Colton and J. W. Rabalais, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 227 (1974).

(32) A. G. Harrison, *J. Am. Chem. Soc.*, **100**, 4911 (1978).

(33) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 7432 (1977).

(34) F. P. Lossing (personal communication, Aug 1978) finds an ionization potential of 7.77 eV for $CH_3S\cdot$ that probably contains $\cdot CH_2SH$. Assuming $\Delta H_f(CH_3S\cdot) = 34.2$ kcal/mol, $\Delta H_f(CH_3S^+) \geq 213$ kcal/mol.

(35) S. W. Benson, *Chem. Rev.*, **78**, 23 (1978).

(36) A similar AP study of COH_3^+ ions[37] gave $\Delta H_f(CH_2{=}OH^+) = 176$ kcal/mol, while monoenergetic electron impact[38] and photoionization[39] data find 169 kcal/mol and ion equilibrium measurements[40] indicate 165 kcal/mol.

(37) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).

(38) F. P. Lossing, *J. Am. Chem. Soc.*, **99**, 7526 (1977).

(39) K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1968). See also F. M. Benoit and A. G. Harrison, *J. Am. Chem. Soc.*, **99**, 3980 (1977).

(40) J. F. Wolf, R. H. Staley, I. Köppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 5417 (1977).

(41) W. G. Richards, T. E. H. Walker, and R. K. Hinkley, "A Bibliography of ab Initio Molecular Wave Functions", Clarendon Press, Oxford, 1971; W. G. Richards, T. E. H. Walker, C. Farnell, and P. R. Scott, "Bibliography of ab Initio Molecular Wave Functions. Supplement for 1970–1973", Clarendon Press, Oxford, 1974.

(42) P. E. Cade and W. M. Huo, *At. Data Nucl. Data Tables*, **12**, 415 (1973); H. P. D. Liu, J. Legentil, and G. Verhaegen, *Sel. Top. Mol. Phys. Proc. Int. 1970*, 19 (1972); M. Raimondi, G. F. Tantardini, and M. Simonetta, *Mol. Phys.*, **30**, 703 (1975).

(43) R. E. Kari and I. G. Csizmadia, *Can. J. Chem.*, **53**, 3747 (1975).

(44) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. I, "Spectra of Diatomic Molecules", 2nd ed., Van Nostrand, Princeton, N.J., 1950.

(45) B. A. Marrow, *Can. J. Phys.*, **44**, 2447 (1966).

(46) T. H. Edwards, N. K. Moncur, and L. E. Snyder, *J. Chem. Phys.*, **46**, 2139 (1967).

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

(48) P. C. Hariharan and J. A. Pople, *Mol. Phys.*, **27**, 209 (1974).

(49) T. Yamabe, T. Aoyagi, S. Nagata, H. Sakai, and K. Fukui, *Chem. Phys. Lett.*, **28**, 182 (1974).

(50) P. E. Stevenson and D. L. Burkey, *J. Am. Chem. Soc.*, **96**, 3061 (1974).

(51) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *J. Am. Chem. Soc.*, **97**, 1131 (1975).

(52) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).

(53) T. Yamabe, S. Nagata, K. Akagi, R. Hashimoto, K. Yamashita, K. Fukui, A. Ohno, and K. Nakamura, *J. Chem. Soc., Perkin Trans. 2*, 1516 (1977).

(54) M.-H. Whangbo, S. Wolfe, and F. Bernardi, *Can. J. Chem.*, **53**, 3040 (1975).

(55) P. K. Bischof and M. J. S. Dewar, *J. Am. Chem. Soc.*, **97**, 2278 (1975).

(56) P. v. R. Schleyer, E. D. Jemmis, and J. A. Pople, *J. Chem. Soc., Chem. Commun.*, 190 (1978).

(57) J. Kojimi and T. Nishikawa, *J. Phys. Soc., Jpn.*, **12**, 680 (1957).

(58) N. L. Allinger and M. J. Hickey, *J. Am. Chem. Soc.*, **97**, 5167 (1975).

(59) Calculated from atomization energies assuming CH and SH bond strengths to remain constant in CH_4, SH_2, C_2H_6, and CH_3SH. See J. D. Dill, Ph.D. Thesis, Princeton University, 1976.

(60) R. R. Lucchese and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **99**, 6765 (1977); B. O. Roos and P. M. Siegbahn, *ibid.*, **99**, 7716 (1977).

(61) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).

(62) J. D. Dill, P. v. R. Schleyer, J. S. Binkley, R. Seeger, J. A. Pople, and E. Haselbach, *J. Am. Chem. Soc.*, **98**, 5428 (1976).

(63) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).

(64) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 289 (1971).

(65) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 5935 (1972).

(66) Carried out using optimized geometries for CSH_3^+ (Table III), affixing a standard-geometry[67] methyl group in place of H in each isomer. For $CH_3CH{=}SH^+$, the methyl was assumed to eclipse the C—S bond, was found to be slightly more stable syn to SH than anti, and was affixed with a CC distance of 1.484 Å (STO-3G value in $C_2H_5^+$);[61] this gave $E = -470.661\,77$ hartrees. For $CH_3CH_2\text{-}S^+$ triplet, methyl was affixed staggering the CS bond at a CC distance of 1.54 Å;[67] this gave $E = -470.689\,33$ hartrees. It was necessary to specify the electronic configuration in the initial guess to obtain this energy. Singlet $CH_3CH_2\text{-}S^+$ at a similar geometry was found to lie ~60 kcal/mol higher than this triplet.

(67) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

Collisional Activation and Theoretical Studies of Gaseous COH_3^+ Ions[1]

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Abstract: Collisional activation spectra of *m/z* 31 ions from a variety of precursors are consistent with a single isomeric structure, $H_2C{=}OH^+$. However, reexamination of published data combined with ab initio calculations indicates a shallow energy minimum for a second structure, a C_{2v} complex of H_2 and HCO^+, heat of formation (ΔH_f) 194 vs. 165 kcal/mol for $H_2C{=}OH^+$. The triplet ground state methoxy ion, $H_3C\text{-}O^+$, is calculated to be unstable, $\Delta H_f = 231$ kcal/mol.

In the preceding paper[2] collisional activation (CA) mass spectra and ab initio calculations showed that two isomers of CSH_3^+, protonated thioformaldehyde ($H_2C{=}SH^+$) and thiomethoxy ion ($H_3C{-}S^+$), are stable in the gas phase, with the latter higher (~10 kcal/mol) in energy. To elucidate further the relative abilities of oxygen and sulfur for carbocation

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