insensitivity of the vibrational branching ratios to angular momentum. Since the comparison summarized above shows that the quasiclassical results are not *quantitatively* reliable for this reaction, however, the remaining discrepancy between the quasiclassical result with converged J_{max} and the experiment must be resolved by further work. Although a quantal calculation with converged J_{max} will be difficult, the results should be very interesting when this calculation is available.

In summary, the main conclusions of this study are as follows. (1) Classical simulation of state-to-state chemical reaction probabilities for $H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$ are reliable to a factor of about 1.5, but not better. (2) Vibrational branching ratios for this reaction are relatively insensitive to total angular momentum for the range 0–4$\hbar$ in both classical and quantal simulations, but the classical results are significantly lower at higher total angular momentum. (3) Classical simulations are in error by a factor of 2 for the final-state rotational partitioning into the two lowest rotational states of $o\text{-}H_2$ in the vibrationally excited level, even when contributions from two initial rotational states and nine total-angular-momentum/parity blocks are included. (4) Since the classical simulations are only semiquantitative at low angular momentum, further study of quantal effects at high angular momentum should prove very interesting.

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Fragmentation and Structure of $C_2H_3S^+$ Ions

R. G. Cooks,*[†] Md. A. Mabud,[†] S. R. Horning,[†] X.-Y. Jiang,[†] Cristina Paradisi,[‡] and Pietro Traldi[§]

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, Dipartimento di Chimica Organica, Centro Meccanismi di Reazioni Organiche del CNR, Via Marzolo 1, 35131 Padova, Italy, and Area di Ricerca del CNR, Corso Stati Uniti 4, 35131 Padova, Italy. *Received October 7, 1987*

Abstract: Daughter spectra for $C_2H_3S^+$ ions, generated from a variety of precursor molecules and activated by different means, are insensitive to the nature of the precursors, but spectra recorded by different methods of activation show unexpectedly large differences. The methyl cation, a fragment characteristic of the thioacylium structure, is the dominant product of collisions at low energy with a gaseous or solid target but is virtually absent for zero scattering angle gas-phase collisions in the kiloelectronvolt range. As the scattering angle is increased, this low-energy fragment increases in abundance, and it is suggested that this is the result of an increased degree of direct vibrational as opposed to electronic excitation. It is shown that (i) the $C_2H_3S^+$ ions sampled by collision-activated dissociation and by surface-induced dissociation have the thioacylium structure, (ii) internal energy differences associated with their formation are not reflected in spectral changes in kiloelectronvolt collision experiments although they do affect the low-energy spectra, (iii) zero-angle, high-energy collisions probably involve fragmentation via excited electronic states, and for this reason they result in different products to those that occur upon low-energy collisions with gaseous or solid targets, and (iv) while activation by collision with a solid surface in the energy range below 100 eV causes very considerable internal excitation, only vibrational and not electronic excitation is involved. Isomerization between the several nascent $C_2H_3S^+$ structures generated from different precursors occurs prior to activation and is favored by the unusually high activation energy required for dissociation. When the highly endothermic charge stripping process is used, it is possible to sample some $C_2H_3S^+$ ions of such low internal energy that they have not completely isomerized.

The structure, energetics, and reactivity of gas-phase ions continues to generate wide interest.[1] Experimental strategies include analysis of gas-phase ion/molecule reactions,[2] which allows structural features to be inferred from the observed reactivity, and ion dissociation characteristics, best accomplished by means of tandem mass spectrometry (MS/MS).[3] The latter approach has gained wide popularity and has stimulated the development of new ion activation techniques. A typical experiment includes the following stages: (i) generation and mass selection of the ionic species of interest, (ii) activation to induce dissociation, and (iii) analysis of the resulting fragmentation products by comparison with the fragments produced by model ions of known structure.

Activation of mass-selected ions can be achieved in photodissociation experiments[4] and through collision with a stationary gas-phase target[5] in either the high-energy (kiloelectronvolt)[6] or low-energy (electronvolt)[7] range of laboratory ion kinetic energies. More recently, procedures have been developed for activation of ionic species through their interaction with a solid surface.[8] Of these methods, collision-activated dissociation (CAD), where activation is achieved through collision with neutral gas-phase targets, has been most widely used. Application of several different methods to a given problem has much to offer, particularly since the different methods can result in deposition of different amounts of internal energy into the ion.[9] In several recent studies of gas-phase ion structure, surface-induced dissociation has proved

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[†] Purdue University.

[‡] Centro Meccanismi di Reazioni Organiche del CNR.

[§] Area di Ricerca del CNR.

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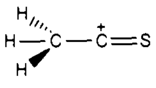
valuable in characterizing isomeric ions. Examples include ionized polynuclear aromatic hydrocarbons[10] and isomeric ions of composition $C_2H_4O^{\bullet+}$,[11] $C_8H_{12}^{\bullet+}$,[12] $C_5H_6^{\bullet+}$,[13] and $C_6H_6^{\bullet+}$.[14] In high-energy CAD experiments, angle-resolved mass spectrometry (ARMS) is a useful feature, since ions with varying internal energies can be selected.[15]

The thioacylium ion is an elusive species in solution. Previous studies on the gas-phase $C_2H_3S^+$ species, of which a–f represent the most likely structures, have left some questions open. Paradisi and co-workers[16] studied $C_2H_3S^+$ ions, derived from various precursors, by high-energy (keV) collision-activated dissociation and the charge stripping technique. The high-energy CAD daughter spectra, which were identical in all cases, were characterized by a CH_3^+ ion of very low abundance, major fragments being due to losses of H$^\bullet$ and 2H$^\bullet$ and to formation of the HCS^+ and $CS^{\bullet+}$ ions. It was concluded that all $C_2H_3S^+$ species examined had isomerized to a single structure, or to a mixture of readily interconverting isomers, prior to activation. Since the methyl cation formed to the extent of only 0.2–0.4% of the total ion current, the thioacylium ion a was assumed to constitute only a minimal portion of the ion beam analyzed. This ion can reasonably be expected to undergo cleavage of the C–C bond to yield CH_3^+ and CS (ionization potentials[17] of $CH_3^\bullet$ and of CS are 9.84 and 11.33 eV, respectively, leading to the expectation[18] of charge retention on the methyl fragment).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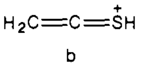
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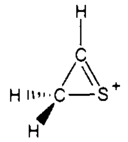
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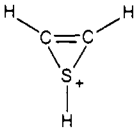
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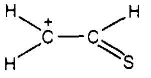
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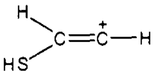
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Charge stripping of the $C_2H_3S^+$ ions derived from the same neutral precursors resulted in $C_2H_3S^{2+}$, $C_2H_2S^{2+}$, and C_2HS^{2+} product ions.[16] The relative abundances of these ions were similar when each of the nine precursors was used to generate $C_2H_3S^+$ parent ions. Paradisi et al. concluded that a common $C_2H_3S^+$ structure was involved. However, the observed differences in the charge stripping data are possibly significant and allow the alternative interpretation that isomerization of the ions sampled in this experiment is incomplete. For example, the normalized abundances for the above three doubly charged ions are 57%, 25%, and 18%, respectively, for thiirane and 65%, 24%, and 11% for diethyl disulfide.

In an independent and simultaneous investigation, Caserio and Kim[19] generated and characterized thioacylium ions in the gas phase. Using ICR techniques, they found that $C_2H_3S^+$ ions, formed according to the ion/molecule displacement reaction 1,

$$CH_3CO^+ + CH_3CSH \rightarrow CH_3CS^+ + CH_3COH \qquad (1)$$

$$CH_3C({=}S)SCH_3 \xrightarrow{e^-} CH_3CS^+ + CH_3S^\bullet \qquad (2)$$

display the same reactivity as the species generated via direct electron impact fragmentation (eq 2) of thiocarbonyl compounds such as methyl ethanedithioate, $CH_3C({=}S)SCH_3$. A common structure, that of the thioacylium ion CH_3CS^+ (a), was inferred for both populations of ions on the basis of their ion/molecule reactions, which included proton transfer and thioacylation.

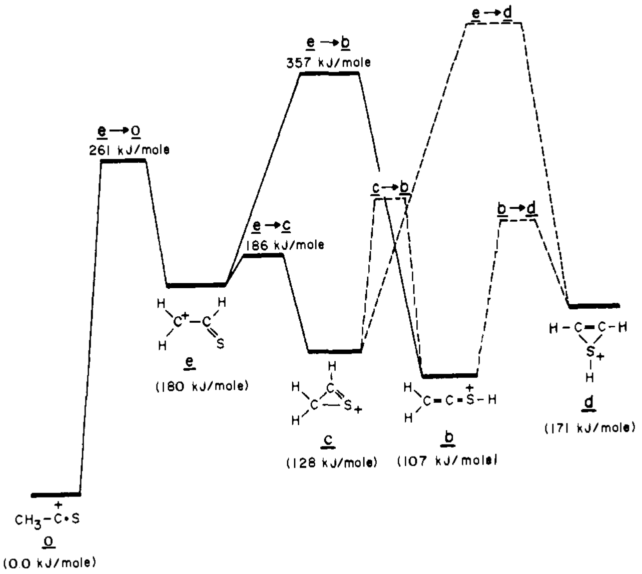

Figure 1. Potential energy diagram for $C_2H_3S^+$, adapted from ref 21.

Caserio et al.[19] estimated the heat of formation of a to be approximately 879 kJ/mol, about 61 kJ/mol lower than that of the S-protonated isomer [$CH_2{=}C{=}SH^+$] (d). Calculated ground-state energies for isomeric $C_2H_3S^+$ species are available in the literature. Csizmadia et al.[20] placed the β-thiovinyl cation, f, at 11.3–12.1 kJ/mol above the thiirenium ion, d. Kollman et al.[21] have calculated the relative energies of b, d, and f to be –165, –43.5, and 0 kJ/mol, respectively. Recently, high-level calculations (6-31g*) have established the relative energies of the $C_2H_3S^+$ isomers a–f with the thioacylium ion a being the most stable *ground-state* species.[22] The order of stability given by these authors is a > b > c > d > e > f (Figure 1).

Isomerization reactions were also examined in the same theoretical investigation.[22] Possible direct interconversions (corresponding energy barriers in kJ mol^{-1}) are e → a (81), e → c (6), and e → b (177) as shown by the solid lines in Figure 1. The transition states, which could not be determined, are shown by dotted lines. The rearrangement a → b should be stepwise and proceed via the intermediacy of e.

In this paper we report results of a comparative study of the fragmentations of mass-selected $C_2H_3S^+$ species, generated from different neutral precursors and induced to fragment by using low-energy CAD, high-energy CAD, angle-resolved mass spectrometry, and surface-induced dissociation (SID). The enquiry is prompted by the apparent discrepancy between the structural conclusions arising from calculations and ion/molecule reactions on the one hand and the high-energy collision activation data on the other.

Experimental Section

High-Energy Gaseous Collisions. These experiments were performed with a VG ZAB-2F instrument operated, unless otherwise specified, in

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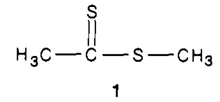
the EI mode (70 eV). The mass spectrometer was coupled with a VG 11-250 data system. Liquid samples were introduced via a septum inlet held at 150 °C, and solid samples, via a direct introduction probe. Collisionally activated dissociation (CAD) yielded mass-analyzed ion kinetic energy (MIKE) spectra from collisions of 8-keV ions with the specified target gas in the second field-free region. The pressure in the collision cell was adjusted so as to reduce the main beam intensity by 10% or 50% as specified. Experiments on $C_2H_3S^+$ ions derived from metastable ions **1** were performed by adjusting the magnetic field strength so as to transmit ions of apparent mass m/z 32.8.[23]

Angle-Resolved High-Energy Gaseous Collisions. Angle-resolved experiments were carried out in a Finnigan MAT 8200 mass spectrometer. The scattering angle was selected by electrical deflection of the ion beam along the xz plane as it leaves the ion source and prior to entering the first field-free region collision cell.[24] Sample pressure was 2×10^{-6} Torr, and Ar collision gas was added to the collision cell to attenuate the main beam by 20%, which resulted in an overall source pressure of 1.4×10^{-5} Torr, as indicated by an ionization gauge located in the ion source housing. Daughter ions generated through 3-keV collisions were examined at selected scattering angles in the range from 0° to 2.5° with a linked (B/E) scan of the sector analyzers.

Surface-Induced Dissociation. The hybrid BQ instrument[8,25] and the method used to acquire SID daughter spectra have been described earlier. Ions were generated by 70-eV electron impact in a source held at a potential in the range of 20–100 V with respect to ground. The ion beam was accelerated to 6 keV prior to mass analysis by the magnetic sector and then decelerated to ground potential prior to collision at a stainless steel surface. Mass analysis of the emerging beam was achieved with a quadrupole mass filter. All data were taken at a nominal incident angle of 25° (estimated uncertainity 3°) with respect to the surface normal. The angle of deviation was 121° from the original beam direction. The pressure in the chamber containing the target surface was maintained at 5.0×10^{-7} Torr. Data acquisition was carried out with a customized system.[26] In order to ensure identical experimental conditions, daughter spectra of all isomeric species were run one after another without adjustment of any instrumental parameters.

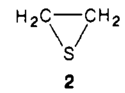
Low-Energy Gaseous Collisions. The low-energy gas-phase data were obtained with a Finnigan triple quadrupole instrument. Ions were generated by 70-eV electron impact. The collision-activated dissociation daughter spectra[27] were obtained at collision energies ranging from 5 to 25 eV with argon as collision target. Argon pressure was monitored by a Bayard–Alpert ionization gauge situated externally to the collision chamber. The indicated pressure was less than 3×10^{-6} Torr, corresponding to single-collision conditions.

The neutral precursors employed to generate $C_2H_3S^+$ are those (**2–9**) used in the earlier CAD investigation,[16] in addition to methyl ethanedithioate (**1**), previously used in the ICR study.[19] Methyl ethanedithioate (**1**) was prepared from acetyl chloride via the thioester CH_3CSCH_3[28] according to the procedure of Pedersen et al.[29] and purified by column chromatography. All other compounds were obtained commercially and used without purification.



$H_3C-\overset{\overset{\displaystyle S}{\|}}{C}-S-CH_3$

1



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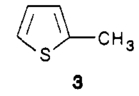

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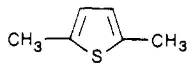

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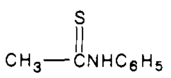


$CH_3-\overset{\overset{\displaystyle S}{\|}}{C}NHC_6H_5$

5

$CH_3SCH_2CH_3$

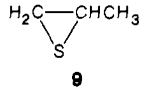
6

$(CH_3CH_2S)_2$

7

$HOCH_2CH_2SCH_3$

8



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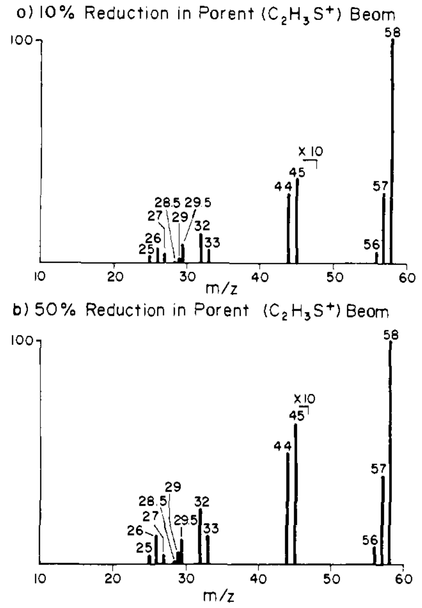

Figure 2. Daughter spectra of $C_2H_3S^+$ ions (m/z 59) obtained from **1**, recorded by 8-keV CAD using a MIKE spectrometer. Corresponds to attenuation of the main beam (a) by 10% and (b) by 50%.

Results

High-Energy CAD. The dithioester **1** was chosen by Kim and Caserio as a probable source of the thioacylium ion a upon electron ionization (eq 2). It might therefore be expected that the daughter spectrum of this ion, recorded using collision-activated dissociation at 8 keV, would yield the methyl cation for the reasons already given. Figure 2 displays this daughter spectrum, which is characterized by the *absence* of the methyl cation. The unexpected behavior of the ion derived from **1**, together with Kim and Caserio's[19] ion/molecule reaction results and Rodriquez and Hopkinson's[22] theoretical data, makes it necessary to reconsider the earlier conclusion[16] that the $C_2H_3S^+$ ions generated from a variety of other sources (**2–9**) do not have the thioacylium structure.

The high-energy experiments were extended by using a variety of conditions. Possible effects on the daughter spectra of $C_2H_3S^+$ species due to changes in (i) target gas pressure, (ii) target gas composition, and (iii) initial internal energy of the ion were investigated. The spectra of the $C_2H_3S^+$ species (m/z 59) from **1**, obtained with air as target at collision cell pressures corresponding to reduction of the main beam intensity by 10% and 50% are *practically superimposable* (Figure 2). They are representative examples of a series of experiments performed at various collision gas pressures resulting in main beam reductions in the range 5–80%. Identical results were also obtained when the target gas was changed from air to argon and oxygen, each used at various pressures, thus proving that changes in target composition and pressure do not alter the daughter spectra. Attempts were also made to study ions of lower initial internal energy by the following: (i) analysis of metastable $C_2H_3S^+$ ions produced in metastable ion fragmentations and (ii) deexcitation of the $C_2H_3S^+$ ions by collisions with argon present at high pressure in the ion source. Neither approach leads to changes in the CAD spectra. To summarize, the results reported here indicate that neither the structure of the neutral precursors used to generate the ions nor other experimental parameters, such as ion initial internal energy and collision conditions, affect the high-energy CAD spectra of $C_2H_3S^+$ ions. The peaks observed in these spectra are due to $C_2H_2S^{\bullet+}$, C_2HS^+ (both also formed in spontaneous decompositions), $C_2S^{\bullet+}$ (m/z 56), HCS^+ (m/z 45), $CS^{\bullet+}$ (m/z 44), SH^+

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Table I. Surface-Induced Dissociation (SID) Daughter Spectra of $[C_2H_3S]^+$ Ions from Various Sources, Recorded by Using 25- and 75-eV Collision Energy

	25-eV fragments at *m/z*					75-eV fragments at *m/z*					
precursors	15	27	33	57	58	15	27	33	45	57	58
ethylene sulfide (**2**)	62	2	5		31	85	7	2	2	1	4
2-methylthiophene (**3**)	64	3	4	2	29	83	9	2	2	1	4
ethyl methyl sulfide (**6**)	55	4	5	2	26	82	10	2	3	1	3
propylene sulfide (**9**)	57	3	4		37	83	9	1	3	1	4

Table II. CAD Daughter Spectra of $[C_2H_3S]^+$ Ions from Various Sources (Single-Collision Conditions), Recorded at 10- and 22-eV Collision Energy (Ion at *m/z* 58 Has Been Excluded (See Text))

	10-eV fragments at *m/z*									22-eV fragments at *m/z*								
precursors	15	26	27	32	33	45	47	56	57	15	26	27	32	33	45	47	56	57
methyl ethanedithioate (**1**)	88	1	1		6				3	82	2	1		4	2			7
ethylene sulfide (**2**)	58	1	2	2	8	2	2	2	10	62	3	2	1	7	4	1	2	15
2-methylthiophene (**3**)	65	1	1	3	11	1	3	1	9	59	3	2	3	7	3	1	2	16
2,5-dimethylthiophene (**4**)	74	1	1	1	10	1		1	6	66	3	2	2	7	3		2	14
thioacetanilide (**5**)	75	1	1	2	8	1		1	8	65	2	2	2	5	3		2	17
ethyl methyl sulfide (**6**)	46	1	3	1	8	2	1		8	52	3	4	2	8	5	1	2	12
hydroxy ethyl methyl sulfide (**8**)	59	1	7		9	2		5	3	51	4	4		12	4		2	9

(*m/z* 33), $S^{\bullet+}$ (*m/z* 32), $C_2H_3^+$ (*m/z* 27), $C_2H_2^{\bullet+}$ (*m/z* 26), C_2H^+ (*m/z* 25), and $C_2^{\bullet+}$ (*m/z* 24). Charge stripping peaks are observed at *m/z* 29.5, 29, and 28.5. Of particular note is the absence (<1% relative abundance) of a peak due to CH_3^+. The kiloelectronvolt CAD daughter spectrum of dithioester **1** is in fact virtually identical with the spectra of the $C_2H_3S^+$ ions generated from compounds **2**–**9** and reported earlier.[16]

Angle-Resolved Mass Spectrometry. High-energy angle-resolved CAD experiments impart amounts of internal energy into the parent ion, which increase with scattering angle.[15,30] Angle-resolved daughter spectra for the $C_2H_3S^+$ species generated from ethylene sulfide **2** (Figure 3) show that at larger scattering angles ionic fragments, which are expected to have high energies of activation (*m/z* 44, 32, 26), increase in abundance, as expected. The feature of most interest is the methyl cation, the relative abundance of which increases steadily with scattering angle. For example, the methyl cation abundance with respect to $C_2H_2S^{\bullet+}$ (*m/z* 58) and $CS^{\bullet+}$ (*m/z* 44) is 0.15% and 1.7%, respectively, at zero scattering angle, while at 2.3° the relative abundance of the *m/z* 15 ion to *m/z* 58 and 44 increases to 13% and 40%. In comparison with the formation of $C_2^{\bullet+}$ (*m/z* 24), the methyl cation increases from 100% to over 140% as the scattering angle is raised. Although these results are consistent with CH_3^+ formation being a highly endothermic process, the low collision energy CAD and SID data (see below) demand a different conclusion, namely that a different mechanism of activation occurs in the two energy regimes. It is argued further below that scattering in the kiloelectronvolt collision experiments favors vibrational excitation.

Surface-Induced Dissociation (SID). Daughter spectra of $C_2H_3S^+$ ions (generated from precursors **2**, **3**, **6**, and **9**) were recorded following collision at a solid target at various energies between 25 and 75 eV. The $C_2H_3S^+$ ions all behaved virtually identically. Table I describes the distribution of fragments obtained at 25 and 75 eV. At 25-eV collision, the only significant fragment ions that appear in the SID daughter spectra of $C_2H_3S^+$ are *m/z* 15 and 58, presumably due to CH_3^+ and $C_2H_2S^{\bullet+}$, respectively. With increasing collision energies other fragment ions of *m/z* 45, 33, and 27 appear in the daughter spectra. At 75-eV collision, few parent ions survive the surface collision without fragmenting, the major product being the methyl cation while minor contributions arise from $C_2H_3^+$ (*m/z* 27), SH^+ (*m/z* 33), and CHS^+ (*m/z* 45). Note that the 75-eV spectra resemble each other more closely than do the 25-eV spectra. This can be readily interpreted in terms of a reduced dependence upon initial internal energy in the more highly activated ions.

The SID data confirm the conclusion of the high-energy CAD experiment that a single $C_2H_3S^+$ fragmenting structure (or mixture of structures) is accessible from compounds **1**–**9**. Moreover, the simplest interpretation of these daughter spectra is that this is the thioacylium structure. Low-energy gaseous collisions were used to test this conclusion further.

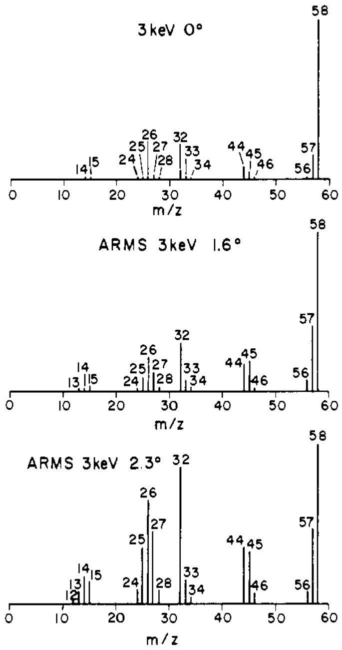

Figure 3. Daughter spectra of $C_2H_3S^+$ ions (generated from **2**) obtained at scattering angles of 0, 1.6, and 2.3° following 3-keV collision with Ar.

Low-Energy CAD. Daughter spectra due to collision-activated dissociation of $C_2H_3S^+$ ions at 5–25-eV energies with a gas-phase target were recorded under single-collision conditions. The spectra recorded for all precursors examined (**1**–**8**) are similar. Typical data obtained at 10- and 22-eV collisions, are reported in Table II. The pattern of fragmentation is similar to that observed in the SID experiments. The dominant ionic product is the methyl cation. Minor products occur at *m/z* 57 ($C_2H_2S^{\bullet+}$), *m/z* 45 (HCS^+), *m/z* 33 (HS^+), and *m/z* 27 ($C_2H_3^+$). Note that pressure-variation experiments establish that a major portion of the fragment ion observed at *m/z* 58 is due to metastable ion dissociation, and it is therefore omitted from Table II. At *minimum*-collision gas pressures, contribution from metastable ion dissociation to give *m/z* 57 and 58 is large, but, even under these mild conditions, CH_3^+ is readily generated. Representative breakdown curves of $C_2H_3S^+$ ions generated from two different precursors (**1** and **4**) are shown in Figure 4. These curves show the dependence of fragment ion abundances on collision energy. The close similarity between the ERMS data of these ions is typical

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[30] McLuckey, S. A.; Cooks, R. G. In *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley: New York, 1983; pp 303–320.

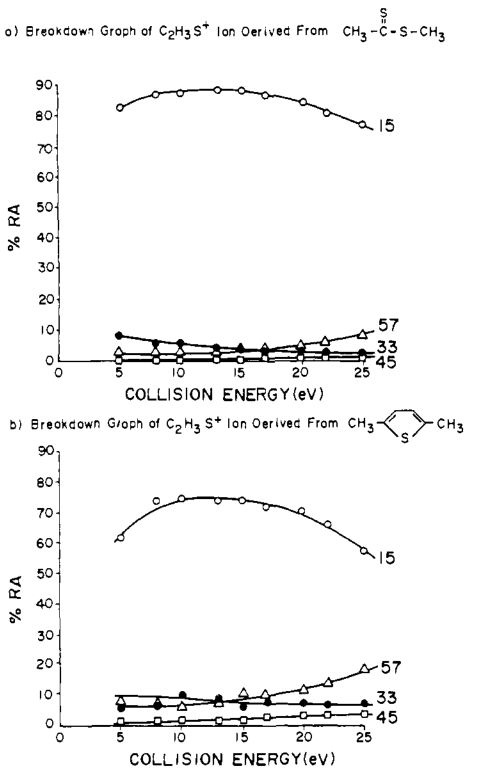
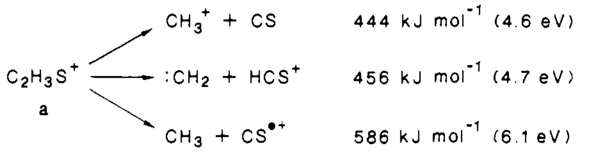


Figure 4. Breakdown curves for $C_2H_3S^+$ ions generated from precursors **1** and **4**. The data show daughter spectra corresponding to ions having a range of internal energies associated with activating collisions of 5–25 eV.

of the $C_2H_3S^+$ ions derived from all precursors.

Discussion

The activation energies for dissociation reactions of $C_2H_3S^+$ are expected to be significantly higher than those for isomerization. A lower limit for the activation energy of a given reaction is provided by the enthalpy of reaction, which can be calculated from the heats of formation[31] of products and reactants. The examples reported in eq 3 for decomposition reactions of the thioacylium ion a are indicative of the large energy barriers involved.



$$\underset{\mathbf{a}}{C_2H_3S^+} \begin{array}{lll} \nearrow & CH_3^+ + CS & 444\ \mathrm{kJ\ mol^{-1}}\ (4.6\ \mathrm{eV}) \\ \longrightarrow & :CH_2 + HCS^+ & 456\ \mathrm{kJ\ mol^{-1}}\ (4.7\ \mathrm{eV}) \\ \searrow & CH_3 + CS^{\bullet +} & 586\ \mathrm{kJ\ mol^{-1}}\ (6.1\ \mathrm{eV}) \end{array} \qquad (3)$$

The different activation methods applied to $C_2H_3S^+$ (low-energy CAD, high-energy CAD, angle-resolved CAD and SID) yield some common fragment ions but also one major discrepancy. This concerns the virtually complete absence of CH_3^+ in the zero-angle, high-energy CAD experiments. This is shown in Figure 5, which compares the daughter spectrum of the $C_2H_3S^+$ ion, derived from ethylene sulfide **2**, generated by each of the activation methods, low-energy (eV) CAD, high-energy (keV) CAD, SID, and ARMS at a 2° scattering angle. The spectra shown in Figure 5 do not include the $C_2H_2S^{\bullet +}$ (*m/z* 58) ion because its abundance changes considerably in the various experiments due to its formation largely via metastable decomposition of the parent ion.[36]

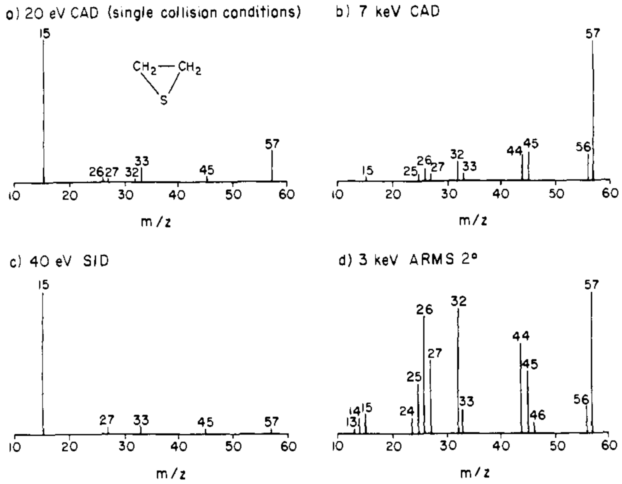


Figure 5. Comparison of daughter spectra of $C_2H_3S^+$ ions (generated from **2**) activated by (a) 20-eV collisions with Ar, (b) 7-keV collisions with air (zero scattering angle), (c) 40-eV SID, and (d) 3-keV collisions with Ar at 2.0° scattering angle.

It is a reasonable assumption that, in most cases, $C_2H_3S^+$ ions formed in the ion source initially have the skeletal features of their neutral precursors. Thus, ions a are expected to be obtained from thiocarbonyl derivatives and ions c from ethylene sulfide **2**. However, common to all the experiments (eV CAD, keV CAD, and SID) is the finding that different $C_2H_3S^+$ ions derived from different precursors produce very similar daughter spectra. A simple explanation for these similarities may be invoked, namely that the ions that are sampled are those that have undergone isomerization prior to collisional activation. The high activation energy for fragmentation and the considerably lower barriers to isomerization (Figure 1) should favor[10] such selective sampling of energetic isomerized ions, which are, nevertheless, stable to fragmentation in the absence of activation. Precedent is found in the case of $C_6H_6^{\bullet +}$ where the energetics of fragmentation and isomerization are comparable.[14] Note, too, that the SID and low-energy CAD spectra are remarkably similar, their main feature being the presence of a dominant peak at *m/z* 15. On these grounds, it is logical to suggest that the species analyzed in these experiments contains a methyl group and is best described by the thioacylium structure a. These data are in agreement with the ICR results already mentioned in the Introduction.[19]

High-energy CAD spectra of $C_2H_3S^+$ species, on the other hand, differ sharply from those of low-energy CAD and SID, particularly in the virtual absence of the peak at *m/z* 15. Factors that may be responsible for this discrepancy are differences in structure and energy, and both must be considered. Consider first the possibility that the ions examined in the kiloelectronvolt and electronvolt energy range experiments have different structures. In the original report on kiloelectronvolts activation,[16] the absence of CH_3^+ ion in the kiloelectronvolt CAD daughter spectra was accounted for by considering b and/or c as the structure of the $C_2H_3S^+$ ions. This proposal is reasonable insofar as $C_2H_3S^+$ ions of original structure b or c are concerned, since *kiloelectronvolt CAD* analysis deals with more short-lived ions than do either electronvolt CAD or *SID*.[3,8,23] However, the same proposal also requires that ions a formed in the ion source isomerize in *kiloelectronvolt CAD experiments* but not in electronvolt CAD and SID experiments where the lifetimes of the ions are longer and the internal energy is varied over a wide range. The strongly hydrogen-bonded structure g was not considered previously, but reports of related

$$\underset{\mathbf{g}}{[H_2C\text{---}H\text{---}CS]^+}$$

structures have appeared.[38] Participation of g does not provide

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[31] The following values were used: CH_3CS^+ (879 kJmol^{-1})[19], CH_3^+ (1093 kJmol^{-1}),[32] CS (230 kJmol^{-1}),[33] $CH_3^\bullet$ (143.5 kJmol^{-1}),[34] $CS^{\bullet +}$ (1322 kJmol^{-1}),[17,33] CH_2 (360 kJmol^{-1}),[33] and HCS^+ (975 kJmol^{-1}).[35]

[32] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. Y. *J. Phys. Chem. Ref. Data* **1977**, Suppl. I, 6.

[33] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

[34] Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

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[36] By contrast, in the SID experiment metastable ion dissociation reactions are discriminated against because of the potential barrier imposed by the acceleration/deceleration sequence used.[8,37]

[37] McLuckey, S. A.; Glish, G. L.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Procresses* **1981**, *39*, 219–230.

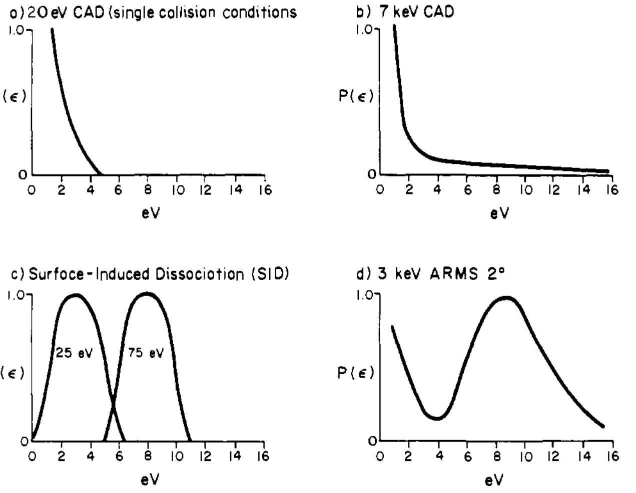

Figure 6. Typical internal energy distributions for the activation methods used in this study (based on experimental data in ref 8b, 9, and 40).

a reasonable explanation of the experimental observations since a and g are expected to fragment in similar fashion.

Another possibility to account for the differences in the kiloelectronvolt and electronvolt range CAD experiments is differences in the amounts of internal energy deposited by the various activation methods. The qualitative internal energy distributions reported in Figure 6 have been suggested on the basis of results recorded for a number of systems.[8,9,39,40] According to these results, the *average* energy deposited in 8-keV CAD should fall within the range covered by 25–75-eV SID.[41,42] The methyl cation is the base peak in the SID daughter spectra over this entire range of collision energies. One therefore expects an abundant CH_3^+ ion to be generated in the kiloelectronvolt CAD experiment. The data of Figures 4 and 5 make it clear that CH_3^+ formation is a facile process even under extremely mild activation conditions (e.g. 5-eV gas-phase collisions). Hence, its virtual absence in the 7-keV CAD data is not explained by the nature of the internal energy distribution. It follows that differences in internal energy in themselves cannot account for the difference in the kiloelectronvolt CAD and SID spectra. This result is in contrast to another case, the retro Diels–Alder fragmentation of limonene, where the differences in behavior are almost as marked as in the present system.[42] However, the differences in the *shapes* of the internal energy distributions account completely for the limonene fragmentation.

There is one way to reconcile the proposal that the $C_2H_3S^+$ ions have isomerized to a common structure prior to CAD or SID with the observed differences in fragmentation behavior observed upon activation by different means. It is generally accepted[3,5,43] that the mechanism of collisional activation of *small* organic ions with kiloelectronvolt kinetic energy involves excitation to an electronically excited state, followed by fast internal energy redistribution. In a few cases, notably in fluorinated compounds, energy redistribution may be slow enough for fragmentation to occur via isolated electronically excited states, leading to spectra that differ from those encountered for ground-state ions.[44] Collisional activation of the thioacylium ion a on an excited electronic surface is expected to occur to yield electronically excited $C_2H_3S^+$ in the kiloelectronvolt experiments. If this ion fragments from this state, the results will differ from those encountered in the low-energy experiments where fragmentation occurs from the vibrationally excited ground state.[45] Note that the lifetime of the excited state need be no greater than the lifetime of the activated ion, a period which is probably less than a nanosecond. There is precedent for isomerization in an excited electronic state by an avoided crossing in ionized methyl acetate.[46] Note also that our results suggest that in both the low- and high-energy experiments (eV CAD, SID) those $C_2H_3S^+$ ions that are sampled have isomerized to the thioacylium structure before undergoing activation.[47]

Photoelectron spectra of simple sulfur compounds[48] (e.g. thioketone) suggest that the first excited states of the $C_2H_3S^+$ ions may lie well below the threshold for the major fragmentation reactions. There is other precedent for striking differences in fragmentation patterns of ionic species in high- and low-energy collision experiments. One example concerns protonated acetonitrile, $C_2H_4N^+$, which gives an intense peak at *m/z* 15 in low-energy CAD experiments[49] and a very weak one in high-energy CAD experiments.[50]

The ARMS data provide evidence for the conclusion that the difference in fragmentation between low and high collision energy experiments is to be found in the *mode* of energy deposition. It is expected that nonzero scattering will increase the amount of energy deposited in a vibrational excitation experiment, as shown explicitly for small molecules by Futrell and co-workers.[51] Nonzero angle scattering can also be expected to increase the probability of vibrational excitation over electronic excitation, and recent data on $Fe(CO)_5^{\bullet+}$ has confirmed this point.[40] Thus, the increasingly abundant ion of *m/z* 15 observed at larger scattering angles is ascribed to the increased contribution from vibrational excitation of the thioacylium ions being sampled.[52]

Conclusion

The $C_2H_3S^+$ ions derived from different precursors yield similar daughter spectra in low-energy (eV) CAD and SID experiments, which are characterized by a large methyl cation (*m/z* 15) abundance. This indicates that the $C_2H_3S^+$ ions have isomerized to the thioacylium structure a before undergoing fragmentation, and evidence is presented that this occurs before activation.[53] Identical daughter spectra of $C_2H_3S^+$ ions, derived from the same

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[38] Blanchette, M. C.; Holmes, J. L.; Hop, C. E. C. A.; Lossing, F. P.; Postma, R.; Ruttink, P. J. A.; Terlouw, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 7589.

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[40] Horning, S. R.; Vincenti, M.; Cooks, R. G., submitted for publication.

[41] For example, limonene molecular ion acquires more internal energy upon 30-eV collisions in SID than upon CAD at 3 keV.[42]

[42] Vincenti, M.; Horning, S. R.; Cooks, R. G. *Org. Mass Spectrom.* **1988**, *23*, 585.

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[45] Little can be said regarding the structure of this state; it may correlate with $CH_3^{\bullet}$ and $CS^{\bullet+}$ and hence fail to yield CH_3^+ fragments.

[46] Heinrich, N.; Schmidt, J.; Schwarz, H.; Apelig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 1317.

[47] Although the methyl cation is always the dominant ion in the low-energy CAD daughter spectra of $C_2H_3S^+$ ions derived from different precursors, its abundance varies from 50% to 80% relative abundance. The methyl cation is expected to be generated only from structure a, and this variation in the abundance of CH_3^+ may be indicative of minor contributions from structures other than a. The small but probably significant differences in the abundances[16] of the charge stripping products of $C_2H_3S^+$ also point to the presence of ions in the beam that have not undergone isomerization.

[48] For example, the difference in energy between the ground and first excited states of $C_2H_3S^{\bullet+}$ is only 2.43 eV, more than 2 eV less than that in the corresponding O-containing species. (a) Rosmus, P.; Solouki, B.; Bock, H. *Chem. Phys.* **1977**, *22*, 453. (b) Bock, H.; Solouki, B.; Bert, G.; Rosmus, P. *J. Am. Chem. Soc.* **1977**, *99*, 1663.

[49] Hayward, M. J.; Cooks, R. G., unpublished data.

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[51] Herman, Z.; Futrell, J. H.; Freidrich, B. *Int. J. Mass Spectrom. Ion Procresses* **1984**, *58*, 181–199.

[52] In both the $C_2H_3S^+$ and the $Fe(CO)_5^{\bullet+}$ study a laboratory scattering angle of 2° was utilized. In the center of mass the corresponding scattering angles are 5° and 12°, respectively. The differences in the center of mass scattering angles account for the small degree of vibrational activation for the $C_2H_3S^+$ ion over that of $Fe(CO)_5^{\bullet+}$.

[53] The high activation energy for the lowest energy dissociation process will also promote activation after excitation, especially under multiple-collision conditions; compare ref 10.

precursors, have also been observed in high-energy (keV CAD) experiments, again suggesting that the common ion a is sampled. The major difference between the low-energy (eV CAD and SID) and high-energy (keV CAD) daughter spectra of $C_2H_3S^+$, the methyl cation (CH_3^+) abundance, is not due to different extents of activation but, it is proposed, to fragmentation via an excited electronic state in those CAD experiments that proceed via electronic excitation. Supporting evidence is presented from angle-resolved experiments, that CH_3^+ is generated competitively by vibrational excitation, a process which is expected to become increasingly favorable, compared with electronic excitation, at nonzero scattering angles.

It can be expected that excitation to still higher internal energies than those used here should make it possible to sample those $C_2H_3S^+$ ions that retain the original $C_2H_3S^+$ structures prior to activation and so lead to characteristically different daughter ion spectra. Not only does this study account for the remarkable difference between the high- and low-energy CAD and SID data but it accommodates the fact that the ion/molecule reactions also suggest a thioacylium structure. A further, although tentative, conclusion that emerges from this work is that the polyatomic ion/surface collisions studied lead chiefly to vibrational excitation of the $C_2H_3S^+$ ion.

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Registry No. 1, 2168-84-5; **2**, 420-12-2; **3**, 554-14-3; **4**, 638-02-8; **5**, 637-53-6; **6**, 624-89-5; **7**, 110-81-6; **8**, 5271-38-5; **9**, 1072-43-1; a, 59348-26-4.

Gas-Phase Reactions of Fe$^-$ and Co$^-$ with Simple Thiols, Sulfides, and Disulfides by Fourier Transform Mass Spectrometry

L. Sallans,[†] K. R. Lane,[‡] and B. S. Freiser*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received January 27, 1988*

Abstract: Fe$^-$ and Co$^-$ are found to react with simple thiols, sulfides, and disulfides. The primary reaction products formed from these metal anions, M$^-$, and thiols include MS^-, MSH^-, and MSH_2^- and suggest a mechanism involving initial insertion of the metal into the weak C–S bond. Similarly, C–S insertion is the main mode of attack in the reactions with the sulfides and disulfides, in analogy to what is observed for the reaction of metal cations. Collision-induced dissociation is used to support the proposed structures for the primary products, H–Fe$^-$–SH and Fe$^-$–SH. Some of the thermochemical data derived from this study include $D^\circ(M^-{-}S) > 103$ kcal/mol and $D^\circ(M^-{-}SH) = 83 \pm 9$ kcal/mol. Finally, a brief survey of the reactivity of V$^-$, Cr$^-$, and Mo$^-$ with selected organosulfur compounds is also reported.

The ion–molecule chemistry of atomic and coordinated metal ions has proven to be a very rich and active area over the past decade. The incentives for these studies include the fact that organometallic compounds and ions are becoming increasingly recognized as essential components in a variety of environmental, chemical, and biological systems.[1] Another major factor fueling the considerable effort dedicated to gas-phase metal ion chemistry is that it provides fundamental kinetic, mechanistic, and thermodynamic information[2] that is crucial to the understanding of catalytic reaction mechanisms.

A considerable data base has already been obtained from gas-phase studies of atomic and molecular metal cations, including homolytic and heterolytic metal–hydrogen, metal–carbon, and metal–oxygen bond strengths[2,3-11] and relative ligand binding energies.[12-17] In addition, gas-phase Lewis basicities,[18-20] hydride affinities,[21,22] electron affinities,[23-27] and ionization potentials[5,13,28] for neutral transition-metal complexes have been obtained.

The majority of studies on gas-phase metal ion chemistry have involved metal cations,[29] primarily due to the ease of their formation. In particular we have shown that laser desorption on pure metal targets is a convenient method of generating virtually any atomic metal cation for study by Fourier transform mass spectrometry.[30-32] The scope of this work has continued to expand to include not only the ion–molecule reactions of the atomic metal cations with various organic molecules but also the chemistry of a variety of ligated metal cations[33-36] and small metal cluster ions.[37-40]

[†] Current Address: PPG Industries, Inc., P.O. Box 31, Barberton, Ohio 44203.

[‡] Current Address: AMOCO Chemicals Corp., P.O. Box 400, Naperville, Illinois 60566.

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