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Experimental and Theoretical Characterization of Long-Lived Triplet State $CH_3CH_2S^+$ Cations

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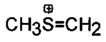
Abstract: Gas-phase $[C_2H_5S]^+$ ions obtained by electron impact ionization from $CH_3SC_2H_5$ at 13 eV undergo three distinct low-pressure ion/molecule reactions with the parent neutral: proton transfer, charge transfer, and hydride abstraction. The kinetics of these reactions studied by FT-ICR techniques clearly suggests the $[C_2H_5S]^+$ species to be a mixture of isomeric ions. While proton transfer and hydride abstraction are consistent with CH_3CHSH^+ and $CH_3SCH_2^+$ reagent ions, the observed charge transfer strongly argues for the presence of thioethoxy cation, $CH_3CH_2S^+$, predicted to be stable only in the triplet state. Charge transfer reactions only occur with substrates having an IE below 8.8 eV and thus yield an upper limit for the recombination energy of the $CH_3CH_2S^+$ ions. Studies using $CD_3SC_2H_5$ show that charge-transfer reactions are promoted by cations originating from a sulfur−methyl carbon bond cleavage. Ab initio calculations at several levels of theory predict that $CH_3CH_2S^+$ ions are only stable in the triplet state. Calculations along the fragmentation pathway of the molecular ion reveal the tendency to generate triplet $CH_3CH_2S^+$ ions upon cleavage of the sulfur−methyl carbon bond. Calculations were also carried out to determine the lifetime of triplet $CH_3CH_2S^+$ using nonadiabatic RRKM theory. The exothermic or near thermoneutral spin-forbidden unimolecular isomerizations and dissociations were first characterized at different levels of theory, and the minimum energy crossing points (MECPs) for all the channels were identified at the CCSD(T) level. The probability for surface hopping was then estimated from the spin−orbit matrix elements. The calculated unimolecular dissociation rate constants predict that triplet $CH_3CH_2S^+$ ions with less than 10 kcal mol^{-1} of internal energy and at any level of rotational excitation should be long-lived, and strongly support the experimental observations.

1. Introduction

Unraveling the structure, atom connectivity, and stability of elusive neutrals and ions remains one of the most exciting and challenging problems in structural chemistry. In recent years, new and powerful experimental techniques coupled with high-level theoretical calculations have paved the way for the direct structural characterization of unusual ions,[1] and of such novel neutral chemical species as ammonium oxide[2] and hydrogen trioxide.[3]

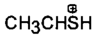
The structure and reactivity of simple organosulfur neutrals and ions are areas of major current interest because of the possible role of these species in atmospheric processes leading to acid rains,[4] and in interstellar clouds.[5] Unlike sulfur-containing stable neutrals or radicals, the structure of the corresponding ions is not always uniquely defined. For example, ions exhibiting the formal $[RS]^+$ (R = alkyl) composition are common fragments observed in the mass spectra of simple thiols and thioethers[6] but structures with different atom connectivities are well-known to be stable species. Collisional activation studies carried out more than 20 years ago suggest that even simple neutrals are prone to yield a mixture of isomeric $[RS]^+$ ions upon isomerization and fragmentation of the parent molecular ion.[7,8] For $[C_2H_5S]^+$ ions, three distinct species (**1**−**3**) have been claimed to be consistent with experimental data. A careful analysis of the fragmentation reactions of the molecular ions of methyl ethyl sulfide (MeSEt), $CH_3SC_2H_5^{+\bullet}$, and their deuterium labeled analogues, has led to the conclusion that fragment ions corresponding to structures **1** and **2** are formed

1



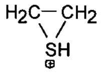
$CH_3\overset{\oplus}{S}{=}CH_2$

2



$CH_3CH\overset{\oplus}{S}H$

3



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as a result of bond cleavage processes,[9] and that these ions do not undergo unimolecular interconversion readily.

Isomers **1**, **2**, and **3** have been shown to be distinguishable by neutralization−reionization techniques.[10] It is also likely that differences in ion reactivity can provide the means for distinction among these isomers as illustrated for the corresponding $[C_2H_5O]^+$ ions[11,12] and the related $[C_2H_4S]^{+\bullet}$ tautomers.[13]

By comparison, no evidence has been advanced for the existence of the thioethoxy cation, **4**, which has been claimed

4 $CH_3CH_2S^{\oplus}$

to be unstable toward rearrangement to isomer **2**.[9a] Other alternative structures for $[C_2, H_5, S]^+$ ions, most noticeably ions such as **5** and **6**, have also been considered as playing a role in the general energy surface of $[C_2H_5S]^+$ ions.[9a]

5 $CH_2CHSH_2^{\oplus}$ **6** $^{\oplus}CH_2CH_2SH$

Early measurements on appearance energies[14] for $[C_2H_5S]^+$ ions obtained by electron ionization from MeSEt revealed that ions **1** and **2** do not differ significantly in their heats of formation. While an appearance energy was also claimed for an ion with a $CH_3CH_2S^+$ structure, these results were inconclusive regarding the possible existence of **4**. A more accurate determination of the thermochemistry of $[C_2H_5S]^+$ ions, assumed to have structure **1**, was first obtained from PEPICO experiments.[15] By comparison, the corresponding neutral radicals of **1** and **4** display significant differences in ionization energies. The photoelectron spectrum of the short-lived $CH_3SCH_2^\bullet$ radical yields an adiabatic IE of 6.85 ± 0.03 eV,[16] while the ionization energy of the $C_2H_5S^\bullet$ radical has been recently determined to be 9.077 ± 0.004 eV by pulsed field ionization photoelectron spectroscopy.[17] This value supersedes an early estimate of 9.6 ± 0.8 eV with formation of an ion of unknown structure.[18]

On the theoretical side, recent ab initio calculations at the G2 level[19] predict **2** to be more stable than **1** and **3** by 2.6 kcal mol^{-1}. The same calculations confirm that ion **4**, in its singlet state, is unstable toward rearrangement to **2**. However, a stable triplet thioethoxy cation **4** is predicted to lie 44 kcal mol^{-1} above **2** but the barriers for intersystem crossings to the singlet surfaces were not explored. Refinements of the early calculations[20] on neutral $[C_2H_5S]^\bullet$ radicals have led to a calculated adiabatic ionization energy of 6.86 eV for $CH_3SCH_2^\bullet$ and of 9.07 eV for $C_2H_5S^\bullet$ to yield triplet $C_2H_5S^+$. This general picture parallels closely the results obtained in some of the early classical ab initio calculations on $[CH_3S]^+$ that predicted the thiomethoxy cation CH_3S^+ to be stable only in the triplet state.[21,22] Likewise, calculations on the ethoxy cation $C_2H_5O^+$ also predict this structure to be stable only in the triplet state.[23]

While some organic cations in high-energy triplet states have been recently identified,[24] there are few examples describing experimentally observed long-lived thioalkoxy or alkoxy cations.[25] In one case, CH_3O^+ cations (presumably in the triplet state) generated by collision-induced charge reversal of methoxide anions were identified by their low-energy ion/molecule reactions.[26] Thus, the key question is whether triplet thioalkoxy cations are sufficiently long-lived to be amenable for experimental characterization.

This paper presents for the first time some unequivocal experimental evidence that long-lived triplet state $CH_3CH_2S^+$ ions can be generated, among other isomeric species, from electron ionization of $CH_3SC_2H_5$. These ions are shown to undergo charge-transfer reactions with neutral substrates of ionization energies below 8.8 eV by ion cyclotron resonance techniques. Theoretical calculations similar to those recently reported for the unimolecular decay of the thiomethoxy cation[27] have also been carried out and clearly support the idea that triplet $CH_3CH_2S^+$ ions with low internal energies are long-lived species.

2. Experimental Methods

Experiments were carried out in a homemade Fourier transform ion cyclotron resonance mass spectrometer that has been described previously.[28] The magnetic field for these experiments was set typically at 1.0 or 1.2 T.

The experiments with $[C_2H_5S]^+$ ions generated from $CH_3SC_2H_5$, or MeSEt, illustrate the basic procedure followed in the present work. Ions were formed in a one-region 1 in. cubic cell by electron bombardment at ionizing energies varying between 11 and 70 eV and at pressures in the range of $2-4 \times 10^{-8}$ Torr as measured by a nude ion gauge located between the cell and the turbomolecular pump. The ions of interest, $[C_2H_5S]^+$ (*m*/*z* 61), were isolated by two different

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methods: (a) soon after ion formation (typically after 200 ms) by a sequence of short frequency swept ejection pulses to remove all unwanted primary and secondary ions (formed before ion isolation) and (b) after Ar gas was introduced in the cell through a pulsed valve and the ion gauge returned to its original base pressure (∼1 s). An aperture time of 3 to 5 ms was used for the pulsed valve and the instantaneous ion gauge reading typically reached 3×10^{-7} Torr. However, the actual instantaneous Ar pressure in the cell may be an order of magnitude higher in this type of experiment. Qualitative differences are observed in the kinetics with these two methods but not in the product distribution as discussed in the Results.

Ion/molecule reactions of neutral MeSEt with $[C_2H_5S]^+$ ions, obtained as fragment ions upon ionization of different sulfur-containing precursors, were carried out with methyl ethyl sulfide introduced through a pulsed valve after isolation of the *m*/*z* 61 ions. A delay of at least 20 s was used between successive FT acquisition cycles to ensure that all the methyl ethyl sulfide was pumped away before ionization. Reactions with other neutral substrates were studied either at a fixed partial pressure of $1.5-3 \times 10^{-8}$ Torr or by pulsing the reagent gas into the cell.

Reagents (except for methyl sulfide) were obtained from Aldrich and used without further purification. Samples were thoroughly degassed and subjected to several freeze, pump, and thaw cycles prior to their introduction in the high-vacuum system of the spectrometer. Mass spectra of these samples obtained by running the FT-ICR spectrometer with continuous ionization and short trapping times revealed no detectable impurities. Methyl sulfide (Me_2S) was prepared and purified by the group of Prof. Liliana Marzorati from this Institute. Prof. Nico M. M. Nibbering of the University of Amsterdam kindly provided $CD_3SC_2H_5$ and the isotopic purity is rated as better than 97%.

3. Computational Methods

Ab initio molecular orbital calculations were carried out with the Gaussian[29] and Gamess[30] suite of programs. Structures corresponding to stable species in the $[C_2H_5S]^+$ energy surface were studied at different levels of theories, namely HF/6-31G(d) and B3LYP/6-31G(d), and harmonic frequencies were obtained for these structures to ensure that they correspond to minima in the energy surface. Critical structures were first optimized and then characterized at different levels of theory, namely HF/6-31G(d), B3LYP/6-31G(d), and MP2/6-31G(d). Single point energy calculations for the optimized structures were then performed at both the B3LYP/6-311G(3df,3pd) and CCSD(T)/6-311+G(p,d) levels of theory.

The critical points[31] concerning the minimal energy crossing points (MECP) between the triplet and singlet surfaces were initially located, without any symmetry restrictions, using a recently developed steepest descent method.[32] To check the effects of the intrinsic limitations of each theoretical approach,[33] the location of the critical points was carried out at three different levels of theory, namely: MP2(full)/6-31G(d), B3LYP/6-31G(d), and CCSD(T)/6-311+G(p,d)//B3LYP/6-31G(d).

Crude estimates of the curvature of the seams were also carried out as described in ref 32 to characterize the located crossing points as actual minima along the 3N-7 hypersurface and thus obtain an estimate for the corresponding harmonic frequencies necessary for the RRKM calculations. To ascertain that the located MECPs actually interconnect the corresponding minima, an approximate IRC-like procedure was also carried out as described in ref 27.

The spin−orbit matrix elements known as the main mechanism responsible for driving the intersystem crossing[34] were then calculated in correspondence with the MECPs between the singlet and all the triplet substates through an approximate monoelectronic spin−orbit Hamiltonian with an effective nuclear charge for all the nuclei as recommended in the literature,[35] using CI wave functions expanded within HF orbitals generated for the singlet state[36] with Dunning's correlation consistent triple-ζ quality basis sets.[37] The reported values are the corresponding root-mean-square values.

Calculations of the unimolecular dissociation rate constants were carried out using a nonadiabatic version of the RRKM theory[38] recently implemented by us,[39] and following a procedure similar to that described in detail for the case of CH_3S^+ and CH_3O^+.[27,40] Briefly, we have used

$$k(E,J) = [2/h\,\rho(E,J)] \int \mathrm{d}E_\mathrm{h}\, \rho(E-E_\mathrm{h},J)P_\mathrm{sh}(E,J)$$

where *h* is the Planck constant, ρ stands for the density of the vibrational states, and $P_\mathrm{sh}(E)$ is the surface-hopping probability for a single passage through the seam at the speed corresponding to the energy E_h. The rotational effects have been introduced by considering four different values of *J* and treating the *K* quantum number as an active rotor.[41] For the rate calculations statistical weights were also considered for each case.

4. Experimental Results and Discussion

$[C_2H_5S]^+$ Ions Obtained from MeSEt. MeSEt is a convenient source of $[C_2H_5S]^+$ ions for studying ion/molecule reactions. The *m*/*z* 61 is a major peak in the mass spectrum of MeSEt, and isolation of this fragment ion is easily achieved since at low electron energies essentially no neighboring fragment ions are observed. Previous mass spectrometric studies[7a,9a] concluded that 75 to 85% of the $[C_2H_5S]^+$ ions, obtained from of ionization of MeSEt at 70 eV, correspond to the sulfonium structure **1**. The remaining fragment ions were assumed to have structure **2**, protonated thioacetaldehyde, resulting from a carbon−sulfur cleavage followed by a 1,2 hydrogen shift in the nascent $CH_3CH_2S^+$ ion.

Reaction of these *m*/*z* 61 fragment ions with the neutral parent MeSEt in our FT-ICR spectrometer reveals the formation of three product ions, identified as $MeS^+{=}CHMe$ (*m*/*z* 75), $(MeSEt)^{+\bullet}$ (*m*/*z* 76), and $(MeSEt)H^+$ (*m*/*z* 77). Figure 1a shows the typical kinetics for formation of these product ions from reactant ions thermalized by pulsing Ar into the ICR cell. The kinetics of the reactions leading to the *m*/*z* 76 and 77 ions is not noticeably affected by thermalization of the reagent ion. By comparison, the rate of formation of $MeS^+{=}CHMe$ (*m*/*z* 75) displays a noticeable slow rise and nonexponential growth in the absence of the Ar gas pulse. However, the final ion product distribution after complete depletion of the reagent ions

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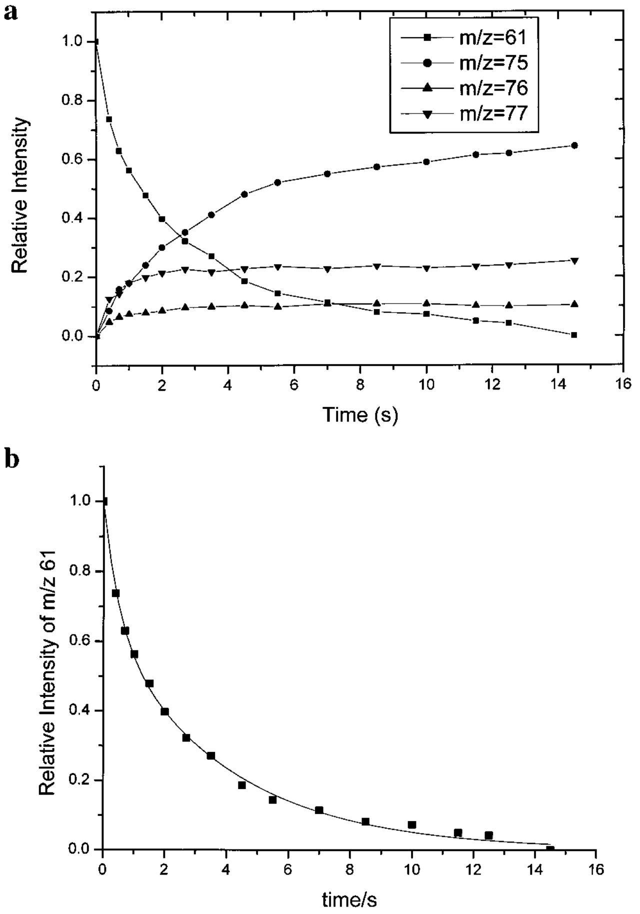

Figure 1. (a) Kinetics of $[C_2H_5S]^+$ ions (*m/z* 61 ions) obtained from MeSEt reacting with neutral MeSEt to yield the products displayed in reaction 1. Pressure = 3.5×10^{-8} Torr and electron energy = 13 eV. (b) Best fit for the double exponential disappearance of $[C_2H_5S]^+$ ions is the following: $I_{61} = (0.65 \pm 0.03)\exp(-0.255 \pm 0.014)t + (0.34 \pm 0.03)\exp(-1.95 \pm 0.34)t$.

is independent, within experimental error, of whether ion selection is performed with or without a rare gas pulse.

The kinetic behavior shown in Figure 1a, and the fact that product ions do not undergo further reaction with neutral MeSEt, suggests that a mixture of isomeric $[C_2H_5S]^+$ ions is responsible for the different reaction channels. In fact, the products can be rationalized as a result of three distinct ion/molecule processes:

(a) Hydride abstraction by the sulfonium ion, **1**,

$$\mathrm{Me{-}S^+{=}CH_2 + MeSEt \rightarrow MeSMe + \underset{m/z\ 75}{Me{-}S^+{=}CH{-}Me}} \quad (2a)$$

The exothermicity of this reaction is not known as the termochemistry of the Me—S$^+$=CHMe ion has not been previously determined.

(b) Fast proton transfer from either **2** or **3**,

$$\mathrm{C_2H_4SH^+ + MeSEt \rightarrow C_2H_4S + \underset{m/z\ 77}{M{-}S^+(H){-}Et}} \quad (2b)$$

Proton transfer from protonated thiirane, **3**, is exothermic by 9.3 kcal mol^{-1} (see Table 1 for the relevant thermochemical properties),[42] and is also expected to be 8 kcal mol^{-1} exothermic for protonated thioacetaldehyde, **2**, according to our ab initio calculations (see Table 1).

Table 1. Ionization Energies (eV) and Proton Affinities (kcal mol^{-1}) of Different Neutrals Used in This Work[a]

	IE /eV	PA /kcal mol^{-1}	calcd (G2)[b]
$CH_3SC_2H_5$	8.55	202.3	201.3
cyclo-CH_2CH_2S	9.0	193	192.44
$CH_3C(H)S$			193.4
$CH_3CH_2S^{\cdot}$	9.077[c]		
CH_3SCH_2•	6.85		
$(CH_3)_2CHSH$	9.15	192.1	
$(CH_3)_2S$	8.69	198.6	
NH_3	10.07	204	
$PhNH_2$	7.72	210.9	
PhOEt	~8.4	~204[d]	
pyridine	9.22	222	
$MeNH_2$	~8.9	214.9	
toluene	8.828	187.4	
acetophenone	9.28	205.8	

[a] Values obtained from ref 42. [b] Calculated in this work. [c] Reference 17. [d] Estimated from the proton affinity tabulated in ref 42.

(c) Fast charge transfer from a $[C_2H_5S]^+$ species of unknown connectivity,

$$\mathrm{[C_2H_5S]^+ + MeSEt \rightarrow [C_2H_5S]^\bullet + \underset{m/z\ 76}{[MeSEt]^{+\bullet}}} \quad (2c)$$

Reaction 2c is in principle energetically feasible since the ionization energy of MeSEt is considerably less than the recombination energy for presumably triplet $CH_3CH_2S^+$ ions to yield $C_2H_5S^\bullet$ radicals.[17] Thus, the observation of the charge transfer reaction strongly suggests the participation of an additional isomeric species such as $CH_3CH_2S^+$. This is an interesting observation since calculations consistently predict that only the high-energy structure corresponding to triplet $CH_3CH_2S^+$ is stable with respect to rearrangement to CH_3CHSH^+ (see below). By comparison, charge transfer is significantly endothermic for the other stable isomeric ions discussed in the Introduction. The MeS$^+$=CH$_2$ ion can be ruled out on energetic grounds since its recombination energy to yield the $MeSCH_2^\bullet$ radical (6.85 eV)[16] is well below the IE of MeSEt. Likewise, the protonated ions **2** and **3** are expected to have very low recombination energies (~3.7 eV) followed by dissociation of a neutral hydrogen atom.[43] The possibility that isomers **1**, **2**, or **3** could promote charge transfer by rearranging in the collision complex can also be ruled out as the barriers for such processes amount to energies two or three times larger[19b] (see also calculations below) than that expected to be available in the collision complexes of these systems (~15 to 20 kcal mol^{-1}).[44]

The presence of more than one isomeric $[C_2H_5S]^+$ can also be inferred from the mathematical fit of the kinetics of disappearance of the reactant ion (Figure 1b). The best fit is obtained for a double exponential decay with the following characteristics: (a) a slow component with $k = 0.25 \pm 0.01$ s^{-1} and a preexponential coefficient of 0.65 ± 0.03 and (b) a fast component with $k = 1.95 \pm 0.32$ s^{-1} and a preexponential coefficient of 0.34 ± 0.04. The first coefficient is in excellent

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[42] Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

[43] Sadilek, M.; Turecek, F. *Int. J. Mass Spectrom.* **1999**, *185/186/187*, 639.

[44] One of the referees raised the question that reaction 2c could also be attributed to a methyl transfer from the neutral substrate. While such an unusual reaction cannot be necessarily distinguished by our isotopic labeling experiments, the observation of charge exchange with aniline, phenetole, and methyl sulfide but not with dimethoxymethane or diethyl ether clearly suggests that reaction 2c proceeds by electron transfer.

Table 2. Product Distribution as a Function of Nominal Electron Energy for the Reaction of $[C_2H_5S]^+$ Ions Generated from MeSEt with the Parent Neutral

product ion	13 eV	70 eV
m/*z* 75	64%	56%
m/*z* 76	11%	5%
m/*z* 77	25%	39%

agreement with the relative intensity of the *m*/*z* 75 ion after complete depletion of the reactant ion, while the other coefficient agrees closely with the sum of the relative intensities of the *m*/*z* 76 and 77 ions. Good agreement with the slow component of the kinetics is also obtained by fitting the growth of the *m*/*z* 75 ion as a function of time, while a similar approach for the individual kinetic curves for the *m*/*z* 76 and 77 ions suffers from a much larger scatter of the experimental points. On the other hand, this mathematical treatment cannot distinguish between two or possibly three different isomeric species, since exothermic proton transfer (from ions such as **2** or **3**) and charge transfer (from ions such as **4** or similar) often proceed at near collision rate.[45] Thus, caution must be exercised before concluding that reactions 2b and 2c originate from common or different isomeric species.

The product distribution was found to depend on the electron energy used in the ionization process. Table 2 lists the final product ion composition obtained under similar pressure and ion isolation conditions at 13 and 70 eV. It is clear that an increase in electron energy considerably enhances the proton-transfer reaction in agreement with the idea that this reaction is promoted by an ion originating from a higher appearance energy fragmentation channel of the molecular ion. At the lowest nominal electron energies used in our experiments (~11 eV), there is a significant increase of the *m/z* 76 ions in the product distribution at the expense of the protonated product ion. The significance of these observations will become apparent during the discussion of the energy surface for triplet−singlet crossing.

Re-isolation of the *m*/*z* 61 ions after 3 s in experiments similar to those shown in Figure 1a shows that these remaining ions react exclusively by hydride transfer and can thus be safely assumed to correspond to pure sulfonium ions **1**. The same product distribution is obtained in experiments where $[C_2H_5S]^+$ ions are allowed to react with neutral MeSEt introduced rapidly at much higher pressures via a pulsed valve. This is particularly relevant with regard to experiments with $[C_2H_5S]^+$ ions generated from different neutral precursors.

More definitive conclusions regarding the characteristic reactivity of $[C_2H_5S]^+$ ions with MeSEt can be drawn from experiments designed to generate specifically isomers **1**, **2**, and **3**.

$[C_2H_5S]^+$ Ions Obtained from 2-Propanethiol, $(Me)_2CHSH$. Fragmentation of the molecular ions of $(Me)_2CHSH$ is usually considered a source of essentially pure protonated thioacetaldehayde, CH_3CHSH^+, isomer **2**. Therefore, the reactivity of these ions in the presence of MeSEt was considered to be an important test of our methodology.

$[C_2H_5S]^+$ ions obtained by electron ionization of $(Me)_2CHSH$ at 20 eV were found to react with MeSEt introduced via the pulsed valve almost exclusively by proton transfer to yield the $(MeSEt)H^+$ (*m*/*z* 77) product ion. The only other product observed, *m*/*z* 75, amounts to about 2%. This result agrees with the idea that ions formed from $(Me)_2CHSH$ presumably retain structure **2**, although proton-transfer reactivity alone cannot distinguish between structures **2** and **3**. However, this experiment clearly shows that these ions do not promote reaction 2c.

$[C_2H_5S]^+$ Obtained from Self-Protonation of Thiirane, *cyclo*-$(CH_2CH_2)S$. At 25 eV, the primary ions of thiirane, namely $M^{+\bullet}$ (*m*/*z* 60), $(M - H)^+$ (*m*/*z* 59), and $(M - CH_3)^+$ (*m*/*z* 45), undergo rapid proton-transfer reactions to yield, presumably, protonated thiirane (structure **3**). Isolation of the resulting *m*/*z* 61 ions followed by reaction with MeSEt introduced through a pulsed valve results in the exclusive formation of the proton-transfer product ion, $(MeSEt)H^+$ (*m*/*z* 77).

The similarity in behavior between $[C_2H_5S]^+$ ions formed by self-chemical ionization of thiirane and by electron impact ionization from $(Me)_2CHSH$ strongly argues against the possibility that either isomers **2** or **3** are capable of undergoing charge-transfer reactions such as shown in (2c).

$[C_2H_5S]^+$ Ions Obtained from $(Me)_2S$. $[C_2H_5S]^+$ ions obtained as fragment ions upon electron impact ionization of Me_2S at 20 eV suggest that these ions undergo reactions with its parent neutral in ways that are reminiscent of the behavior of a mixture of isomeric ions. Since our main interest in using Me_2S was as a precursor of pure sulfonium ions **1**, a different approach was used to generate the *m*/*z* 61 ions in this case. Initially, $MeO^+{=}CH_2$ ions were formed by electron ionization and subsequent fragmentation of $MeOCH_2OMe$ at 20 eV. These ions were then isolated and allowed to react with Me_2S. The ensuing reaction proceeds exclusively by hydride abstraction to yield $[C_2H_5S]^+$ ions, presumably structure **1** (reaction 3).

$$CH_3O^+{=}CH_2 + (CH_3)_2S \rightarrow CH_3S^+{=}CH_2 + (CH_3)_2O \qquad (3)$$

These *m*/*z* 61 product ions were then isolated following the procedure outlined in the Experimental Section and allowed to react with MeSEt introduced into the cell through the pulsed valve. The only reaction observed under these circumstances corresponds to reaction 2a resulting in the formation of *m*/*z* 75 ions.

This latter experiment reveals two important points: (a) this methodology is a clean way to generate pure sulfonium ions and (b) $CH_3S^+{=}CH_2$ reacts exclusively by hydride abstraction with MeSEt.

Reactions of $[C_2H_5S]^+$ and $[C_2D_3H_2S]^+$ Ions Obtained from d_3-MeSEt. The FT-ICR spectrum of d_3-MeSEt at 14 eV yields the fragment ions $[C_2D_3H_2S]^+$ (*m*/*z* 64) and $[C_2H_5S]^+$ (*m*/*z* 61) in a roughly 3:1 ratio. This is similar to what has been reported previously[7a] but somewhat less than the 4:1 ratio observed in the mass spectrum obtained at 70 eV in a sector mass spectrometer at the University of Amsterdam.[46]

Reaction of the *m*/*z* 64 ions with the parent neutral yields almost exclusively the $(M - 1)$ ion of d_3-MeSEt (*m*/*z* 78). This is consistent with the idea that these ions are formed by cleavage of the carbon−carbon bond to yield the sulfonium ions, d_3-$MeSCH_2^+$, and that hydride abstraction occurs at the methylene carbon of MeSEt.

By comparison, reaction of the *m*/*z* 61 ions with the parent neutral yields a more complex pattern: 71% of $(d_3\text{-MeSEt})H^+$ (*m*/*z* 80), 20% of $(d_3\text{-MeSEt})^{+\bullet}$ (*m*/*z* 79), and 9% of $(d_3\text{-MeSCHMe})^+$ (*m*/*z* 78). Some important points emerge from these results:

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[45] Previous experiments have shown that a reliable measurement of the composition of a mixture of isomers in ionic processes can be derived from these rate constant fits provided that the rate constants are significantly different. See, for example: (a) Gaumann, T.; Zhu Z.; Kida, M. C.; Riveros, J. M. *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 372. (b) Gaumann, T.; Zhu Z.; Kida, M. C.; Riveros, J. M. *Helv. Chim. Acta* **1990**, *73*, 2218. (c) Riveros, J. M.; Zhu, Z. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 387.

[46] (a) Ingemann, S. Private communication. (b) van Amsterdam, M. W.; Zappey, H. W.; Ingemann, S.; Nibbering, N. M. M. *Org. Mass Spectrom*. **1993**, *28*, 30.

(a) The $[C_2H_5S]^+$ ions obtained from d_3-MeSEt cannot be considered as originating only from a simple sulfur−methyl carbon cleavage as observation of hydride abstraction (product ion of *m/z* 78) suggests the formation of a fraction of $CH_3S^+{=}CH_2$ ions (larger than that expected from the isotopic purity of the parent neutral). This observation also agrees with metastable studies that reveal that loss of CD_3 may involve other processes besides a simple cleavage.[46]

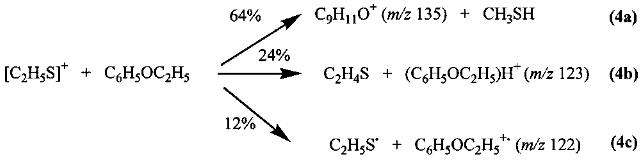
(b) These experiments are consistent with our contention that the charge-transfer reaction is promoted by fragment ions originating from cleavage of the sulfur−methyl bond in the molecular ion and retaining the structure of thioethoxy cations.

(c) The product ratio $(MH^+)/M^{+\bullet}$ in this case is considerably higher than that obtained with the ions generated from undeuterated MeSEt. While our experiments do not provide mechanistic details about the ionization processes leading to the formation of the primary ion, previous studies have shown significant isotope effects in the $(M - CD_3)$ fragmentation of MeSEt.[9a]

Results obtained with other neutral substrates (see below) yield further support to these conclusions and are consistent with the participation of thioethoxy cations in the reactivity pattern.

Reaction of $[C_2H_5S]^+$ Ions with Other Neutral Substrates. Additional experiments were carried out to explore the nature of the $[C_2H_5S]^+$ ions obtained from MeSEt and to better characterize the behavior of the proposed EtS^+ cations. For this purpose, we initially explored substrates of different ionization energies and proton affinities. At the outset, we expected that complex reaction patterns could occur since $CH_3S^+{=}CH_2$ ions, by analogy with the corresponding oxonium ions $CH_3O^+{=}CH_2$, could display a rich variety of ion/molecule reactions including proton transfer to substrates of high proton affinity.[11] Furthermore, the kinetic analysis in these cases is considerably more difficult since under our experimental conditions the $[C_2H_5S]^+$ ions react both with neutral MeSEt and with the additional neutral substrate. The study of reaction product distribution in the presence of excess additional neutral substrate was verified whenever possible by pulsing the neutral reagent through a pulsed valve. However, no reliable kinetic information could be extracted from these experiments.

The best studied example pertains to reactions with phenetole, PhOEt (IE ∼ 8.4 eV and PA ∼ 204 kcal mol^{-1}, see Table 1). At 13 eV, $[C_2H_5S]^+$ ions obtained from MeSEt were observed to react with PhOEt in a fashion reminiscent of the behavior described in reaction 2. Reaction 4a is an addition−elimination reaction involving methylene insertion, presumably in the aromatic system, followed by elimination of CH_3SH. This type of reaction, leading to a product ion with an $[M + CH]^+$ composition, was first observed in the gas-phase ion/molecule reactions of oxonium ions with benzene.[47] The overall product distribution observed for the reaction of $[C_2H_5S]^+$ ions with phenetole shows remarkable agreement with that observed for the reaction of the same ions with neutral MeSEt (see Table 2).



By comparison, reaction of $CH_3S^+{=}CH_2$ ions generated from Me_2S as described above, or of $CD_3S^+{=}CH_2{}^+$ ions from d_3-MeSEt, with phenetole yields ∼91% of reaction 4a and ∼6% of reaction 4b. A small fraction of charge transfer is observed in this case (less than 3%). Whether the proton affinity of PhOEt is high enough to allow for proton transfer from the sulfonium ion or whether the small percentage of reactions 4b and 4c originates from some other isomeric species remains unclear.

On the other hand, $[C_2H_5S]^+$ ions, obtained from d_3-MeSEt, react with PhOEt to yield $[M + CH]^+$, charge transfer, and proton transfer in very close agreement with the results obtained upon reaction with d_3-MeSEt.

Additional experiments with some of the substrates shown in Table 1 reveal some additional features that can be qualitatively summarized as follows:

(a) Charge transfer is distinctly observed to take place between $[C_2H_5S]^+$ ions generated from MeSEt with neutral substrates whose ionization energies lie below 8.8 eV. While this threshold value is consistent with the recombination energy calculated by G2 calculations for triplet $C_2H_5S^+$ ions,[19] it is well-known that threshold values for charge transfer reactions do not necessarily provide the correct recombination or ionization energies.[48]

(b) For substrates of high proton affinity (pyridine, methylamine) and ionization energies above 8.8 eV, proton transfer is the only reaction observed.

(c) The reactivity of $[C_2H_5S]^+$ ions with substrates of higher ionization energies than 8.8 eV can be quite diverse depending on the chemical nature of the neutral and a more thorough analysis will be the subject of a separate report.

Summary of Experimental Results. The results clearly establish that the observed charge-transfer reactions are consistent with the presence of stable thioethoxy cations. Furthermore, the results suggest that a significant fraction of the $[C_2H_5S]^+$ ions formed by cleavage of the methyl−sulfur bond in the molecular ion of MeSEt yield thioethoxy cations that theoretical calculations predict to be possible only in the triplet state (see below).

The results displayed in Table 2 allow us to estimate that approximately 11% of the long-lived $[C_2H_5S]^+$ ions obtained by electron ionization of MeSEt at 13 eV correspond to thioethoxy cations. Nevertheless, we emphasize the fact that caution must be exercised before concluding that ion/molecule reactivity alone can unequivocally establish the percentage composition of isomeric $[C_2H_5S]^+$ ions obtained from precursors such as MeSEt. The degree of synergism observed between the reactivity of the thioethoxy cations and the proton affinity, ionization energy, and chemical bonding of the neutral substrates raises the possibility that isomerization may occur in the collision complex through spin-forbidden processes. This is an area that needs to be explored in more details as a function of the nature of the neutral reagent and is presently under investigation.

The main conclusions from our experimental results regarding the thioethoxy cation find strong and important theoretical support in the calculations described below.

5. Theoretical Results and Discussion

Theoretical Calculations: Structure and Energetics of $[C_2H_5S]^+$ Ions. The recent ab initio calculations at the G2 level for different isomeric $[C_2H_5S]^+$ structures, and the transition states connecting some of the ionic species in the singlet state, are probably a reliable guide for the thermochemical characterization of the different species.[19b] The results obtained in that

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(47) Dunbar, R. C.; Shen, J.; Melby, E.; Olah, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7200.

(48) For a very recent discussion on this point, see: Irikura, K. K. *J. Am. Chem. Soc.* **1999**, *121*, 7689.

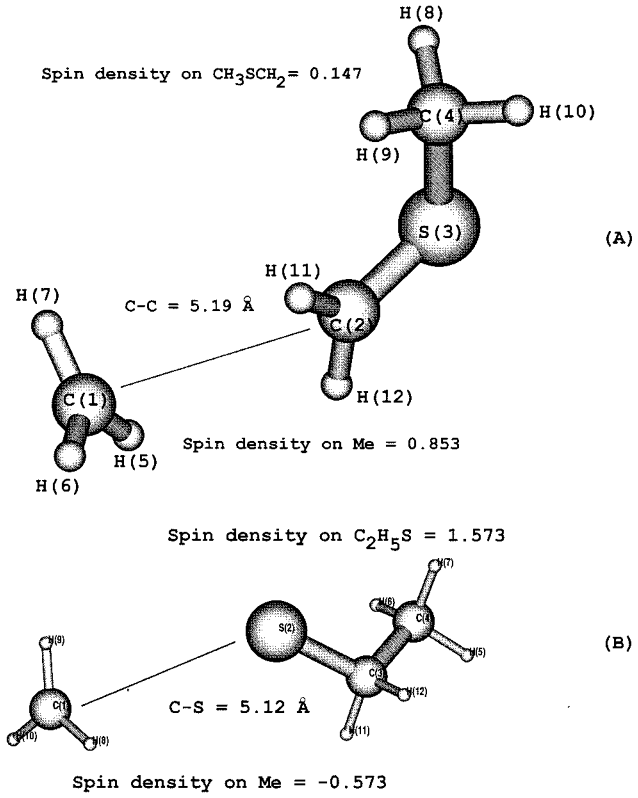

Figure 2. (a) Calculated total spin density of the nascent fragments resulting from carbon−carbon cleavage of the molecular ion of MeSEt. (b) Calculated total spin density of the nascent fragments resulting from sulfur−methyl carbon cleavage of the molecular ion of MeSEt.

study showed that the thioethoxy cation, structure **4**, is only stable in the triplet state. Our own calculations at the B3LYP/6-311G(3df,3pd)//B3LYP/6-31G(d) level yield very similar results with the triplet thioethoxy cation, **4**, calculated 41 kcal mol^{-1} above **2**, while isomers **1** and **3** are predicted to lie 3.8 kcal mol^{-1} above **2**. Thus, the general picture obtained from different levels of ab initio calculations is quite consistent with regard to the structure and stability of the different ions.

A second aspect that was also investigated concerns the fragmentation process of the molecular ion of MeSEt: What are the expected nascent structures from cleavage of the carbon−carbon bond and of the methyl carbon−sulfur bond? To address this question, calculations were carried out at the B3LYP/6-31G(d) level along the two bond cleavage fragmentation processes of the molecular ion $CH_3SCH_2CH_3]^{+\bullet}$:

(i) The first set of calculations involved single-point calculations as a function of increasing carbon−carbon distance along the cleavage $[CH_3SCH_2\text{---}CH_3]^{+\bullet}$. At a C−C distance of 5.19 Å, the energy of the system is 1.999 eV above the calculated energy of the molecular ion and has reached a stage where the energy varies very slowly upon further separation of the fragments. Figure 2a shows a qualitative picture of this structure with the total spin densities calculated for each moiety. It is clear that the nascent sulfonium ion displays a distinct singlet state character.[49]

(ii) The same type of calculations for the dissociation resulting from the cleavage of $[CH_3{-}SCH_2CH_3]^{+\bullet}$ is shown in Figure 2b for a C−S bond distance of 5.12 Å and an energy of 2.889 eV above the molecular ion. The most noticeable result of this calculation is the fact that the nascent $CH_3CH_2S^+$ displays a positive spin density of 1.57 and a very clear tendency to form a triplet state ion.[49]

Thus, calculations along the dissociation path of the molecular ion $CH_3SCH_2CH_3]^{+\bullet}$ predict the likelihood that triplet state thioethoxy cations can be generated in our experiments. A correlation diagram of the electronic states[50] of $CH_3SCH_2CH_3]^{+\bullet}$ reinforces this idea. The ground state of this ion arises from removal of a nonbonding sulfur p electron from neutral $CH_3SCH_2CH_3$ resulting in a ground-state wave function of A″ symmetry (assuming C_s symmetry for the ion). Formation of the nascent $CH_3CH_2S^+$ ion by cleavage of the sulfur−methyl bond requires an antisymmetric spatial part of the wave function with a totally symmetric spin wave function and thus this dissociation correlates with the triplet state of the $CH_3CH_2S^+$ ion. By comparison, the second electronic state of the molecular ion (∼11.3 eV above the ground neutral species)[50] corresponding to removal essentially of a 3s electron from S is of A′ symmetry and thus expected to yield singlet ions by dissociation of the sulfur−methyl bond.

Lifetime and Unimolecular Dissociation of Triplet $CH_2CH_2S^+$. While the ab initio calculations support the existence of a stable triplet thioethoxy cation and its likely formation upon fragmentation of the molecular ion of $MeSEt^{+\bullet}$, a key question is whether the lifetime of such a species is long enough for experimental observation in the time scale of FT-ICR experiments. Thus, establishing the possible pathways for isomerization and/or dissociation along more than a single energy surface is necessary to understand all the likely mechanisms for spin-forbidden processes. The importance of these spin-forbidden processes in the unimolecular decay of the methoxy cation is a good example of this type of problem.[40]

Thus, the initial calculations were directed to find the possible pathways for fragmentation and isomerization of the triplet thioethoxy cation. Unlike some of the singlet species for which fragmentation pathways have been previously reported,[51] this problem has not been explored. As reported in the computational details, we have addressed this problem at three different levels of theory to compare with the G2 literature data.[18,51] This initial investigation was necessary to test the reliability of the methods for subsequently locating the crossing points as described below.

Table 3 lists the five possible decomposition channels for low-energy triplet thioethoxy cations predicted to be exothermic or essentially thermoneutral by the G2 calculations. All the other conceivable adiabatic or nonadiabatic unimolecular pathways are strongly endothermic at the same level of theory and were therefore ignored in our kinetic investigation. Table 3 also lists the results obtained by us at different levels of theory.[52] A comparison of our results with the G2 data reveals a satisfactory and rather homogeneous agreement at all the different levels of theory with an average error not exceeding the 8 kcal mol^{-1} of the B3LYP approach. Therefore, since no single approach shown in Table 3 reveals itself as the most reliable method, the corresponding MECPs were located at all three different levels of theory. The resulting general potential energy diagram is shown in Figure 3 while the MECPs geometries are displayed in Figure 4 and the structural features reported in Table 4.

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(49) The individual atomic spin densities are available from the authors upon request.

(50) For an orbital description of the photoelectron spectrum of the related CH_3SCH_3, see: Aue, D. H.; Webb, H. M.; Davidson, W. R.; Vidal, M.; Bowers, M. T.; Goldwhite, H.; Vertal, L. E.; Douglas, J. E.; Kollman, P. A.; Kenyon, G. L. *J. Am. Chem. Soc.* **1980**, *102*, 5151.

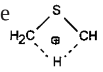
(51) (a) Chiu, S.-W.; Cheung, Y.-S.; Ma, N. L.; Lee, W.-K.; Ng, C. Y. *J. Mol. Struct. (THEOCHEM)* **1999**, *468*, 21. (b) Chiu, S.-W.; Lau, K.-C.; Li, W.-K.; Ma, N. L.; Cheung, Y.-S.; Ng, C. Y. *J. Mol. Struct. (THEOCHEM)* **1999**, *490*, 109.

(52) Optimized geometries and harmonic frequencies of all the species are available from the authors upon request.

Table 3. Calculated Thermochemistry for Dissociation and Isomerization Pathways of Triplet $C_2H_5S^+$ Cations (at 0 K and in kcal mol^{-1})

reaction	G2	MP2/6-31G(d)	B3LYP/6-31G(d)	CCSD(T)/6311+G(p,d)//B3LYP/6-31G(d)
(1) triplet $C_2H_5S^+ \rightarrow$ singlet CH_3CHSH^+ spin forbidden 1,2 H shift	−38	−38	−36	−36
(2) triplet $C_2H_5S^+ \rightarrow$ singlet $CH_3CS^+ + H_2$ α−α H_2 elimination	−25	−26	−17	−20
(3) triplet $C_2H_5S^+ \rightarrow CH_4 +$ singlet HCS^+ elimination of methane	−11	−7	0	−6
(4) triplet $C_2H_5S^+ \rightarrow$ singlet $[H_2C(H)CH_2]S$ (structure **11** of ref 16b corresponding to a bridged C_{2v} structure[a]	0	+11	+9	+8
(5) triplet $C_2H_5S^+ \rightarrow$ singlet $CH_3SCH_2^+$	−36	−30	−33	−32

[a] This ion corresponds to the structure



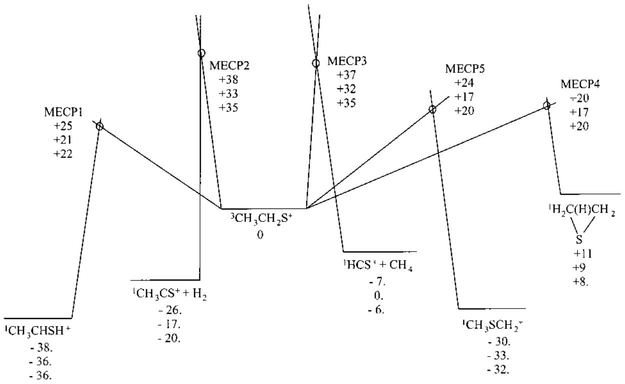


Figure 3. Calculated potential energy surface for the unimolecular decomposition of the triplet $C_2H_5S^+$ at 0 K. The values refer to the energy differences calculated respectively at the following levels: MP2-(full)/6-31G(d), B3LYP/6-31G(d), and CCSD(T)/6-311+G(p,d)//B3LYP/6-31G(d).

The picture that clearly emerges from these calculations is that all of the crossing points, just as in the previous similar case of the CH_3S^+ ion,[27] are rather high in energy at all levels of theory. These findings qualitatively imply that the triplet thioethoxy cation at a low level of internal energy would not be expected to undergo unimolecular decay very easily. A more quantitative analysis of the problem, as indicated in the computational details, was subsequently carried out within the context of the nonadiabatic RRKM theory using the CCSD(T) results. Table 5 reports the MECPs harmonic frequencies, moments of inertia, and spin−orbit coupling root-mean-sqaure values used in these calculations.

Rate constants were calculated for the five channels (see Table 3) following the procedure outlined above as a function of the internal energy and rotational excitation of the ion. The calculated unimolecular rate constants for each channel are displayed in Figure 5 for various values of *J*, while the total calculated unimolecular rate constant for $J = 0$ at 300 K is shown in Figure 6.

The results of these calculations clearly point out that triplet $CH_3CH_2S^+$ ions with low internal energies (less than 10 kcal mol^{-1}) and at any level of rotational excitation are expected to

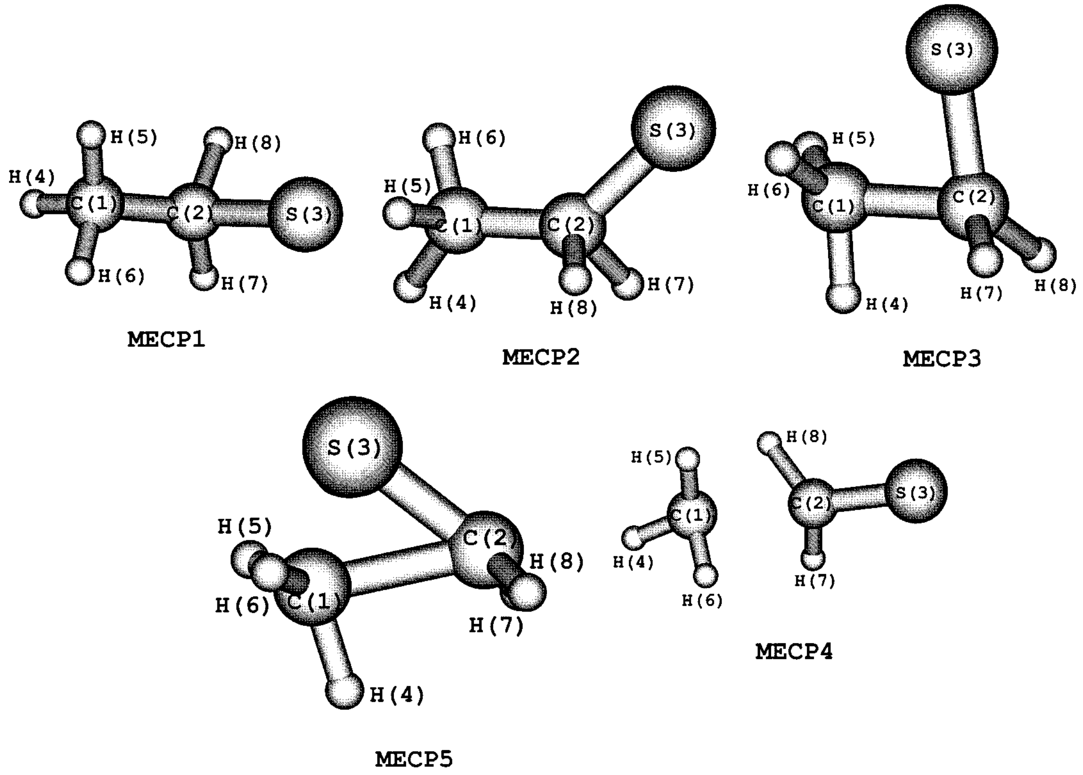


Figure 4. Geometry of the different MECPs for the exothermic and near-thermoneutral isomerization of triplet $C_2H_5S^+$. Geometric parameters are shown in Table 4.

Table 4. Geometric Parameters of the Minimum Energy Crossing Points Obtained at the Indicated Level of Theory (M = MP2(full)/6-31G(d), B = B3LYP/6-31G(d), CB = CCSD(T)/6-311+G(p,d)//B3LYP/6-31G(d))[a]

	MECP1			MECP2			MECP3			MECP4			MECP5		
	M	B	CB	M	B	CB	M	B	CB	M	B	CB	M	B	CB
R12	1.504	1.508	1.508	1.496	1.494	1.494	1.662	1.668	1.666	1.73	1.79	1.74	2.707	2.77	2.768
R23	1.701	1.717	1.72	1.639	1.648	1.648	1.697	1.714	1.714	1.64	1.641	1.644	1.715	1.721	1.715
R14	1.09	1.09	1.09	1.091	1.091	1.09	1.102	1.108	1.107	1.09	1.09	1.087	1.09	1.09	1.09
R15	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.089	1.089	1.09	1.09	1.09	1.09	1.09	1.09
R16	1.09	1.09	1.09	1.09	1.09	1.09	1.089	1.089	1.089	1.09	1.09	1.09	1.09	1.09	1.09
R27	1.095	1.09	1.098	1.173	1.175	1.175	1.09	1.091	1.091	1.087	1.089	1.089	1.09	1.09	1.09
R28	1.214	1.214	1.219	1.178	1.178	1.178	1.089	1.091	1.09	1.137	1.136	1.14	1.09	1.09	1.09
A321	123.6	122.5	123.5	128.3	130.1	129.0	85.3	85.2	85.3	121.5	121.2	121.6	38.5	40.1	40.8
A412	110.2	111.0	111.4	112.4	112.5	112.7	92.3	93.3	92.8	103.6	102.2	103.5	71.5	72.1	71.7
A512	111.9	110.6	111.5	107.8	110.2	110.3	116.2	116.2	116.2	115.1	114.5	114.8	123.0	123.6	122.5
A612	107.7	108.8	111.5	108.0	109.1	108.3	114.8	114.7	114.8	99.1	97.9	98.8	122.0	121.6	121.8
A723	114.7	115.1	113.8	110.0	108.9	109.6	107.8	117.2	117.3	109.9	108.0	109.7	118.5	119.1	119.1
A823	72.6	73.2	72.6	105.1	104.8	104.9	108.4	116.9	117.0	66.0	65.0	66.0	118.5	118.5	119.4
D4123	158.5	177.3	159.4	164.9	165.9	165.3	176.1	175.8	175.9	−175.4	−173.4	−175.8	178.1	179.5	177.8
D5123	35.7	54.8	35.9	−73.2	−73.2	−73.1	64.8	64.8	64.9	60.7	62.7	60.1	74.6	74.7	73.7
D6123	−84.0	−62.6	−83.1	44.4	43.7	43.9	−71.4	−71.6	−71.6	−58.0	−56.0	−57.0	−78.0	−75.7	−76.1
D7231	−158.7	−161.2	−157.6	149.9	150.2	149.7	−66.6	−108.3	−108.1	−23.1	−146.8	−149.4	96.9	94.8	96.4
D8231	102.6	101.4	100.82	−148.4	−147.3	−148.0	59.0	109.1	108.8	88.0	72.3	72.1	−76.8	−80.1	−79.2

[a] Distances (*R*) are in angstroms and angles (*A*) and dihedrals (*D*) are in degrees.

Table 5. B3LYP/6-31G(d) Harmonic Frequencies[a] (cm^{-1}), Moments of Inertia[b] (GHz),and S.O.C. rms (cm^{-1}) Calculated in Correspondence to the MECPs Located at the CCSD(T)/6-311+G(p,d)//B3LYP/6-31G(d) Level of Theory

$C_2H_5S^+$	MECP1	MECP2	MECP3	MECP4	MECP5
frequencies (cm^{-1})					
204	66	90	80	99	120
259	215	101	266	487	276
673	250	431	411	797	483
702	671	746	749	873	608
881	740	869	944	941	779
981	1012	940	1021	1037	820
992	1067	1089	1096	1174	834
1194	1174	1127	1170	1189	1008
1238	1310	1349	1391	1339	1322
1373	1408	1472	1419	1427	1363
1422	1455	1520	1492	1508	1425
1488	1477	1523	1502	1525	1439
1512	1946	2481	2692	3028	3000
2971	2848	2539	3132	3150	3105
3014	3064	3121	3251	3250	3127
3078	3125	3218	3261	3276	3203
3162	3174	3244	3299	3282	3259
3186					
moments of inertia (GHz)					
32	39	40	37	22	20
5	5	5	5	8	7
5	5	5	5	7	7
S.O.C. (cm^{-1})					
	105.0	93.0	100.0	117.0	90.0

[a] The frequencies below 150 cm^{-1} have been considered as free rotors. [b] All the species have been treated as symmetric top rotors.

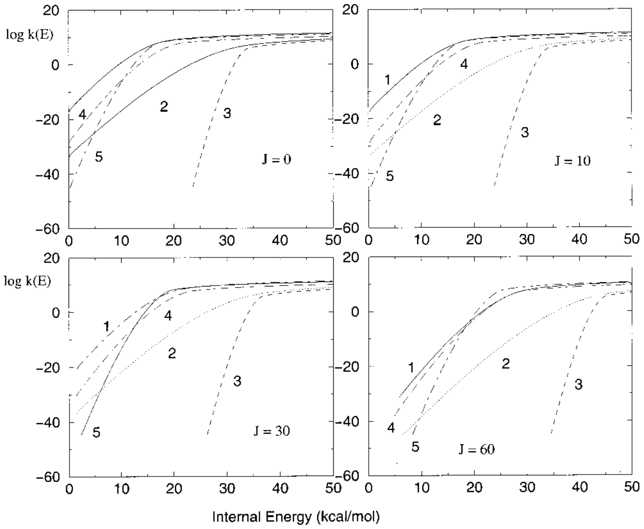


Figure 5. Calculated unimolecular rate constants for the pathways shown in Table 3 plotted as log *k* vs ion internal energy and for different levels of rotational excitation.

be very long-lived species. Thus, it is expected that triplet state $CH_3CH_2S^+$ ions can be observed within the time scale of ion cyclotron resonance experiments. The results displayed in Figure 5 also illustrate that as the internal energy of the ions increases the most important channel will be isomerization to CH_3CHSH^+ (pathway 1 in Table 3). This has an important bearing on the results displayed in Table 2. At the highest ionization energies, and subsequently higher ion internal energies, it is expected that a larger fraction of the triplet $CH_3CH_2S^+$ ions will undergo isomerization to CH_3CHSH^+ prior to being sampled in the time scale of ion cyclotron resonance experiments. This is exactly what is observed at 70 eV where the surviving triplet $CH_3CH_2S^+$ ions only amount to approximately 5%. Furthermore, these lifetime calculations predict that metastable studies and collisional activation of triplet $C_2H_5S^+$ will be similar and indistinguishable from that observed for ion **2** as reported in earlier studies.[7a,9a] At internal energies above 15 kcal mol^{-1} pathways 4 and 5 can also become increasingly important while direct methane elimination is predicted to be a minor channel even at high internal energies.

Summary of Theoretical Results. The theoretical calculations support the idea that triplet thioethoxy cations are likely to be formed upon cleavage of the sulfur−methyl carbon bond of the molecular ion of methyl ethyl sulfide. Furthermore, the identification of the possible spin-forbidden isomerization and dissociation processes and an analysis of the unimolecular rate constants for these different channels predict that triplet thioethoxy cations should be long-lived at low levels of internal energies. Thus, these predictions are very consistent with our observations carried out at low energies and with a time-resolved technique such as ion cyclotron resonance mass spectrometry that allows for ion trapping during several seconds.

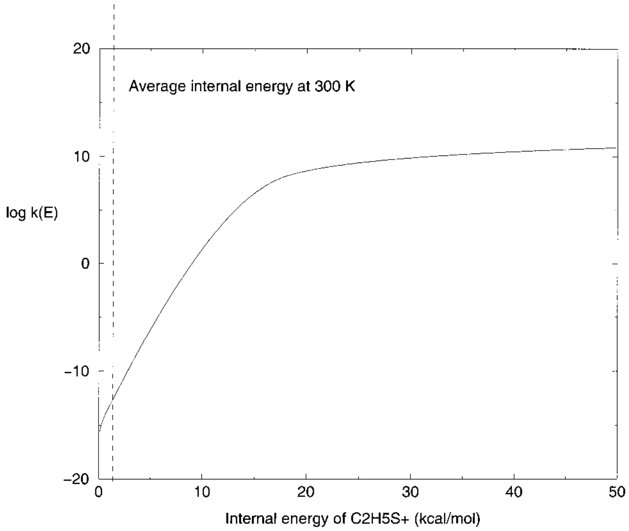


Figure 6. Total unimolecular rate constant for triplet $C_2H_5S^+$ ions at 300 K for $J = 0$.

Conclusions

The ion/molecule reactions observed for $[C_2H_5S]^+$ ions obtained from MeSEt are indicative that a significant fraction of ions originating from the methyl carbon−sulfur bond cleavage retain the triplet thioethoxy structure. The main evidence relies on the ability of these ions to promote charge-transfer reactions with neutral substrates of ionization energies less than 8.8 eV.

Ab initio calculations at different levels of theory consistently predict that the $CH_3CH_2S^+$ structure is only stable in the triplet state lying considerably above the most stable singlet structures of $[C_2H_5S]^+$ ions. Lifetime calculations for triplet thioethoxy cations show that at low internal energies these ions are long-lived and thus provide strong support for the experimental observations.

The present approach suggests the possibility that other triplet thioalkoxy cations may display similar behavior. Furthermore, the present study paves the way for a more careful study of fragment ions obtained from sulfur-containing compounds by ion cyclotron resonance techniques.

Finally, the fate of triplet thioethoxy cations in the absence of exothermic charge-transfer channel remains a very interesting problem from the experimental and theoretical point of view.

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