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C_2H_2S radical cations: Application of tandem mass spectrometry methodologies☆

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Abstract

Attempts have been made to characterize ionic and neutral $C_2H_2S^{\bullet+/o}$ isomers, *viz.*, thioketene ($\mathbf{1}^{\bullet+}$), ethynylthiol ($\mathbf{2}^{\bullet+}$), and thiirene ($\mathbf{3}^{\bullet+}$) using various tandem mass spectrometric methodologies. Dissociative electron ionization of thiophene, 1-propane thiol and thiirane were used to produce the $C_2H_2S^{\bullet+}$ (*m/z* 58) ions. The collisional activation (CA) mass spectrum of *m/z* 58 ions from thiophene is highly compatible with thioketene ions which has been supported by the CA mass spectrum of metastably generated *m/z* 58 ions and by comparison with the previously reported CA mass spectrum of thioketene ions. Theoretical calculations at the B3LYP/6-311G(d,p), and G2/G2(MP2) levels predict that low energy thioketene ions equilibrate with other isomeric ions *viz.*, ethynylthiol and thiirene prior to dissociation by loss of $H^\bullet$ (*m/z* 57) and $CH^\bullet$ (*m/z* 45). The CA spectra of $C_2H_2S^{\bullet+}$ ions from 1-propane thiol and thiirane are nearly identical indicating a facile isomerization of the initial structures at energies lower than the dissociative threshold. The low energy CID spectra of the *m/z* 58 ions from three precursors are found to be similar. However, significant differences are noticed in the relative abundances of product ions in the NR spectra of *m/z* 58 ions from the three precursors. While the NR mass spectra of *m/z* 58 ions from thiophene and thiirane confirms the stability of thioketene neutrals, the NR spectra of *m/z* 58 ions from 1-propane thiol suggests formation of a mixture of ethynylthiol and thioketene ions. Calculations predict a different thermo-chemistry for $\mathbf{1}^{\bullet+}$–$\mathbf{3}^{\bullet+}$, but, due to a mixture of reacting isomeric ions whatever the precursor molecule is, similar results were obtained for the associative ion/molecule reactions between the $C_2H_2S^{\bullet+}$ ions with methylisocyanide.

Keywords: Thioketene; Ethynylthiol; Thiirene; Tandem mass spectrometry; Computational chemistry

1. Introduction

The formation and characterization of C_2H_2S isomers has been frequently reported in the past; these works mainly concerned with identification of reactive molecules [1] such as thioketene **1**, ethynylthiol **2**, or also thiirene **3** (Scheme 1). The preparation of these target molecules, defined as reactive intermediates, inevitably requires matrix isolation procedures after flash-vacuum pyrolysis (FVP) [2] or photolysis of suitable precursors.

Contrasting with the abundant literature concerning the *neutral* molecules shown in Scheme 1, the corresponding *radical cations* have only been scarcely described [3–5]. In particular, recent methods of tandem mass spectrometry have not been systematically applied to these radical cations. Collisional activation techniques will be used in the present work together with associative ion/molecule reactions in order to try the characterization of the $C_2H_2S^{\bullet+}$ isomers $\mathbf{1}$–$\mathbf{3}^{\bullet+}$. The experimental results will also be supported by quantum chemical calculations in order to evaluate the structures, relative energies, and the potential dissociation products of the different ions under investigation, as well as the transition states connecting them.

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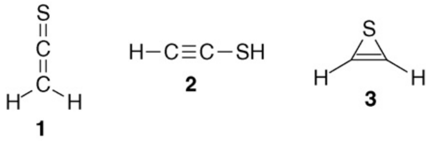
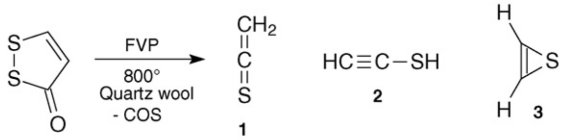


Scheme 1.



Scheme 2.

2. Experimental

The spectra were recorded on a hybrid tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of $cE_1B_1cE_2ccE_3B_2cE_4$ geometry (E_i stands for electric sector, B_i for magnetic sector, and c for conventional collision cells) and on a trisector mass spectrometer (Micromass AutoSpec M, Manchester) of $cE_1B_1ccE_2$ geometry. Typical conditions have been reported elsewhere [6–8]. Recently, an RF-only hexapole collision cell (H_{cell}) has been installed inside the six-sector instrument between E_2 and E_3. This cell allows, *inter alia*, the study of associative ion/molecule. Briefly, the experiments utilizing the hexapole consist of the selection of a beam of fast ions (8 keV) with the three first sectors ($E_1B_1E_2$), the deceleration of these ions to approximately 5 eV kinetic energy. The interaction between the ions and the reagent gas is thereafter realized in the H_{cell} and, after re-acceleration at 8 keV, all the ions generated in the hexapole are separated and mass measured by scanning the field of the second magnet. The high-energy collisional activation (CA) spectra of mass-selected ions generated in the H_{cell} can be recorded by scanning the field of E_4 after selection of the ions with E_3 and B_2.

The details of the neutralization–reionization (NR) experiments have been reported previously [8]. The elimination of un-reacted ions was performed by deflection along the *z*-axis.

Thiophene, 1-propane thiol, and thiirane were commercially available (Aldrich) and used without any further purification.

Structures and energies of the C_2H_2S ions (and neutrals) pertinent to this study, connecting transition states and dissociation products were probed by density functional methods B3LYP/6-311G(d,p) [9] and, for comparison, we also used ab initio methods G2 [10] and G2(MP2) [11] as implemented in Gaussian 03w [12]. Stationary points were characterized as either minima (all real frequencies) or transition structures (one imaginary frequency) by calculation of the frequencies using analytical gradient procedure. The minima connected by given transition structures were confirmed by intrinsic reaction coordinate (IRC) calculations. The calculated frequencies were also used to determine zero-point vibrational energies, which were used as a zero-point correction for the electronic energies. Spin unrestricted calculations were used for all open shell systems and the spin contamination was not found to be high (0.75–0.76) for doublets.

3. Results and discussion

Flash-vacuum pyrolysis (FVP) of the dithiol-3-one shown in Scheme 2 produces thioketene **1** in the gas phase as indicated [13] by two independent experiments: (1) FVP/MS which confirms the molecular mass and the composition and (2) FVP/IR which clearly indicates the presence of the ketene connectivity. These combined pieces of information strongly support the data shown in Scheme 2.

The data of the FVP/MS/MS method applied to the *m/z* 58 ions were nevertheless not straightforward as an intense signal at *m/z* 45 (thioformyl cation) was seen in the collisional activation (CA) spectrum. This observation requires the production in the gas phase of another neutral C_2H_2S isomer or the occurrence of a post-collisional isomerization process after ionization of thioketene. Most probable candidates are of course ethynylthiol **2** and thiirene **3** (neutral or ionized).

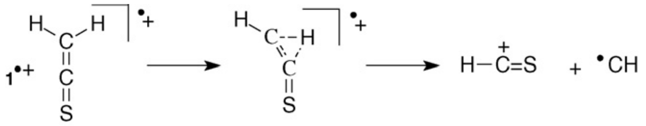
4. Collisional activation mass spectrometry

The CA spectrum of the *m/z* 58 ions generated by dissociative ionization of thiophene (loss of ethyne) is completely identical to the spectrum obtained after direct ionization of the pyrolyzate as described in Scheme 2 (see Fig. 1a). The loss of 13 amu (*m/z* 45) corresponds to the loss of a carbyne ($HC^{\bullet}$) for which a heat of formation of 596 kJ mol^{-1} has been reported in the literature [14]. The reported heat of formation of the ionized product, namely the thioformyl cation, amounts to 1018 kJ mol^{-1} [14].

Using a calculated (*vide infra*) heat of formation of 1063 kJ mol^{-1} for ionized thioketene, this fragmentation which is likely to proceed by a [1,2] hydrogen shift as suggested in Scheme 3, is therefore endothermic by 551 kJ mol^{-1} (even more if one considers the reported [14] 1011 kJ mol^{-1} value for $\mathbf{1}^{\bullet+}$).

This endothermicity is definitively higher than the isomerization barriers calculated (*vide infra*) to amount to 451 kJ mol^{-1} and 390 kJ mol^{-1} for the $\mathbf{1}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}$ and $\mathbf{1}^{\bullet+} \rightarrow \mathbf{3}^{\bullet+}$ processes. In other words, if *m/z* 45 is present in the CA spectrum of ionized thioketene, its equilibration with the isomeric ionized species is certainly feasible prior to the fragmentation.

Actually, the $HC^{\bullet}$ loss does not dominate the CA spectrum (Fig. 1) of ionized thioketene but instead the loss of $H^{\bullet}$. Using the following heat of formations, 1063 kJ mol^{-1} for ionized thioketene, 218 kJ mol^{-1} for the hydrogen atom [14] and 1286 kJ mol^{-1} for *C*-protonated di carbon sulfide $HC^{+}{=}C{=}S$ [15]. An endothermicity of 441 kJ mol^{-1} is readily estimated, such a value is again higher (but to a lesser extent) than the isomerization critical energies. Further confirmation that the loss of $H^{\bullet}$ is the lowest energy demanding reaction is also confirmed by



Scheme 3.

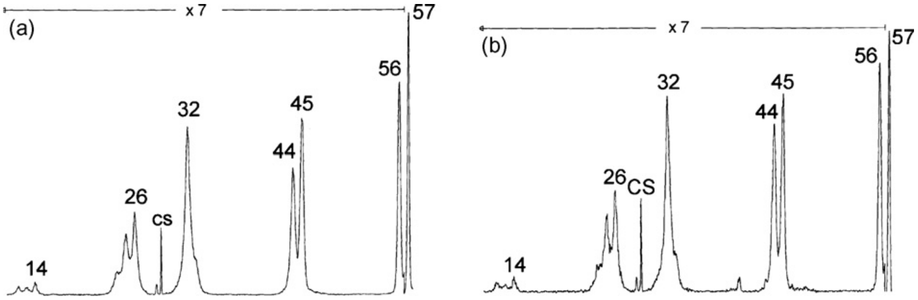


Fig. 1. (a) CA mass spectrum of the source generated *m*/*z* 58 ions from thiophene and (b) CA mass spectrum of metastably generated *m*/*z* 58 ions of thiophene. CS refers to charge stripping.

the fact that it is the lone reaction of *metastable* thioketene ions. The kinetic energy release measured for the peak at *m*/*z* 57 at half maximum $T_{0.5}$ is, for thioketene 100 meV (9.6 kJ mol^{-1}) [16]. It is also worthy of note that the CA spectrum of the metastably generated *m*/*z* 58 ions is perfectly superimposable to the corresponding spectrum of the source generated ions (Fig. 1b). All these results indicate that the majority of the $C_2H_2S^{\bullet+}$ ions from thiophene possess the thermodynamically more stable thioketene connectivity and a portion of ions equilibrate with isomeric structures ethynylthiol and thiirene prior to dissociation by loss of H$^\bullet$ and CH$^\bullet$.

$C_2H_2S^{\bullet+}$ ions are also generated by dissociative ionization of 1-propane thiol ($CH_3CH_2CH_2SH$, losses of CH_4 and H_2) and thiirane (cyclic CH_2SCH_2, loss of H_2). The CA spectra shown in Fig. 2 are nearly identical to the spectrum of thioketene ions suggesting again facile isomerization of the initial structures at energies lower than the dissociation threshold. This is inline with similar $T_{0.5}$ values, 8 meV (0.75 kJ mol^{-1}) and 10 meV (0.96 kJ mol^{-1}) obtained for H$^\bullet$ loss from *m*/*z* 58 ethynylthiol and thiirene ions. Given the fact that, according to the Massey's adiabatic criterion [17], high-energy collisional activation samples preferentially the higher energy species within the global population of "stable" ions, the observation of nearly identical spectra starting with the three different precursors is really not unexpected. In this situation, high-energy collisional activation does not allow a clear-cut C_2H_2S isomer differentiation. Therefore, we have turned to use alternative tandem mass spectrometry methodologies such as (1) collision induced dissociations (CID) in the low translational energy regime, (2) neutralization–reionization experiments and (3) associative ion/molecule reactions. Experiments (1) and (3) require the use of the sector mass spectrometer in its hybrid configuration (see Section 2), while experiment (2) is expected to be more informative on the actual structures than conventional CA. Actually, as a higher energy deposition in the ions is usually observed in NRMS [18], less discrimination towards isomeric ions differing in internal energy contents is expected.

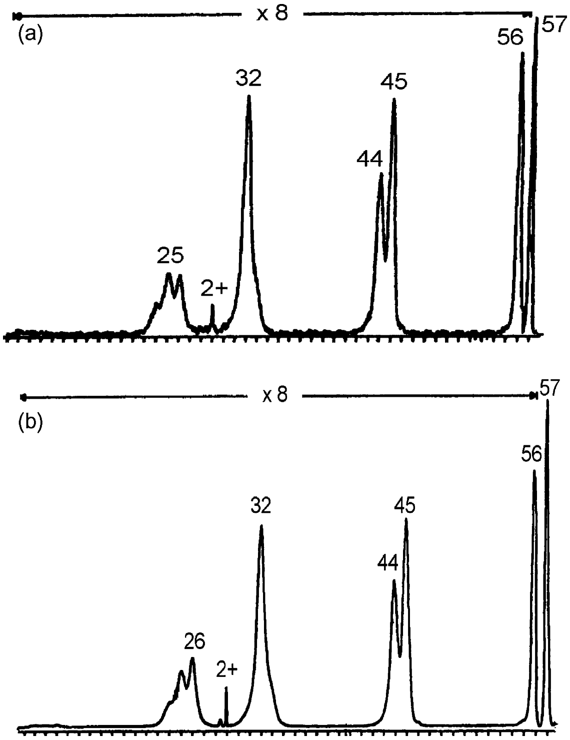


Fig. 2. CA mass spectra of the *m*/*z* 58 ions generated by dissociative ionization of 1-propane thiol (a) and thiirane (b).

5. Collision induced dissociations (low energy collision regime)

It has been reported in some instances that the CID spectra obtained in the low kinetic energy regime may complement the high kinetic energy results [19]. The spectrometer of the Mons' laboratory in its hybrid configuration is appropriate for performing this kind of experiments. Using argon as the collision gas, the CID spectra of the *m*/*z* 58 ions are nevertheless found deceptively simple featuring only two fragmentations, the loss of H$^\bullet$ (*m*/*z* 57) and the loss of C_2H_2 (*m*/*z* 32). Moreover, branching ratios (*m*/*z* 57):(*m*/*z* 32) are found nearly identical whatever the nature of the precursor: 2.3 for thiophene, 1.9 for 1-propane thiol, and 2.4 for thiirane.

6. Neutralization–reionization experiments

Neutralization–reionization mass spectra (NRMS [20]) are shown in Fig. 3. Compared to the conventional CA spectra (see Figs. 1 and 2), more significant differences are detected, but again, these differences concern relative intensities of peaks,

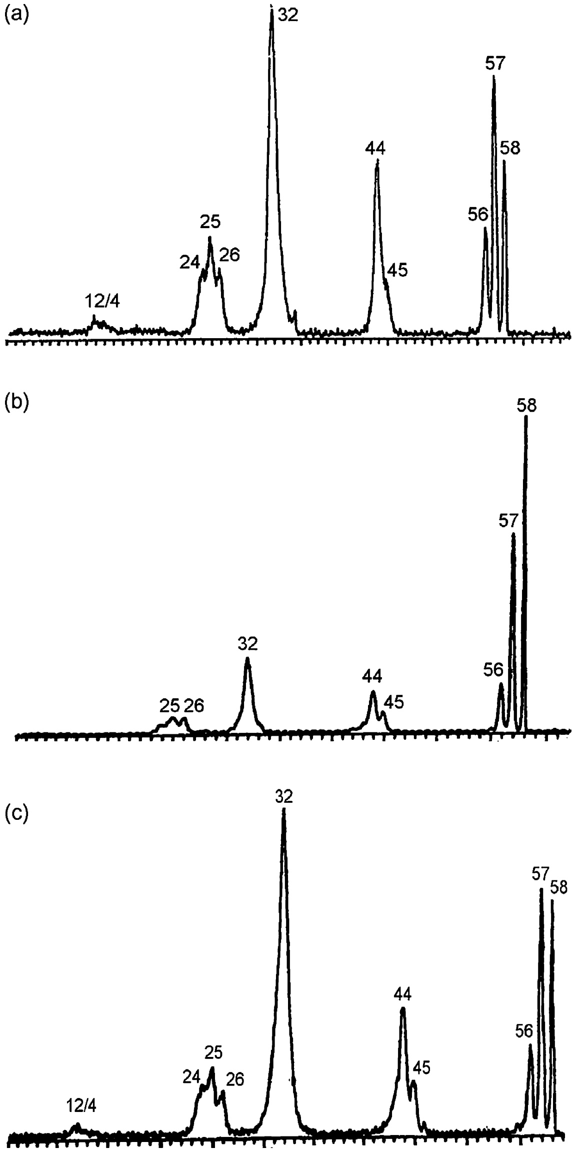


Fig. 3. NR (Xe/O_2) spectra of the m/z 58 ions generated from thiophene (a), 1-propane thiol (b), and thiirane (c).

and no tell-tale peaks appeared. As already mentioned before, it is generally accepted [18] that, upon NR, more internal energy is deposited in the ions and in such situations one may expect a marked preference for simple bond cleavage reactions and a better sampling of all the "stable" ions. Compared to the CA spectrum, one assists in the NR spectrum shown in Fig. 3a to an inversion of the m/z 45/m/z 44 abundance ratio and a base peak appearing now at m/z 32. The peak at m/z 58 attests that a neutral molecule of composition C_2H_2S has survived the neutralization reaction for at least a fraction of a microsecond, that is the flight time before re-ionization. We interpret these data on the basis of a *preferential* production of thioketene ions upon dissociative ionization of thiophene.

In the case of 1-propane thiol, the NR spectrum of the m/z 58 ions (Fig. 3b) clearly demonstrates the presence of another isomer; the recovery signal represents now the base peak of the NR spectrum and the fragmentation (similar to the previous case) is now severely reduced. Possibly, a mixture dominated by ethynyl thiol ions and thioketene ions could justify these observations. A quite favourable Franck–Condon effect associated with high dissociation energies could explain the particularly strong intensity of the recovery signal. Such considerations will be discussed later in the theoretical part.

Concerning the spectrum in Fig. 3c, it appears quite similar to the spectrum shown in Fig. 3a; the beam of m/z 58 ions generated from thiirane could therefore be mainly constituted by thioketene ions.

7. Associative ion/molecule reactions

Methyl isocyanide (CH_3NC) has been used on several occasions as an efficient reagent gas for the characterization of distonic [21] or distonoïd [22] ions in the gas phase. For instance, interaction between ionized ketene radical cations and methyl isocyanide affords two main chemical reactions: a proton transfer reaction yielding CH_3NCH^+ (m/z 42) ions and an ionized methylene transfer reaction yielding $CH_3N{=}C{=}CH_2{}^{\bullet+}$ (m/z 55) [19]. Both reactions are calculated exothermic by 16 kJ mol^{-1} and 193 kJ mol^{-1}, respectively:

$$CH_3NCH^+ \leftarrow CH_2{=}C{=}O^{\bullet+} \rightarrow CH_3N{=}C{=}CH_2{}^{\bullet+}$$

Such a behavior has of course induced the study of the reactions of the C_2H_2S radical cations with methyl isocyanide and, in fact, the two major processes found are the same, see Fig. 4a for the reactions of thioketene ions. The thermo-chemistry is nevertheless somewhat different, as the methylene transfer reaction is calculated only slightly exothermic by 7 kJ mol^{-1} and protonation is found slightly endothermic by about 8 kJ mol^{-1}. The absence of thermalisation in our experimental conditions allows indeed the occurrence of slightly endothermic processes:

$$CH_3NCH^+ \leftarrow CH_2{=}C{=}S^{\bullet+} \rightarrow CH_3N{=}C{=}CH_2{}^{\bullet+}$$

In the high mass region (>m/z 58), one observes a more complex spectrum, but signals are less intense by one order of magnitude. Possible attributions are collected in Table 1.

The formation of a "dimer" formally consists of a [2 + 1] cycloaddition reaction of a vinylidene (methyl isocyanide) on the thioketene ions producing a monoimine of cyclopropane dithione (see Scheme 4).The occurrence of such a cyclic structure (or a tautomer) justifies the presence of most of the reaction products seen in Fig. 4a and Table 1. Considering

Table 1

m/z	Possible attribution
99	A "dimer" combining the C_2H_2S radical cation and methyl isocyanide
98	Loss of $H^\bullet$ from the "dimer"
84	Loss of $CH_3{}^\bullet$ from the "dimer"
73	Methyl isothiocyanate ions and consecutive hydrogen losses
66	Loss of $HS^\bullet$ from the "dimer"
57	Collision induced dissociation
55	Ionized methylene transfer to methyl isocyanide
42	Proton transfer to methyl isocyanide

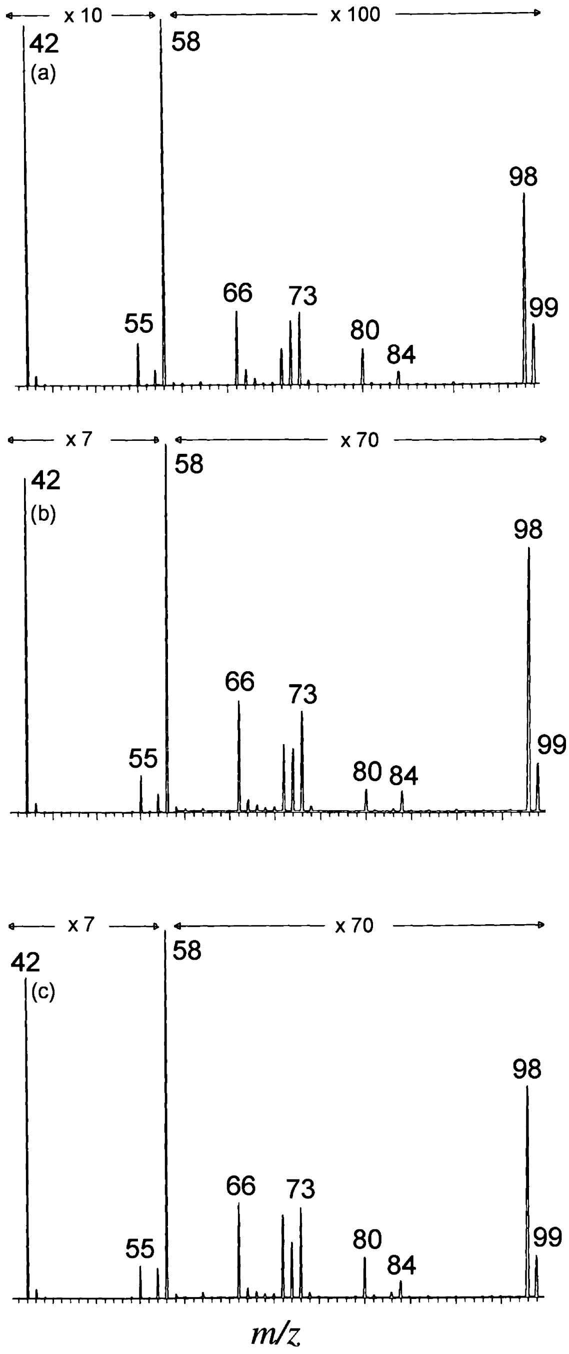


Fig. 4. Mass spectra of the ions generated in the hexapole collision cell when decelerated mass selected *m/z* 58 ions interact with methyl isocyanide. Neutral precursors: thiophene (a), 1-propane thiol (b), and thiirane (c).

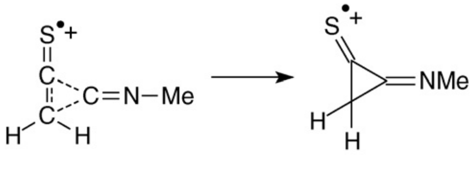
now Fig. 4b and c, it is clear that the spectra are quite similar without any significant differences. This may suggest that ethynylthiol ions or thiirene ions are not reactive towards methyl isocyanide.

8. Quantum chemical considerations

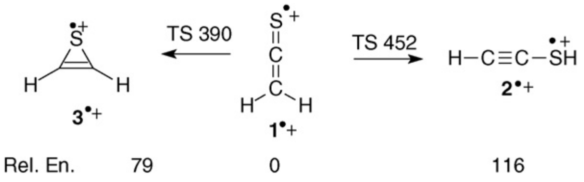
From the computational results presented in Table 2 and the potential energy diagram of Scheme 5, it follows that all three isomeric ions $\mathbf{1}^{\bullet+}$–$\mathbf{3}^{\bullet+}$ are minima on the potential energy surface. The high-energy isomers $\mathbf{4}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ are not further considered (Fig. 5). Ion $\mathbf{1}^{\bullet+}$ (thioketene ion) is the most stable species having a linear structure with C_{2v} symmetry. Ion $\mathbf{3}^{\bullet+}$ (thiirene ion) is the second most stable structure followed by $\mathbf{2}^{\bullet+}$ (ethynylthiol ion), which are less stable than $\mathbf{1}^{\bullet+}$ by 79 kJ mol^{-1}, and 116 kJ mol^{-1}, respectively. These species are separated by significant energy barrier of 311 kJ mol^{-1} (above $\mathbf{3}^{\bullet}$and 336 kJ mol^{-1} (above $\mathbf{2}^{\bullet+}$). Our G2 calculations using the atomization method also predict $\Delta_f H_0$ [23] values for the ionic $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, and $\mathbf{3}^{\bullet+}$ which are 1063 kJ mol^{-1}, 1179 kJ mol^{-1}, and 1124 kJ mol^{-1}, respectively. It should be noted that the stability order $\mathbf{1}^{\bullet+}$–$\mathbf{3}^{\bullet+}$ is in contrast to the stability order of oxygen analogues wherein ethynol radical cation, $HC{\equiv}C{-}OH^{\bullet+}$, is the second most stable isomer followed by oxirene ion, cyclic–$CH{=}CH{-}O^{\bullet+}$, which are reported to be less stable than the ketene ion, $H_2C{=}C{=}O^{\bullet+}$, by 189 kJ mol^{-1} and 257 kJ mol^{-1}, respectively [24]. However, the stability order of the isomers of selenoketene ions [8] is very much similar to that of thioketene.

Calculated dissociation energies for various fragmentation channels are also found to be in fairly good agreement with the fragment ion abundances in the CA mass spectrum (Table 2). For example, the most abundant peak in the CA mass spectra at *m/z* 57 (loss of $H^{\bullet}$), corresponds to the fragmentation channel of lowest dissociation energy. It is nevertheless worthy of note that all the calculated critical energies of dissociation are found largely higher than isomerization critical energies.

Theoretical calculations (Table 3) at the B3LYP/6-311G(d,p), G2 level of theory predict that *neutral* **1** is the global minimum with C_{2v} symmetry and stable with respect to dissociation. In contrast to the stability order of the isomeric ions, the linear isomer ethynylthiol **2** becomes the second most stable structure followed by **3** which are less stable than **1** by 80 kJ mol^{-1}, and 155 kJ mol^{-1}, respectively (Scheme 6; Fig. 6). Our G2 calculations using the atomization method also predict $\Delta_f H_0$ [23] values for the neutral **1**–**3**, which are 200 kJ mol^{-1}, 265 kJ mol^{-1}, and 342 kJ mol^{-1}, respectively. These calculations are in good



Scheme 4.



Scheme 5.

Table 2
Total (a.u.) and relative energies (kJ mol^{-1}) of [C_2, H_2, S]$^{\bullet+}$ ions calculated using various methods

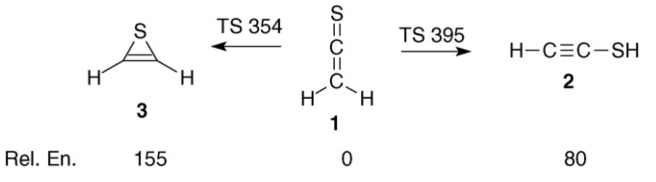
Cations	B3LYP/6-311G(d,p) (+ZPC)	B3LYP ($\Delta_f H_0$)	G2 (0 K)	G2 ($\Delta_f H_0$)	G2(MP2) (0 K)
$^{2}\mathbf{1}^{\bullet+}$ (C_{2v})	−475.248537 (0.0)	1078.2	−474.629137 (0.0)	1064.0	−474.62228 (0.0)
$^{2}\mathbf{2}^{\bullet+}$ (C_1)	−475.204266 (116.3)	1194.5	−474.5849 (115.9)	1180.3	−474.57787 (116.3)
$^{2}\mathbf{3}^{\bullet+}$ (C_1)	−475.218414 (79.0)	1157.3	−474.606049 (60.2)	1124.6	−474.59944 (59.8)
$^{2}\mathbf{4}^{\bullet+}$ *anti* (C_1)	−475.125729 (322.1)	1400.8	−474.507792 (318.4)	1382.8	−474.501282 (317.5)
$^{2}\mathbf{4}^{\bullet+}$ *syn* (C_1)	−475.123467 (328.0)	1406.6	−474.503388 (329.7)	1394.1	−474.496723 (329.3)
$^{2}\mathbf{5}^{\bullet+}$ (C_s)	−475.086074 (426.3)	1504.4	−474.454329 (458.9)	1522.9	−474.448356 (456.4)
^{2}Ts (**1–3**)$^{\bullet+}$ (C_1)	−475.099843 (390.3)	1468.5	−474.489053 (367.7)	1431.7	−474.482836 (366.1)
^{2}Ts (**1–2**)$^{\bullet+}$ (C_1)	−475.076222 (452.3)	1529.6	−474.525103 (272.8)	1337.2	−474.51808 (273.2)
^{2}Ts (**3–4**)$^{\bullet+}$ (C_1)	−475.124211 (326.3)	1404.5	−474.510602 (310.8)	1375.3	−474.504363 (309.1)
^{2}Ts (**4–5**)$^{\bullet+}$ (C_1)	−475.038799 (550.6)	1628.8	−474.413584 (565.6)	1630.8	−474.407768 (563.1)
^{2}Ts [**2–4** (*syn*)]$^{\bullet+}$ (C_1)	−475.112475 (356.8)	1435.5	−474.494339 (353.5)	1418.3	−474.487697 (353.1)
^{2}Ts [**2–4** (*anti*)]$^{\bullet+}$ (C_1)	−475.113306 (354.8)	1433.4	−474.495075 (351.8)	1539.7	−474.488372 (351.4)
$HC_2S^+ + {}^{\bullet}H$	−475.06038 (493.7)	1572.3	−474.447861 (457.3)	1540.1	−474.44101 (475.3)
$C_2S^{\bullet+} + H_2$	−475.05374 (511.2)	1589.9	−474.441225 (493.3)	1557.2	−474.43226 (498.3)
$CS^+ + {}^{\bullet}CH_2$	−474.95014 (782.8)	1861.8	−474.349819 (732.6)	1797.4	−474.34343 (731.7)
$HC_2{}^+ + {}^{\bullet}SH$	−474.90587 (899.5)	1977.7	−474.288356 (894.1)	1958.9	−474.28038 (897.4)
$HCS^+ + {}^{\bullet}CH$	−475.030465 (572.3)	1651.0	−474.424414 (536.8)	1601.6	−474.418612 (534.3)
$HC^+ + {}^{\bullet}HCS$	−474.91430 (877.3)	1956.0	−474.308682 (840.9)	1905.4	−474.30189 (841.0)
$H_2C_2{}^{\bullet+} + {}^{1}S$	−474.92041 (861.5)	1939.7	−474.310329 (836.8)	1901.2	−474.29989 (846.0)
$H_2C_2{}^{\bullet+} + {}^{3}S$	−474.98184 (281.5)	1778.6	−474.354491 (720.9)	1785.3	−474.34496 (727.6)
${}^{2}S^+ + C_2H_2$	−474.884587 (954.7)	2033.8	−474.323542 (802.0)	1866.4	−474.315865 (804.1)

Relative energies in parenthesis.

Table 3
Total (a.u.) and relative energies (kJ mol^{-1}) of [C_2, H_2, S] neutrals calculated using various methods

Neutrals	B3LYP/6-311G(d,p) (+ZPC)	B3LYP ($\Delta_f H_0$)	G2 (0 K)	G2 ($\Delta_f H_0$)	G2(MP2) (0 K)
^{1}**1** (C_{2v})	−475.57338 (0.0)	225.5	−474.958074 (0.0)	200.4	−474.95094 (0.0)
^{1}**2** (C_s)	−475.542768 (80.3)	305.8	−474.933224 (65.2)	265.7	−474.92568 (66.1)
^{1}**3** (C_s)	−475.514257 (155.2)	380.7	−474.904279 (141.0)	341.8	−474.89703 (141.4)
^{1}**4** [*anti* (C_1)]	−475.469439 (272.8)	498.3	−474.857659 (263.6)	464.0	−474.85018 (264.4)
^{1}**4** [*syn* (C_1]	−475.480670 (243.0)	469.0	−474.873311 (222.1)	423.0	−474.86671 (221.0)
^{1}**5** (C_s)	−475.413778 (418.8)	644.3	−474.808981 (391.2)	592.0	−474.80287 (388.7)
^{1}**6** (C_s)	−475.491688 (214.2)	440.1	−474.887237 (185.7)	386.6	−474.88081 (184.0)
^{1}Ts (**1–3**)(C_1)	−475.438432 (354.0)	580.0	−474.827765 (341.8)	542.6	−474.82058 (341.8)
^{1}Ts (**1–2**)(C_1)	−475.419698 (403.3)	628.8	−474.810177 (388.2)	588.6	−474.80326 (387.4)
^{1}Ts (**3–4**) (C_1)	−475.457196 (305.0)	530.5	−474.847076 (292.8)	492.0	−474.83992 (291.2)
^{1}Ts (**4–5**) (C_1)	−475.378643 (510.8)	736.8	−474.773962 (483.2)	683.6	−474.76781 (480.7)
^{1}Ts (**3–6**) (C_1)	−475.372951 (526.0)	751.8	−474.771188 (490.3)	691.1	−474.76491 (488.2)
$HC_2S^{\bullet} + {}^{\bullet}H$	−475.432792 (369.)	594.5	−474.810367 (388.2)	588.2	−474.80192 (390.7)
$C_2S^{\bullet} + H_2$	−475.402889 (447.2)	673.2	−474.794152 (430.1)	631.0	−474.78414 (437.2)
$CS^{\bullet} + {}^{\bullet}CH_2$	−475.371062 (530.5)	756.4	−474.769394 (494.6)	695.8	−474.76302 (493.3)
$HC_2{}^{\bullet} + {}^{\bullet}SH$	−475.382181 (501.6)	727.6	−74.745466 (557.7)	758.5	−474.73629 (563.1)
$HC^{\bullet} + {}^{\bullet}HCS$	−475.316761 (673.6)	899.1	−74.696805 (685.3)	886.6	−474.68874 (688.2)
${}^{1}S + C_2H_2$	−475.332429 (631.7)	858.1	−474.728252 (603.0)	803.7	−474.7178 (611.7)
${}^{3}S + C_2H_2$	−475.393857 (471.1)	697.0	−474.772414 (487.0)	687.8	−474.76287 (493.7)

Relative energies in parenthesis.



Scheme 6.

agreement with previously reported calculations of the potential energy surface of neutral thioketene and its isomers thiirene and ethynyl thiol [25]. The stability order is very much similar to those of neutral oxygen and selenium analogues, *i.e.*, isomers of selenoketene and ketene [8,26]. The high-energy barriers for interconversion of isomers from one to another suggest that neutral **1–3** are viable molecules in the rarefied gas phase.

Further support for the stability of the transient neutral species comes from an examination of the Frank–Condon effects on

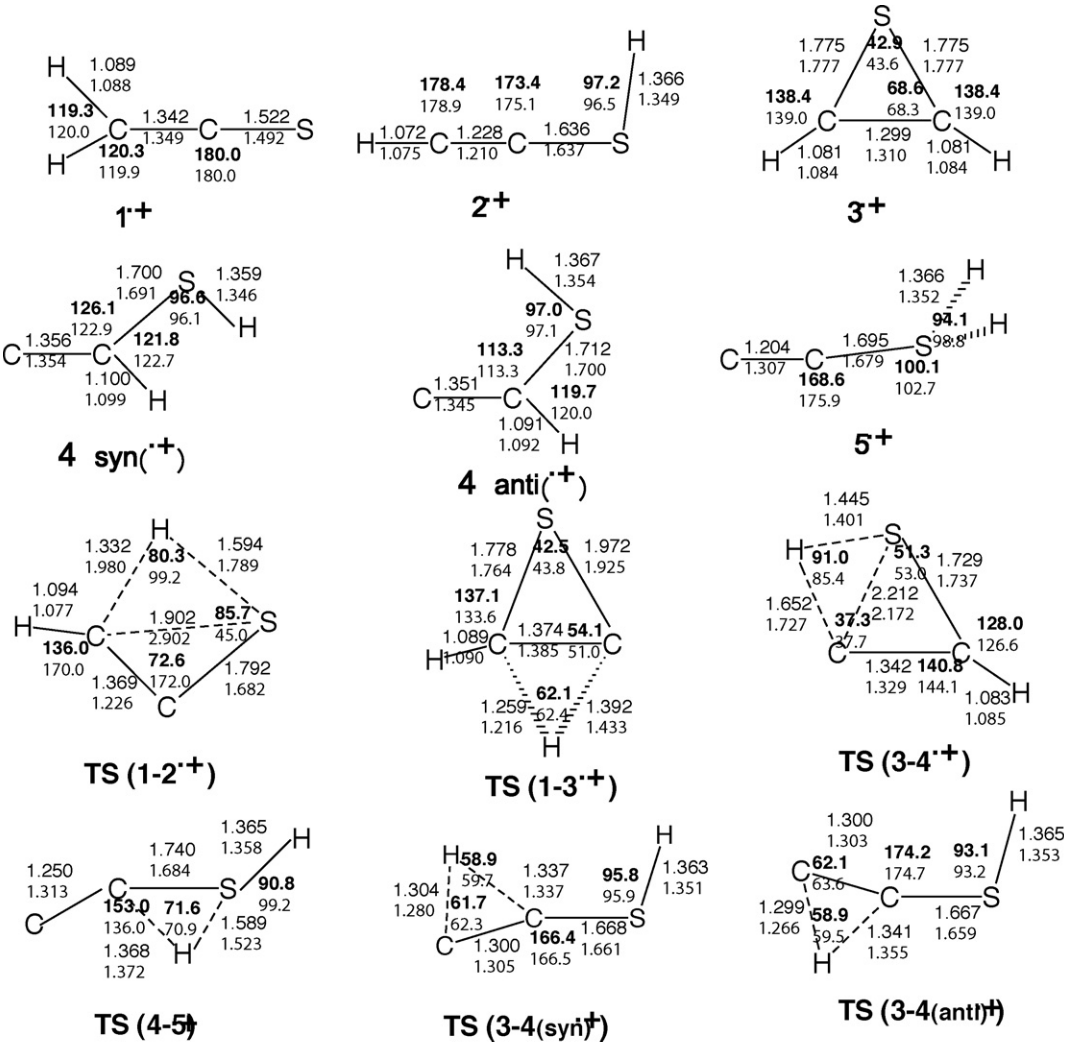


Fig. 5. Selected optimized geometries [B3LYP/6-311G(d,p)] of ionic $H_2C{=}C{=}S^{\bullet+}$ **1**$^{\bullet+}$, its isomers **2**$^{\bullet+}$–**5**$^{\bullet+}$, connecting transition states. Bond lengths in angstroms, bond angles in degrees, values in italics correspond to G2 level.

vertical electron transfer from the corresponding cations. The calculated vertical ionization of neutral **1** (IEv) is found to be only 7 kJ mol^{-1} (Table 4) higher than the adiabatic process and vertical neutralization (REv) of thermalised $C_2H_2S^{\bullet+}$ ions differs by only 8 kJ mol^{-1} from the adiabatic process. The calculated vertical ionization of neutral **2** (IEv) is found to be only 8 kJ mol^{-1} more than the adiabatic process and vertical neutralization (REv) of thermalised $C_2H_2S^{\bullet+}$ ions differs by only 9 kJ mol^{-1} from the adiabatic process. Similarly, the calculated vertical ionisation of neutral **3** (IEv) is found to be only 16 kJ mol^{-1} more than the adiabatic process and vertical neutralization (REv) of thermalised $C_2H_2S^{\bullet+}$ ions differs by only 17 kJ mol^{-1} from the adiabatic process. The minimum excess Frank–Condon energy of C_2H_2S for **1**–**3** is only 8 kJ mol^{-1}, 9 kJ mol^{-1}, and 17 kJ mol^{-1} which are insufficient to induce any fragmentation, or dissociation as the threshold energy of dissociation or isomerization lies at very high in energy. These results are consistent with similar geometry found for both ionic and neutral isomers of **1**–**3**.

Table 4
Calculated adiabatic energies (IE_a) and vertical one-electron transition energies (in eV) of ions and neutrals of $[C_2H_2S]^{\bullet+/o}$ and $[C_2H_2S]$ isomers at B3LYP/6-311G(d,p) level

Transitions	$IE_a{}^*$	RE_v	IE_v
1$^{\bullet+}$–**1**	8.85	8.76	–
1–**1**$^{\bullet+}$	–	–	8.92
2$^{\bullet+}$–**2**	9.22	9.13	–
2–**2**$^{\bullet+}$	–	–	9.30
3$^{\bullet+}$–**3**	8.02	7.85	–
3–**3**$^{\bullet+}$	–	–	8.19
4$^{\bullet+}$(a)–**4**(a)	9.34	9.15	–
4(a)–**4**$^{\bullet+}$(a)	–	–	9.50
4$^{\bullet+}$(s)–**4**(s)	9.75	9.17	–
4(s)–**4**$^{\bullet+}$(s)	–	–	10.07
15$^{\bullet+}$–**5**	8.88	8.68	–
5–**5**$^{\bullet+}$	–	–	9.09

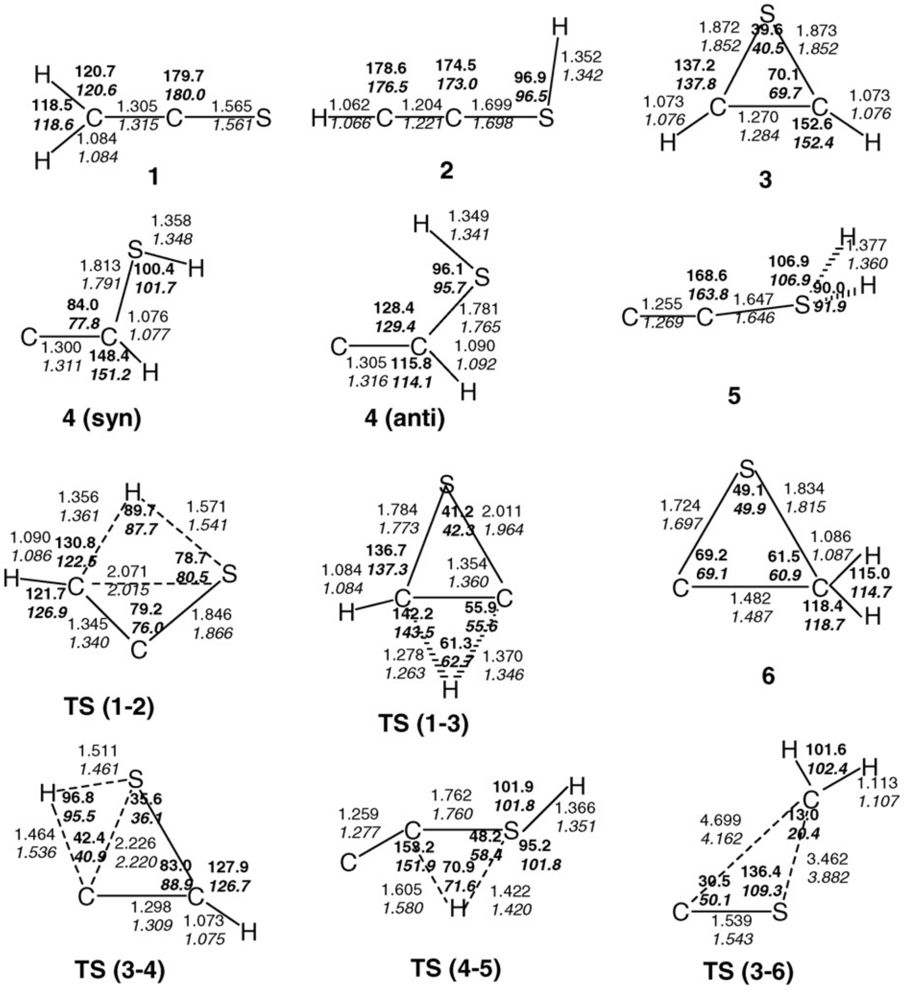


Fig. 6. Selected optimized geometries [B3LYP/6-311G(d,p)] of neutral $H_2C{=}C{=}S$, **1**, its isomers **2**–**6**, connecting transition states. Bond lengths in angstroms, bond angles in degrees, values in italics correspond to G2 level.

9. Conclusions

From the combined results of various tandem mass spectrometric experiments including associative ion–molecule reactions and theoretical calculations at B3LYP/6-311G(d,p) and G2/G2(MP2) levels, it is proposed that dissociative electron ionization of thiophene, 1-propane thiol, and thiirane yields a mixture of $[H_2,C_2,S]^{\bullet+}$ ions of the connectivities $H_2CCS^{\bullet+}$, $HCCSH^{\bullet+}$, and cyclic-$HCCHS^{\bullet+}$. Attempts to differentiate these three isomeric ions using associative ion–molecule reactions also produced non-conclusive results. NR experiments confirm the theoretical prediction that neutral thioketene, ethynylthiol, and thiirene are stable species in the rarefied gas phase. However, the present experimental conditions do not produce these species in their 'pure' form except for thioketene.

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