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Thiosulfoxides ($X_2S{=}S$) and disulfanes (XSSX): first observation of organic thiosulfoxides

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Abstract

Using a combination of tandem mass spectrometry methodologies, collisional activation of fast (8 keV) or slow (20–30 eV) ion beams, neutralization–reionization and ion–molecule reactions, it is shown that thiosulfoxides $X_2S{=}S$ ($X = H$, CH_3, C_2H_5) are stable in the gas phase as radical cations as well as neutral molecules. The absence of isomerization into the more conventional disulfane structure, XSSX, is firmly demonstrated by ion-molecule reactions of the isomeric ions with methyl isocyanide and by collisional activation of "survivor" ions generated in neutralization–reionization experiments. All the mass spectral data have been recorded with a single hybrid mass spectrometer of sectors-quadrupole-sectors configuration. Molecular orbital calculations demonstrate that ionized thiosulfoxides and disulfanes are local minima on the MP2/6-31G* potential energy surface. The disulfane structures are found to be the most stable species by 91, 65 and 59 kJ/mol for $X = H$, CH_3 and C_2H_5, respectively. Heat of formation values of 1000, 810 and 760 kJ/mol are estimated for $X_2SS^{\cdot+}$ ions ($X = H$, CH_3 and C_2H_5, respectively). (Int J Mass Spectrom 195/196 (2000) 239–249) © 2000 Elsevier Science B.V.

Keywords: Thiosulfide; Disulfane; Tandem mass spectrometry; Collisional activation; Neutralization-reionization; Ion-molecule reactions

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1. Introduction

Disulfur difluoride (FSSF) and thiothionyl difluoride ($F_2S{=}S$) rank among the more curious isomers of few-atom molecules. Their syntheses were first reported independently in 1963 by Kuczkowski and Wilson [1] and Seel and Gölitz [2]. Both isomers were prepared by reacting silver fluoride with sulfur and were isolated from the reaction mixture by distillation at low temperature [2]. They were identified by microwave and mass spectrometry studies [3]. Surprisingly, FSSF appears to be thermally less stable and, even at temperatures lower than −50 °C, slowly isomerizes into $F_2S{=}S$. Photoelectron [4] and infrared [5] spectroscopies, as well as theoretical studies [6], have described their molecular properties.

From calculated isomerization energy surfaces of the XSSX $\Leftrightarrow$ $X_2S{=}S$ system (X = F, CI, H) [7], it was concluded that, as expected from the previous experimental observations, $F_2S{=}S$ is slightly more stable than FSSF (~10 kJ/mol) and that the barrier to the transition state amounts to about 150 kJ/mol. Both isomers were thus calculated to be stable and isolable molecules. On the other hand, their calculations sup-

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Dedicated to the memory of Professor Robert R. Squires.

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ported that the experimentally observed HSSH [8] and ClSSCl [9] are the lone species to be stable.

Thiothionyl dichloride and dibromide were nevertheless obtained shortly thereafter by photolysis of the corresponding disulfur dihalide in argon or nitrogen matrices at very low temperatures [10], and identified by infrared spectroscopy. It is also worthy of note that, to the best of our knowledge, the unstable ISSI molecule has not yet been observed [7,11].

A more recent theoretical reinvestigation of the possible HSSH $\Leftrightarrow$ $H_2S{=}S$ isomerism concluded that, although HSSH is roughly 160 kJ/mol more stable, $H_2S{=}S$ is a true local minimum [12]. Finally, Steudel and coworkers, using ab initio MO calculations, showed that H_2SS and Me_2SS should be thermodynamically and kinetically stable toward unimolecular isomerization at low temperature. Actually, the calculated barriers for isomerization of X_2SS to XSSX or vice versa are so high that no thermal isomerization is expected at temperatures at which the X_2S_2 species are stable (<50 °C) [13]. Therefore, it should be possible to isolate and identify $X_2S{=}S$ (X = H, Alkyl) in matrix experiments or in the gas phase. However, organic thiosulfoxides have never been isolated or directly observed, but their implication as reaction intermediates has been discussed on several occasions [14].

With the development of neutralization-reionization mass spectrometry (NRMS) [15], identification of neutral reactive molecules with lifetimes longer than ~0.1–0.5 μs has been readily achieved on several occasions provided fast beams (8–10 keV range) of the corresponding ions are available. In fact, we have discovered in recent works that ionized sulfur ($S^{\cdot+}$) can be efficiently transferred to various functional groups with the production of dipole (distonic) radical cations. Typical examples described concerned the production of ionized nitrile *N*-sulfides [16], pyridine *N*-sulfides [17], transfer of sulfur to alkyl halides [18], and carbon disulfide *S*-sulfide, $S{=}C{=}S^{+}{-}S^{\cdot}$, generated by self-chemical ionization of carbon disulfide appeared to be an efficient reagent for these $S^{\cdot+}$ transfer reactions [16]. Other reagents of choice were cyanogen *N*-sulfides ($RCNS^{\cdot+}$, R = CN or Cl) readily accessible by dissociative ionization of substituted 1,2,5-thiadiazoles [19].

This methodology has been used in the present work for the first observation of three thiosulfoxides, $X_2S{=}S$ (X = H, CH_3, and C_2H_5), as ions and neutrals in the gas phase. Thus, the $X_2S{=}S^{\cdot+}$ radical cations have been generated by $S^{\cdot+}$ transfer from $CS_3^{\cdot+}$ or $ClCNS^{\cdot+}$ radical cations to X_2S neutrals and the connectivities of the so-produced ions have been studied by tandem mass spectrometry experiments such as collisional activation (CA) in the high (8 keV) or low (~20–30 eV) kinetic energy regime and ion–molecule reactions at near thermal energies. The stability of the corresponding neutrals has been estimated owing to the use of NRMS. All these experiments have been performed in the same hybrid mass spectrometer of sectors-quadrupole-sectors configuration.

To determine the structures and stabilities of ionized disulfanes and thiosulfoxides, we have carried out ab initio molecular orbital calculations on $[XSSX]^{\cdot+}$ and $[X_2SS]^{\cdot+}$ ions (X = H, CH_3, C_2H_5). The transition structures for their isomerization via a 1,2-X shift has been also investigated.

2. Experimental and computational section

The spectra were recorded on a large-scale tandem mass spectrometer (Micromass AutoSpec 6F, Manchester) combining six sectors of $E_1c_1B_1c_2E_2c_3c_4E_3B_2c_5E_4$ (E_i stands for electric sector, B_i for magnetic sector, and c_i for collision cell) [20]. General conditions were 8 kV accelerating voltage, 200 μA trap current (in the electron ionization mode, EI), 1 mA (in the chemical ionization mode, CI), 70 eV ionizing electron energy and 200 °C ion source temperature. The solid samples were introduced with a direct insertion probe, while the liquid samples were injected into the ion source via a heated (180 °C) septum inlet.

Collisional activations [21] (CA/O_2/8 keV kinetic energy) of mass-selected ions were performed in c_4 and the CA spectra were recorded by a linked scanning of the fields of the three last sectors ($E_3B_2E_4$).

The NR (Xe/O_2) unit is situated in the fourth field-free region, c_3 and c_4 being the neutralization and the reionization cells, respectively. The NR spectra were recorded by scanning the field of E_3. The NR/CA experiment was performed after mass selection of the survivor ions with B_2 by colliding these ions with O_2 in c_5 and mass-analysis of the fragments by scanning the field of E_4.

The installation of an rf-only quadrupole collision cell (Qcell) inside the instrument between E_3 and E_4 has also been reported elsewhere [22]. This modification allows the study of associative ion-molecule reactions and the study of collisional activation of decelerated ions (~20–30 eV kinetic energy). Briefly, the experiments utilizing the quadrupole 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 approximatively 5 eV (to maximize ion–molecule reactions) or 20–30 eV (to maximize collision induced dissociations). The interaction between the ions and the reagent gas (the pressure of the gas is estimated to be about 10^{-3} Torr) is thereafter realized in the Qcell and, after reacceleration at 8 keV, all the ions generated in the quadrupole are separated and mass measured by scanning the field of the second magnet. The high-energy CA spectra of mass-selected ions generated in the Qcell can be recorded by a linked scanning of the fields of the three last sectors.

All the samples used were commercially available (Aldrich, Resco Trade), except for methyl isocyanide, CH_3NC, which was prepared according to the literature [23].

Standard ab initio molecular orbital calculations have been carried out using the GAUSSIAN-94 series of programs [24]. The geometries of the different species were first optimized at the Hartree–Fock (HF) level with the *d*-polarized 6-31G* basis set of atomic orbitals. Harmonic vibrational frequencies have been determined at this level in order to characterize stationary points as minima (equilibrium structures) or saddle points (transition structures). The zero-point energies (ZPE) of the species considered have been calculated at this level after scaling by a 0.9135 factor [25]. Geometrical parameters have subsequently been reoptimized at the MP2(full)/6-31G* level of theory to take electron correlation effects explicitly into account. Finally, energies were improved by single point calculation using the 6-311+G** basis set at the UMP2 level on the MP2/6-31G* optimized geometries. The relative energies discussed throughout this article are those obtained at the UMP2/6-311+G**// MP2/6-31G* + ZPE(HF/6-31G*) level.

For the open-shell stable species investigated here, the unprotected $\langle S^2 \rangle$ values were within 0.759–0.767 indicating negligible spin contamination. The transition structures have $\langle S^2 \rangle$ expectation values situated between 0.802 and 0.940, these values are, however, not very different from 0.75 and, in any case, far from the quartet value (3.75) thus suggesting that spin contamination has no significant effect here.

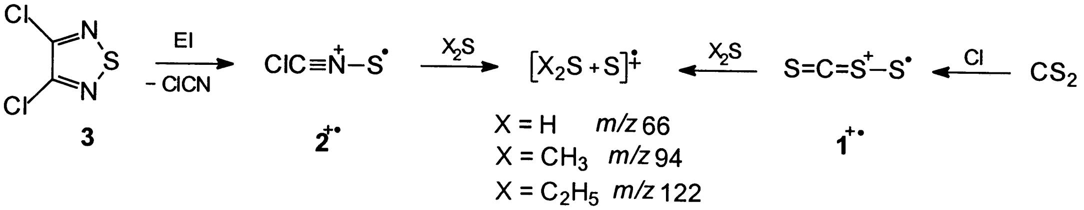
Detailed geometries obtained at the UMP2/6-31G* level are available upon a request to the authors. Some relevant geometrical parameters are presented in Fig. 4.

3. Results and discussion

3.1. Production of $[X_2S,S]^{\cdot+}$ radical cations

The chemical ionization (CI) [26] of X_2S (X = H, Me, Et) using carbon disulfide as the reagent gas leads to the generation in good yields of $[X_2S,S]^{\cdot+}$ radical cations (Scheme 1). The origin of these ions is readily established by using the quadrupolar collision cell: the carbon disulfide *S*-sulfide ions $\mathbf{1}^{\cdot+}$ react indeed readily with the X_2S neutral molecules by $S^{\cdot+}$ transfer. A similar reaction is also observed starting with $Cl\text{-}C{\equiv}N^+\text{-}S^{\cdot}$ ions ($\mathbf{2}^{\cdot+}$). These reagent ions are prepared in an EI source by dissociative ionization of 3,4-dichloro-1,2,5-thiadiazole (**3**) [19].

The sulfur distonic ions [27], $(CH_3)_2S^+\text{-}CH_2^{\cdot}$, have been previously generated by transfer of a methylene radical cation from ionized oxirane [28] to dimethyl sulfide (dimethyl thioether) [29]. The stable ions were characterized by comparison of their CA fragmentations [29] with those observed for the $CH_3CH_2SCH_3$ isomeric ions and their ion-molecule reactions toward several neutral reagents were investigated [30]. Experimental results have indicated that the *metastable*



Scheme 1.

$(CH_3)_2S^+$-$CH_2^{\cdot}$ ions slowly isomerize into the ethyl methyl thioether structure, $CH_3CH_2S^{\cdot+}CH_3$, prior to dissociation [29]. Before probing the stability of the neutral [X_2S,S] in the gas phase by the NRMS methodology, it is therefore necessary to determine the actual atom connectivity of the corresponding radical cations expected to be thiosulfoxide ions, X_2S^+-$S^{\cdot}$.

Three reference structures are readily prepared in an EI source by direct ionization of neutral precursors (MeSSMe$^{\cdot+}$ and EtSSEt$^{\cdot+}$) or by dissociative ionization of diethyl disulfide (HSSH$^{\cdot+}$). HSSH can also be generated by the dimerization of HS$^{\cdot}$ radicals in the gas phase [31], but this procedure is not applicable in our mass spectrometer.

3.2. Metastable and collision-induced dissociations of [X_2S,S]$^{\cdot+}$ radical cations

Table 1 summarizes the dissociations of the metastable ions under investigation. It is not unexpected that both XSSX and X_2SS connectivities present similar behavior toward unimolecular, slow fragmentations so that structural information cannot be obtained.

Table 1
Dissociations of metastable XSSX$^{\cdot+}$ and $X_2SS^{\cdot+}$ isomeric ions and kinetic energy release measured at half-height ($T^{0.5}$)

Ions		Fragments	Loss of	$T^{0.5}$ (meV)
HSSH$^{\cdot+}$	**4**$^{\cdot+}$	—	—	—
HS(S)H$^{\cdot+}$	**5**$^{\cdot+}$	—	—	—
MeSSMe$^{\cdot+}$	**6**$^{\cdot+}$	*m/z* 61	HS$^{\cdot}$	28
MeS(S)Me$^{\cdot+}$	**7**$^{\cdot+}$	*m/z* 61	HS$^{\cdot}$	41
EtSSEt$^{\cdot+}$	**8**$^{\cdot+}$	*m/z* 94	C_2H_4	55
EtS(S)Et$^{\cdot+}$	**9**$^{\cdot+}$	*m/z* 94	C_2H_4	53

In contrast, collisional activation experiments, at high or low translational energies of the ions (Tables 2–4), provide some experimental evidence for the production of the thiosulfoxide isomers, **5**$^{\cdot+}$, **7**$^{\cdot+}$, and **9**$^{\cdot+}$, in the sulfur transfer reactions.

Indeed, the three collision-excited α-distonic ions, **5**$^{\cdot+}$, **7**$^{\cdot+}$, and **9**$^{\cdot+}$, expel a sulfur atom and the corresponding signals are more intense than in the CA spectra of the reference disulfide ions; moreover, this decomposition is completely absent in the case of MeSSMe$^{\cdot+}$ and EtSSEt$^{\cdot+}$ ions, even in the high kinetic energy regime. Moreover, beside this structural indicative dissociation, the CA spectra of the isomers are also characterized by quantitative differences in the signal intensities. It is therefore concluded that the S$^{\cdot+}$ transfer reaction to neutral X_2S leads, at least partly, to the thiosulfoxide ions, $X_2S^+S^{\cdot}$.

3.3. Ion-molecule reactions between isomeric $X_2S_2^{\cdot+}$ ions and methyl isocyanide

Stronger confirmation of the distonic structures of **5**$^{\cdot+}$, **7**$^{\cdot+}$, and **9**$^{\cdot+}$ is found in the study of their ion-molecule reactions with methyl isocyanide (CH_3NC). Distonic ions are indeed recognized as potential reagents for the transfer of charged odd-electron groups to neutral molecules [32]. In previous works, we have successfully used methyl isocyanide as a neutral reagent for the characterization of different distonic ions such as pyridine *N*-selenide [33] and ethenedithione *C*- or *S*-sulfide ions [34]. Therefore, we decided to analyze the reactivity of **4–9**$^{\cdot+}$ radical cations toward MeNC in order to ascertain our previous conclusions derived from the CA experiments.

Table 2
Collisional activation (high and low kinetic energy) and NR spectra of $HSSH^{\cdot+}$, **4**$^{\cdot+}$, and $H_2SS^{\cdot+}$, **5**$^{\cdot+}$, ions (*m/z* 66)

m/z	66	65	64	34	33	32.5	32
	CA(O_2)-8 keV kinetic energy						
4$^{\cdot+}$	—	75	100	1	25	<0.1	12
5$^{\cdot+}$	—	67	100	6	17	1	14
	CA(Ar)-30 eV kinetic energy						
4$^{\cdot+}$	—	36	100	1	7	0	1
5$^{\cdot+}$	—	28	100	7	10	0	3
	NR(Xe/O_2)						
4$^{\cdot+}$	100	52	90	6	50	0	58
5$^{\cdot+}$	100	26	44	13	27	0	40

The associative interaction between $H_2SS^{\cdot+}$, **5**$^{\cdot+}$, and methyl isocyanide leads to ionized methyl isothiocyanate (*m/z* 73) by $S^{\cdot+}$ transfer. Secondary products are also detected and correspond to proton and HS^+ transfer to neutral CH_3NC (Table 5). The isomeric ions, **4**$^{\cdot+}$, react also with MeNC and the same ions are generated, but with quite different yields. Methyl isothiocyanate molecular ions, produced in very low amounts, are likely to result here from the loss of $H^{\cdot}$ starting from *m/z* 74 ions, CH_3NCSH^+. Indeed, the main collision-induced fragmentation of these *m/z* 74 ions is the loss of a hydrogen atom leading to ionized methyl isothiocyanate.

When $(CH_3)_2S^+S^{\cdot}$ ions, **7**$^{\cdot+}$, are allowed to react with methyl isocyanide, methyl isothiocyanate ions are not detected. However, a signal corresponding to dimethyl disulfide molecular ions, $CH_3SCH_3^{\cdot+}$, *m/z* 62, is recorded when energy conditions appropriate for the observation of ion-molecule reactions are applied (~5 eV kinetic energy of the mass-selected ions) [Fig. 1(a)]. That this signal is not due to collisional fragmentation is clearly shown by Fig. 1(b) (CA-argon), where the most intense reaction is the loss of a methyl group (*m/z* 79). This fragmentation is not observed in the ion-molecule reaction with methylisocyanide. This apparently contrasting behavior of **5**$^{\cdot+}$ and **7**$^{\cdot+}$ is in fact readily explained on the basis of relative ionization energies (IE) [35]. The sulfur transfer reaction also occurs for **7**$^{\cdot+}$, but the transition complex expels the neutral possessing the highest ionization energy; in this case, methyl isothiocyanate (see Table 6). In contrast, hydrogen sulfide ($IE = 10.45$ eV) having a higher IE than methyl isothiocyanate ($IE = 9.25$ eV), the interaction between *S*-sulfurated H_2S radical cation and CH_3NC gives $CH_3NCS^{\cdot+}$ molecular ions. Dimethyl disulfide ions, **6**$^{\cdot+}$, were found to be completely unreactive toward MeNC and this interesting observation indicates the absence of isomerization processes on the time scale imposed by the mass spectrometer configuration.

Similarly, $(C_2H_5)_2SS^{\cdot+}$, **9**$^{\cdot+}$, also reacts with MeNC producing ionized diethyldisulfide and neutral

Table 3
Collisional activation (high and low kinetic energy) and NR spectra of $MeSSMe^{\cdot+}$, **6**$^{\cdot+}$, and $Me_2SS^{\cdot+}$, **7**$^{\cdot+}$, ions (*m/z* 94)

m/z	94	79	78	64	62	61	49	48	47	46	45	44	32
	CA(O_2)-8 keV												
6$^{\cdot+}$	—	100	8	24	0	16	2	7	19	23	35	2	1
7$^{\cdot+}$	—	100	7	27	2	53	1	6	19	25	27	1	1
	CA(Ar)-30 eV												
6$^{\cdot+}$	—	100	0	3	0	7	0	0	0	0	0	0	0
7$^{\cdot+}$	—	100	0	2	8	52	0	0	0	0	0	0	0
	NR(Xe/O_2)												
6$^{\cdot+}$	13	34	2	48	0	3	1	28	45	59	100	43	38
7$^{\cdot+}$	78	77	19	98	14	38	2	29	42	69	100	35	64

Table 4
Collisional activation (high and low kinetic energy) and NR spectra of $EtSSEt^{\cdot+}$, $\mathbf{8}^{\cdot+}$, and $Et_2SS^{\cdot+}$, $\mathbf{9}^{\cdot+}$, ions (*m/z* 122)

m/z	122	94	93	90	89	79	75	66	64	61	60	59	45	32	29
CA(O_2)-8 keV															
$\mathbf{8}^{\cdot+}$	—	100	30	0	0	6	0	33	11	6	5	11	8	1	16
$\mathbf{9}^{\cdot+}$	—	100	10	2	2	0	1	5	0	2	0	0	0	<1	2
CA(Ar)-30 eV															
$\mathbf{8}^{\cdot+}$	—	100	16	0	0	6	0	18	0	3	6	0	0	0	<1
$\mathbf{9}^{\cdot+}$	—	100	6	2	7	1	1	7	4	2	1	3	2	0	5
NR(Xe/O_2)															
$\mathbf{8}^{\cdot+}$	2	13	17	0	0	1	2	9	100	12	12	16	26	13	9
$\mathbf{9}^{\cdot+}$	5	14	14	1	3	1	2	8	100	9	14	17	25	20	6

CH_3NCS in agreement with the relative ionization energies. This reaction is again not observed with mass-selected $\mathbf{8}^{\cdot+}$ ions.

3.4. Neutralization-reionization experiments of isomeric $X_2S_2^{\cdot+}$ ions

As summarized in Table 2, the NR spectrum of $\mathbf{5}^{\cdot+}$ [Fig. 2(a)] features a very intense recovery signal (*m/z* 66) and fragmentations very similar to those observed in the CA spectrum. Again, the peak at *m/z* 34, corresponding to ionized H_2S, is more important than in the NR spectrum of the isomeric $HSSH^{\cdot+}$ ions [Fig. 2(b)]. The stability of neutral $H_2S{=}S$ is therefore established for the first time by the present experiment.

The NR spectrum of $(CH_3)S^+\text{-}S^{\cdot}$ ions also features an intense recovery signal [Table 3; Fig. 3(a)]. The signal at *m/z* 62, corresponding to the loss of sulfur, is also present in this spectrum. This peak is not observed in the NR spectrum of the dimethyl disulfide molecular ions (Table 3). All these experimental data, together with the calculations of Steudel [13], clearly indicate that neutral dimethyl thiosulfoxide is a stable molecule in the gas phase.

Table 5
Products of ion-molecule reactions of **4** to $\mathbf{9}^{\cdot+}$ radical cations and MeNC. The last entry (Yield) represents the relative intensities of the signals associated to the ion-molecule reaction products

Ions		Product ions	*m/z*	Yield (%)
$HSSH^{\cdot+}$	$\mathbf{4}^{\cdot+}$	CH_3NCH^+	42	94
		$CH_3NCS^{\cdot+}$	73	0.5
		CH_3NCSH^+	74	5.5
$H_2SS^{\cdot+}$	$\mathbf{5}^{\cdot+}$	CH_3NCH^+	42	82
		$CH_3NCS^{\cdot+}$	73	14
		CH_3NCSH^+	74	4
$MeSSMe^{\cdot+}$	$\mathbf{6}^{\cdot+}$	no reaction	—	—
$Me_2SS^{\cdot+}$	$\mathbf{7}^{\cdot+}$	$CH_3SCH_3^{\cdot+}$	62	100
$EtSSEt^{\cdot+}$	$\mathbf{8}^{\cdot+}$	CH_3NCH^+	42	100
$Et_2SS^{\cdot+}$	$\mathbf{9}^{\cdot+}$	CH_3NCH^+	42	40
		$C_2H_5SC_2H_5^{\cdot+}$	90	60

Moreover, further conclusions can be deduced from the comparison of the NR/CA spectrum of $\mathbf{7}^{\cdot+}$ [Fig. 3(b)] with the conventional CA spectrum recorded under the same conditions [Fig. 3(c)]. Both spectra being completely similar, it can be concluded that neutral **7** does not isomerize to **6** during the flight between the neutralization and reionization collision cells. On the other hand, as far as the ions are concerned, the high level of purity of the parent ion beam, already deduced from the previous ion-molecule reactions, is confirmed. In other words, it seems that the sulfur transfer reaction to dimethyl disulfide leads specifically to $\mathbf{7}^{\cdot+}$ without further isomerization into $\mathbf{6}^{\cdot+}$.

In the case of $\mathbf{9}^{\cdot+}$, a weak but significant recovery signal is also recorded and the fragmentations are in keeping with those observed in the corresponding CA experiment (Table 4). Given the fact that the recovery signal featured in the NR spectrum of $\mathbf{8}^{\cdot+}$ is of very low intensity, we can conclude that, even if isomerization of $\mathbf{9}^{\cdot+}$ to $\mathbf{8}^{\cdot+}$ or of **9** to **8** occurs, the contribution of $\mathbf{8}^{\cdot+}$ in the recovery signal of the NR spectrum of $Et_2SS^{\cdot+}$ should be negligible. Therefore, neutral **9** is very likely a stable species in the gas phase.

It is quite surprising that the NR spectra of $\mathbf{4}^{\cdot+}$, $\mathbf{6}^{\cdot+}$, and $\mathbf{8}^{\cdot+}$ feature recovery signals less intense than the

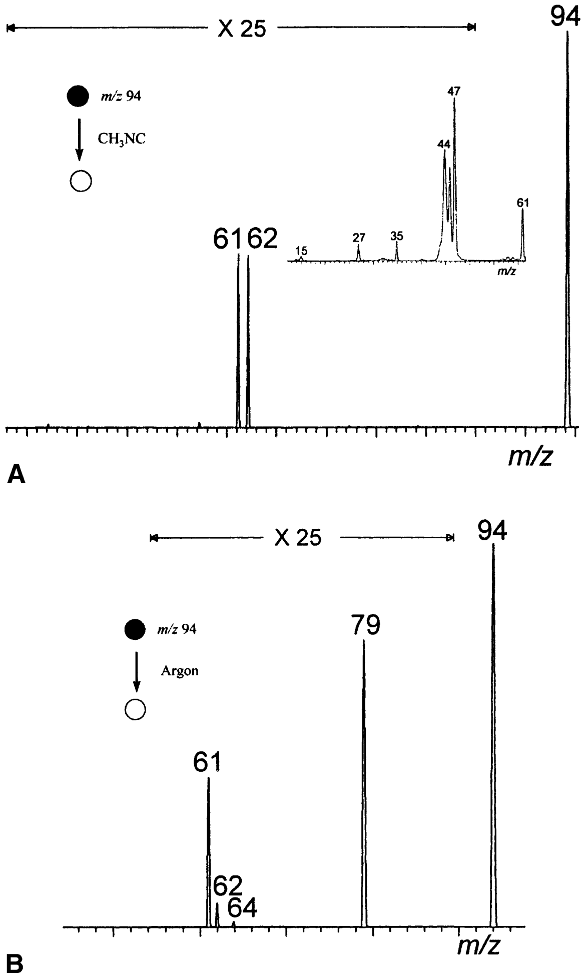


Fig. 1. (a) Mass spectrum of the ions produced by reactions between $(CH_3)_2S^+$-$S^\cdot$ ($\mathbf{7}^{\cdot+}$) and methyl isocyanide in the quadrupolar collision cell and (b) low energy CA (argon) spectrum of the same ions. The inset in (a) shows the high energy CA spectrum of the *m/z* 62 ions formed in the ion-molecule reaction. The terminology, introduced by Schwartz et al. (Anal. Chem. 62 (1990) 1809), is used to schematize the sequence of reactions: a filled circle represents a fixed (or selected) mass; an open circle, a variable (or scanned) mass, whereas the neutral reagent or collision gas that causes the mass transitions is shown between the circles.

Table 6
Relevant ionization energies [35]

Neutral	IE (eV)	Neutral	IE (eV)
HSH	10.45	EtSEt	8.43
HSSH	9.3	EtSSEt	8.00
MeSMe	8.69	MeNCS	9.25
MeSSMe	8.18		

corresponding peaks in the $\mathbf{5}^{\cdot+}$, $\mathbf{7}^{\cdot+}$, and $\mathbf{9}^{\cdot+}$ NR spectra. Actually, upon ionization, the XSSX dihedral angle of about 90° in HSSH or MeSSMe is calculated to change to 180° in the corresponding ionized molecules [36]. Because of the resulting very poor Franck-Condon factors for vertical transition, neutral HSSH and MeSSMe are generated in excited states and thus fragmentation processes occur during the flight between the neutralization and the reionization cells. These very important changes of the geometries between the neutral and ionized states explain that the true adiabatic ionization energy of HSSH and

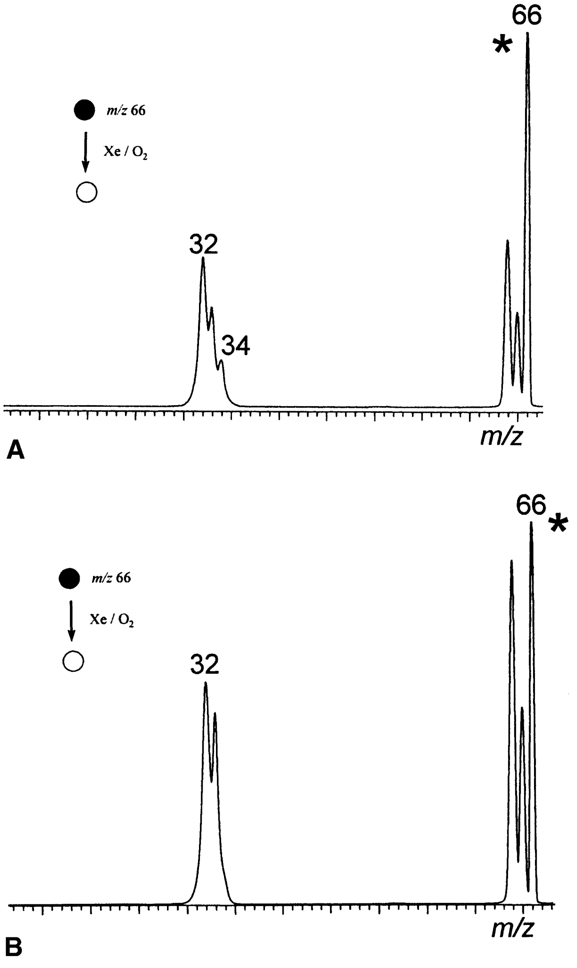


Fig. 2. NR (Xe/O_2) mass spectrum of (a) H_2S^+-$S^\cdot$ ($\mathbf{5}^{\cdot+}$) and (b) $HSSH^{\cdot+}$ ($\mathbf{4}^{\cdot+}$). The asterisk (*) shows the recovery signal.

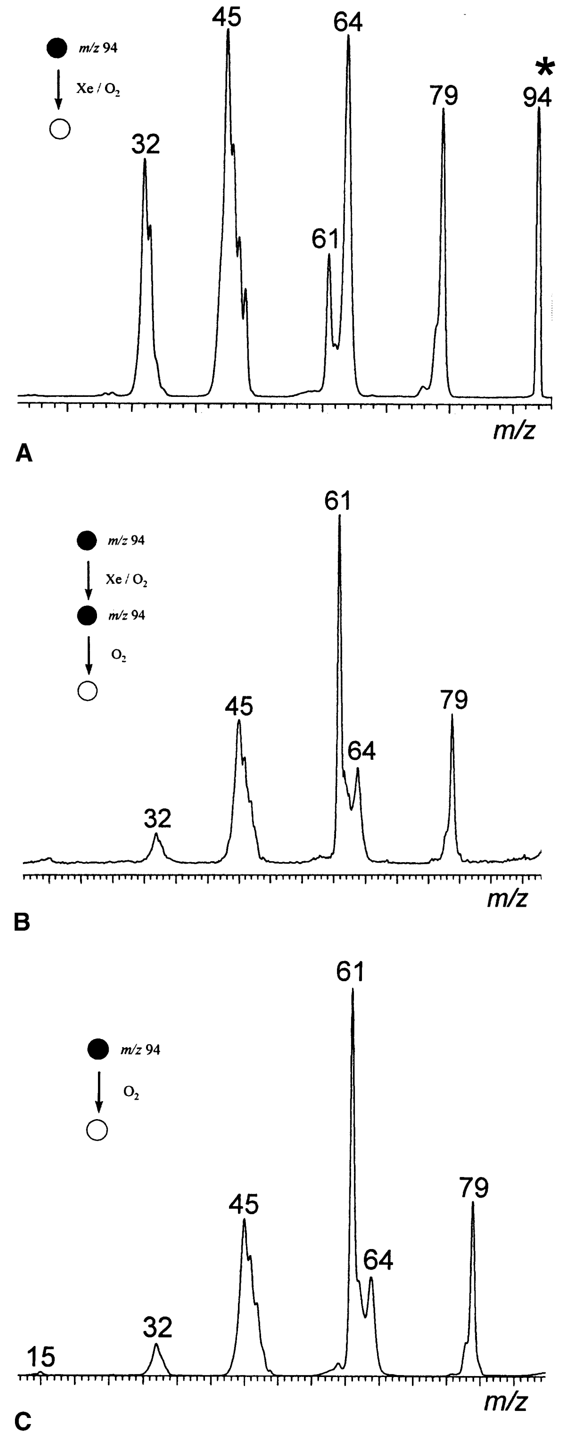


Fig. 3. (a) NR (Xe/O$_2$) mass spectrum of $(CH_3)_2S^+\text{-}S^\cdot$ ($7^{\cdot+}$). (b) NR (Xe/O$_2$)/CA(O$_2$) and (c) conventional CA(O$_2$) mass spectra of $(CH_3)_2S^+\text{-}S^\cdot$ ($7^{\cdot+}$). The asterisk (*) shows the recovery signal.

MeSSMe cannot be observed by photoionization (PI) or photoelectron spectroscopy (PES) [36].

3.5. Molecular orbital results

The calculated total and relative energies of the various $[XSSX]^{\cdot+}$, $[X_2SS]^{\cdot+}$ ions and the transition structures connecting these minima are presented in Table 7. In the three cases investigated (X = H, CH_3, C_2H_5) the disulfane structure $[XSSX]^{\cdot+}$ is found to be more stable than the thiosulfoxide isomer $[X_2SS]^{\cdot+}$. This situation is reminiscent of the case of the neutral systems [13]. The energy difference is, however, slightly lower for the ionized species. For example, the energy difference amounts for 91 kJ/mol between $[HSSH]^{\cdot+}$, $\mathbf{4}^{\cdot+}$, and $[H_2SS]^{\cdot+}$, $\mathbf{5}^{\cdot+}$, while Steudel *et al.* [13] found 143 kJ/mol between neutrals HSSH and H_2SS. Similarly, $[CH_3SSCH_3]^{\cdot+}$, $\mathbf{6}^{\cdot+}$, is more stable than $[(CH_3)_2SS]^{\cdot+}$, $\mathbf{7}^{\cdot+}$, by 65 kJ/mol but neutral dimethyl disulfide CH_3SSCH_3 is more stable than dimethylthiosulfoxide $(CH_3)_2SS$ by 84 kJ/mol [13]. For the three disulfanes $\mathbf{4}^{\cdot+}$, $\mathbf{6}^{\cdot+}$, and $\mathbf{8}^{\cdot+}$, the s-trans structures presented in Fig. 4 are the most stable conformations.

Isomerization of $[XSSX]^{\cdot+}$ ions into $[X_2SS]^{\cdot+}$ structure may occur via a simple 1,2-X shift. This type of reaction has been studied in the case of neutral disulfanes [13] but has never been investigated for the corresponding ionized species. The three transition structures $\mathbf{4}^{\cdot+}/\mathbf{5}^{\cdot+}$, $\mathbf{6}^{\cdot+}/\mathbf{7}^{\cdot+}$, and $\mathbf{8}^{\cdot+}/\mathbf{9}^{\cdot+}$ are presented in Fig. 4. Their energies are well above the energy level of the reactants. Calculated critical energies are 197, 262, and 223, respectively. For the sake of comparison, values of 210 and 340 kJ/mol have been estimated for reactions HSSH → H_2SS and $CH_3SSCH_3 \rightarrow (CH_3)_2SS$, respectively. Thus, again, a decrease of energy is observed when passing from ionized to neutral species. However, the most prominent result is that the 1,2-X shifts $[XSSX]^{\cdot+} \rightarrow [X_2SS]^{\cdot+}$ need considerable energy suggesting the possible identification of both stable ionic structures. This is illustrated in Fig. 5 for the case of X=H. The potential energy profile associated with isomerization $[HSSH]^{\cdot+}$, $\mathbf{4}^{\cdot+}$, → $[H_2SS]^{\cdot+}$, $\mathbf{5}^{\cdot+}$, is completed by the possible dissociation routes leading to products: $[SH]^+ + SH^\cdot$ and $[H_2S]^{\cdot+}$ + S and $[S]^{\cdot+} + H_2S$.

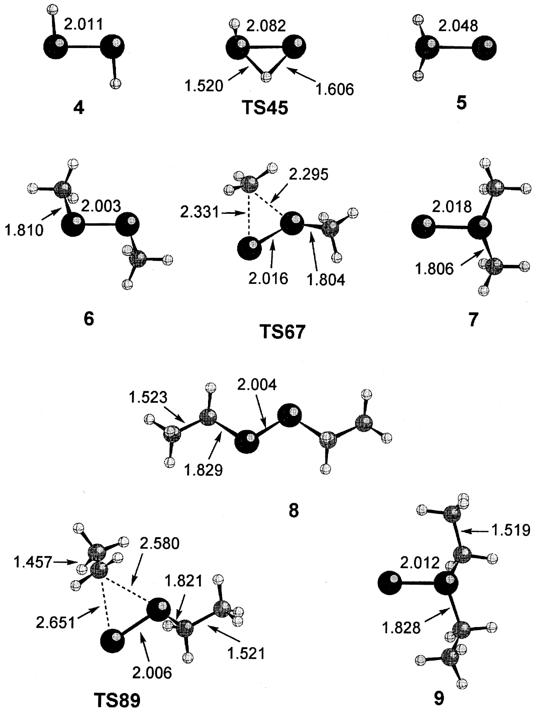


Fig. 4. Optimized geometries of ionized disulfanes, thiosulfoxides, and transition structures investigated (MP2/6-31G* molecular orbital calculations, bond length in Å).

The fragmentation of lowest enthalpy needs at least 45 kJ/mol more than the isomerization $\mathbf{4}^{\cdot+} \rightarrow \mathbf{5}^{\cdot+}$. Although a large population of ions of low internal energy cannot interconvert, isomerization is possible for ions $\mathbf{4}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$ of high internal energy. That could explain why characterization of $\mathbf{4}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$ by collisional experiments is not straightforward. For the other two couples, **6–7** and **8–9**, isomerization barriers by 1,2-X shift are as high as 262 and 223 kJ/mol. However, for these species, other isomerization reactions are possible, particularly via hydrogen atom migrations. It was not the goal of the present work to examine all these possibilities but it can be noted that 1,2-, 1,3-, or 1,4-H atom migrations on radical cations are generally associated with nonnegligible critical energies (in the range 150–80 kJ/mol). There is, consequently, again a large number of stable ions which cannot isomerize and which may be sampled by collision.

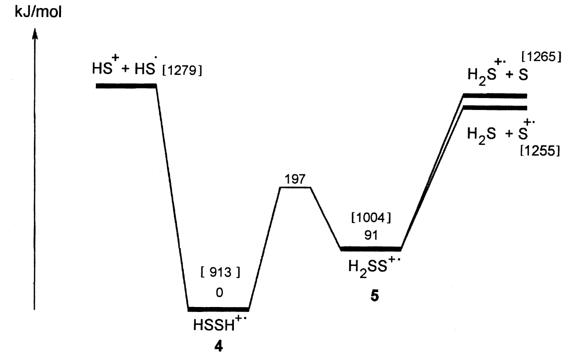


Fig. 5. Potential energy profile for isomerization and dissociation of ionized disulfane $[HSSH]^{+\cdot}$, $\mathbf{4}^{+\cdot}$, and thiosulfoxide $[H_2SS]^{+\cdot}$, $\mathbf{5}^{+\cdot}$, (MP2/6-311+G**MP2/6-31G*+ZPE calculated relative energies; in brackets: experimental heats of formation).

Using the 298 K calculated relative enthalpies (Table 7), it is possible to estimate the heats of formation of $H_2SS^{\cdot+}$, $\mathbf{5}^{\cdot+}$, $Me_2SS^{\cdot+}$, $\mathbf{7}^{\cdot+}$, and $Et_2SS^{+\cdot}$, $\mathbf{9}^{\cdot+}$, starting from the known heats of formation of the isomeric ions, 913, 765, and 800 kJ/mol for $HSSH^{+\cdot}$, $\mathbf{4}^{\cdot+}$, $MeSSMe^{\cdot+}$, $\mathbf{6}^{\cdot+}$, and $EtSSEt^{\cdot+}$, $\mathbf{8}^{\cdot+}$, respectively [35]. These energies for $H_2SS^{\cdot+}$, $\mathbf{5}^{\cdot+}$, $Me_2SS^{\cdot+}$, $\mathbf{7}^{\cdot+}$, and $Et_2SS^{\cdot+}$, $\mathbf{9}^{\cdot+}$, are, in this way, calculated to be about 1003, 812, and 759 kJ/mol, respectively.

From these estimations, the heats of the sulfur transfer reactions from $X_2SS^{\cdot+}$ ions to CH_3NC are also accessible. The calculated values (Table 8) are again in keeping with the experimental observations.

The interaction between $H_2SS^{\cdot+}$, $\mathbf{5}^{\cdot+}$, and MeNC leads to ionized methyl isothiocyanate and accordingly this reaction is estimated to be 173 kJ/mol exothermic. On the other hand, the potentially competitive reaction, that would produce ionized H_2S and neutral CH_3NCS, is only 57 kJ/mol exothermic.

As far the reactions of $Me_2SS^{\cdot+}$, $\mathbf{7}^{\cdot+}$, or $Et_2SS^{\cdot+}$, $\mathbf{9}^{\cdot+}$, are concerned, the estimated heats of reaction (Table 8) agree with the production of ionized MeSMe or EtSEt instead of the generation of the molecular ions of methyl isothiocyanate.

4. Conclusion

By using a combination of tandem mass spectrometry methodologies, collisional activation (low and

Table 7
Total (Hartree) and relative (kJ/mol) energies of ionized disulfane and thiosulfoxides

Structure	Name	ZPE [a]	S^2	UMP2/6-311+G** [b]	ΔE [c]
$HSSH^{\cdot+}$	$\mathbf{4}^{\cdot+}$	50	0.767	−796.179642	0
$H_2SS^{\cdot+}$	$\mathbf{5}^{\cdot+}$	52	0.759	−796.145793	+91 (90)
TS ($\mathbf{4}^{\cdot+} \rightarrow \mathbf{5}^{\cdot+}$)	$\mathbf{4}^{\cdot+}/\mathbf{5}^{\cdot+}$	37	0.802	−796.099610	+197 (197)
$MeSSMe^{\cdot+}$	$\mathbf{6}^{\cdot+}$	200	0.767	−874.883098	0
$Me_2SS^{\cdot+}$	$\mathbf{7}^{\cdot+}$	202	0.760	−874.858906	+65 (64)
TS ($\mathbf{6}^{\cdot+} \rightarrow \mathbf{7}^{\cdot+}$)	$\mathbf{6}^{\cdot+}/\mathbf{7}^{\cdot+}$	192	0.940	−874.780196	+262 (262)
$EtSSEt^{\cdot+}$	$\mathbf{8}^{\cdot+}$	348	0.767	−953.324482	0
$Et_2SS^{\cdot+}$	$\mathbf{9}^{\cdot+}$	349	0.760	−953.302481	+59 (58)
TS ($\mathbf{8}^{\cdot+} \rightarrow \mathbf{9}^{\cdot+}$)	$\mathbf{8}^{\cdot+}/\mathbf{9}^{\cdot+}$	335	0.823	−953.234730	+223 (217)

[a] Zero-point energies based on UHF/6-31G(d) harmonic vibrational wavenumbers scaled by a factor of 0.91.

[b] Using the UMP2(full)6-31G* optimized geometries.

[c] Relative energies (kJ/mol) at the UMP2/6-311+G**//UMP2/6-31G* level, including ZPE corrections. Corrections for 298 K enthalpies are given in parentheses.

high translational energies), neutralization–reionization and ion–molecule reactions, it is shown that ionized or neutral thiosulfoxides X_2SS ($X = H, CH_3, C_2H_5$) are stable species in the gas phase. In particular, the ion-molecule reactions of ionized dimethyl thiosulfoxide with methyl isocyanide and the close analogy of the CA and NR/CA spectra indicate that isomerization into the more conventional dimethyldisulfane ions does not occur. It is also worthy of note that all these experiments have been performed in a hybrid mass spectrometer having the sectors-quadrupole-sectors configuration. Molecular orbital calculations demonstrate that ionized thiosulfoxides and disulfanes are local minima on the MP2/6-31G* potential energy surface. The disulfane structures are found to be the most stable species by 91, 65, and 59 kJ/mol for $X = H$, CH_3 and C_2H_5, respectively. Heat of formation values of 1000, 810, and 760 kJ/mol are estimated for $X_2SS^{\cdot+}$ ions ($X = H$, CH_3, and C_2H_5, respectively).

Table 8
Estimated heats [ΔH (kJ/mol)] of the sulfur transfer reactions from $X_2SS^{\cdot+}$ to neutral CH_3NC

Reactions	ΔH (kJ/mol)
$H_2SS^{\cdot+} + CH_3NC \rightarrow H_2S + CH_3NCS^{\cdot+}$	**−173**
$Me_2SS^{\cdot+} + CH_3NC \rightarrow Me_2S^{\cdot+} + CH_3NCS$	**−70**
$Et_2SS^{\cdot+} + CH_3NC \rightarrow Et_2S^{\cdot+} + CH_3NCS$	**−72**

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References

[1] (a) R.L. Kuczkowski, E.B. Wilson, J. Am. Chem. Soc. 85 (1963) 2028; (b) R.L. Kuczkowski, J. Am. Chem. Soc. 85 (1963) 3047.

[2] (a) F. Seel, D. Gölitz, Chimia 17 (1963) 207; (b) F. Seel, D. Gölitz, Chimia 17 (1963) 335.

[3] R.L. Kuczkowski, J. Am. Chem. Soc. 86 (1964) 3617.

[4] (a) G. Wagner, H. Bock, R. Budenz, F. Seel, Chem. Ber. 106 (1973) 1285; (b) X. Cao, C. Qiao, D. Wang, Chem. Phys. Lett. 290 (1998) 405.

[5] R.D. Brown, G.P. Pez, Spectrochim. Acta Part A 26 (1970) 1375.

[6] (a) A. Hinchliffe, J. Mol. Struct. 55 (1979) 127; (b) C.J. Marsden, H. Oberhammer, O. Lösking, H. Willner, J. Mol. Struct. 193 (1989) 233.

[7] B. Solouki, H. Bock, Inorg. Chem. 16 (1979) 665.

[8] G. Wagner, H. Bock, Chem. Ber. 107 (1974) 68.

[9] F. Runge, Z. El-Hewehi, H.J. Renner, R. Steudel, J. Prakt. Chem. 11 (1960) 284.

[10] (a) B.M. Chadwick, J.M. Grzybowski, D.A. Long, J. Mol. Struct. 48 (1978) 139; (b) M. Feuerhahn, G. Vahl, Chem. Phys. Lett. 65 (1979) 322.

[11] F. Fehér, H. Münzner, Chem. Ber. 96 (1973) 933.

[12] C.J. Marsden, B.J. Smith, J. Phys. Chem. 92 (1988) 347.

[13] R. Steudel, Y. Drozdova, K. Miaskiewicz, R.H. Hertwig, W. Koch, J. Am. Chem. Soc. 119 (1997) 1990.

[14] (a) S.W. Benson, Chem. Rev. 78 (1978) 23; (b) R.D. Baechler, J.P. Hummel, K. Mislow, J. Am. Chem. Soc. 95 (1973) 4442; (c) G. Höfle, J.E. Baldwin, J. Am. Chem. Soc. 93 (1971) 6307; (d) M. Green, E.M. Lown, O.P. Strausz, J. Am. Chem. Soc. 106 (1984) 6938; (e) I.W.J. Still, S.K. Hasan, K. Turnbull, Can. J. Chem. 56 (1978) 1423.

[15] For reviews, see: (a) C.A. Schalley, G. Hornung, D. Schröder, H. Schwarz, Chem. Soc. Rev. 27 (1998) 91; (b) C. Wesdemiotis, F.W. McLafferty, Chem. Rev. 87 (1987) 485; (c) N. Goldberg, H. Schwarz, Acc. Chem. Res. 27 (1994) 347; (d) F.W. McLafferty, Science 247 (1990) 925; (e) R. Feng, C. Wesdemiotis, M.A. Baldwin, F.W. McLafferty, Int. J. Mass Spectrom. Ion Processes 86 (1988) 95.

[16] P. Gerbaux, R. Flammang, M.W. Wong, C. Wentrup, J. Phys. Chem. 101 (1997) 6970.

[17] P. Gerbaux, Y. Van Haverbeke, R. Flammang, J. Mass. Spectrom. 32 (1997) 1170.

[18] P. Gerbaux, Ph.D. thesis, University of Mons-Hainaut (1999).

[19] R. Flammang, P. Gerbaux, E.H. Mørkved, M.W. Wong, C. Wentrup, J. Phys. Chem. 100 (1996) 17452.

[20] R.H. Bateman, J. Brown, M. Lefevere, R. Flammang, Y. Van Haverbeke, Int. J. Mass Spectrom. Ion Processes 115 (1992) 205.

[21] K. Levsen, H. Schwarz, Angew. Chem., Int. Ed. Engl. 15 (1976) 509.

[22] R. Flammang, Y. Van Haverbeke, C. Braybrook, J. Brown, Rapid Commun. Mass Spectrom. 9 (1995) 795.

[23] R.E. Shuster, J.E. Scott, J. Casanova Jr., Org. Synth. 46 (1966) 75.

[24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94, Revision B.2, GAUSSIAN, Inc., Pittsburgh PA (1995).

[25] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.

[26] A.G. Harrison, Chemical Ionization Mass Spectrometry, 2nd ed., CRC, Boca Raton, 1992.

[27] (a) S. Hammerum, Mass Spectrom. Rev. 7 (1988) 123; (b) H.I. Kenttämaa, Org. Mass Spectrom. 29 (1994) 1.

[28] (a) W.J. Bouma, J.K. McLeod, L. Radom, J. Chem. Soc., Chem. Commun. (1978) 724; (b) C. Lange, Org. Mass Spectrom. 28 (1997) 1285; (c) F.C. Gozzo, M.N. Eberlin, J. Am. Soc. Mass Spectrom. 6 (1995) 554.

[29] M.W. van Amsterdam, H.W. Zappey, S. Ingemann, M.M.N. Nibbering, Org. Mass Spectrom. 28 (1993) 30.

[30] (a) M.W. van Amsterdam, P.O. Staneke, S. Ingemann, M.M.N. Nibbering, Org. Mass Spectrom. 28 (1993) 919; (b) R.L. Smith, L.J. Chyall, K.M. Stirk, H.I. Kenttämaa, Org. Mass Spectrom. 28 (1993) 1623.

[31] B.-M. Cheng, W.-C. Hung, J. Phys. Chem. 100 (1996) 10210.

[32] K.M. Stirk, K.M. Kiminkinen, H.I. Kenttämaa, Chem. Rev. 92 (1992) 1649.

[33] P. Gerbaux, Y. Van Haverbeke, R. Flammang, Int. J. Mass Spectrom. 184 (1999) 39.

[34] P. Gerbaux, R. Flammang, C.T. Pedersen, M.W. Wong, J. Phys. Chem. A 103 (1999), 3666.

[35] (a) S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, D. Delvin, W.G. Mallard, J. Phys. Chem. Ref. Data, 17, Suppl. 1 (1988); (b) C.Y. Ng, The Structure, Energetics and Dynamics of Organic Ions, Wiley, New York, 1996.

[36] (a) W.-K. Li, S.-W. Chiu, Z.-X. Ma, C.-L. Liao, C.-Y. Ng, J. Chem. Phys. 99 (1993) 8440; (b) B.-M. Cheng, J. Eberhard, W.-C. Chen, C.-H. Yu, J. Chem. Phys. 107 (1997) 5273.