$[C_2H_4OS]^{\cdot+}$ Radical cations derived from alkyl thioformates: tandem mass spectrometry and molecular orbital calculations

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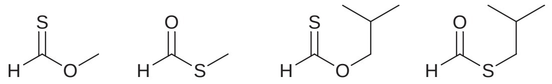
$[C_2H_4OS]^{\cdot+}$ radical cations have been generated upon dissociative ionization of some *S*-alkyl and *O*-alkyl thioformates and characterized by tandem mass spectrometry methodologies and molecular orbital calculations at the UQCISD(T)/6-311++G(d,p)//UMP2/6–31G(d,p) level. Use of a combination of collisional activation (high and low energy translational energies), neutralization–reionization and ion–molecule reaction experiments performed in a single instrument, combining different magnetic and electric sectors and a radiofrequency-only quadrupole collision cell, led to the identification of distonic radical cations and ion–molecule complexes such as $HC^+(OH)SCH_2^{\cdot}$ and $CH_3S^{\cdot+}(H)\cdots CO$, beside ions having a more classical structure, $HC(=S)OCH_3^{\cdot+}$ and $HC(=O)SCH_3^{\cdot+}$. Experimental evidence for the existence of the isomeric distonic $HC^+(SH)OCH_2^{\cdot}$ species has not been found, but calculations of the related $[C_2H_4OS]^{\cdot+}$ potential energy surface suggest that the latter ion is stable and likely to play a role in the fragmentation processes.

Introduction

Mass spectrometery has been (and still is) often used to detect interesting and novel stable structures of ions and neutrals in the gas phase. It is now generally recognized that many unimolecular mass spectrometric fragmentations do not occur directly from the ionized intact molecules, but involve several primary isomerizations to reactive intermediates as critical steps of the fragmentation mechanism. In addition to the results obtained by these advanced experimental methods, much valuable information about ion structure and reactivity can be obtained from theoretical approaches to gas-phase ion chemistry.[1] During the last decade, two types of reactive intermediate have attracted considerable and increasing interest, namely distonic ions[2] and ion/neutral complexes.[3] Distonic radical cations are species in which both charge and radical sites are formally separated.[4] They have been explored in the gas phase by a variety of mass spectrometric methods.[2,5] In previous work, we have shown that the distonic radical cation $HC^+(OH)OC^{\cdot}H_2$, an isomer of ionized methyl formate $HC(=O)OCH_3^{\cdot+}$, can be generated upon fragmentation of ionized isobutyl formate by loss of propene.[6] Identification of the distonic structure was based on collisional activation (CA) and neutralization–reionization (NR) mass spectrometry. Subsequently MO calculations[7] have shown in fact that the distonic ion is the more stable isomer. Further support for the occurrence of the distonic $HC^+(OH)OC^{\cdot}H_2$ species has been found recently in our laboratories making use of a new type of hybrid tandem mass spectrometer (see Experimental), that is, a loss of water is actually observed in the low energy CA spectrum of the distonic species, but not in the classical ester species.[8]

Recently, we have prepared and studied a large series of alkyl thioformates, as either *O*-alkyl or *S*-alkyl derivatives. Their behavior upon electron ionization was extensively investigated using tandem mass spectrometry methodologies and several complex rearrangement and fragmentation reactions were identified and rationalized with the aid of molecular orbital calculations.[8–12]

In the present paper, we report on the structural identification of several *m*/*z* 76 ions having $[C_2H_4OS]^{\cdot+}$ composition derived from direct electron ionization of *O*-methyl and *S*-methyl thioformates **I** and **II** or dissociative ionization (loss of propene) of *O*-isobutyl and *S*-isobutyl thioformates **III** and **IV** (Scheme 1). In addition, *ab initio* molecular orbital calculations have also been carried out in order to assist the interpretation of observed results.



I	**II**	**III**	**IV**
(100%)	(100%)	(<1%)	(22%)

Scheme 1 Thioformates **I**–**IV** used to generate the *m*/*z* 76 ions (relative abundance in the 70 eV EIMS indicated in parentheses).

Experimental

The spectra were recorded using a large scale tandem mass spectrometer with EBEEBE geometry (E stands for electric sector and B for magnetic sector) fitted with five collision cells and, in its hybrid configuration, with an additional radiofrequency-only quadrupole collision cell. The characteristics of the mass spectrometer have already been presented in previous papers.[13–15] General conditions of experiments were 8 kV accelerating voltage, 200 μA trap current, 70 eV ionizing electron energy and 200 °C source temperature. The samples were introduced *via* a heated (160 °C) septum inlet.

Collisional activation (CA) and neutralization–reionization (NR) spectra were recorded by scanning the field of the third

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Table 1 Calculated total energies (hartree)[a] and zero-point energies (kJ mol^{-1})[b] of the $[C_2H_4OS]^{\bullet+}$ radical cations considered

	Structures	UMP2/6-31G(d,p)	UMP2/6-311++G(d,p)	UQCISD(T)/6-31G(d,p)	ZPE	$<S^2>$
1	$HC(=S)OCH_3^{\bullet+}$	−550.68113	−550.77580	−550.74233	167.5	0.783
1d	$HC^+(SH)OCH_2^{\bullet}$	−550.64871	−550.74645	−550.71150	154.3	0.785
1/1d	TS 1,4-H	−550.63153	−550.73193	−550.69478	149.5	0.792
1c	$H_3C{-}OH{-}CS^{\bullet+}$	−550.60180	−550.69976	−550.67068	161.6	0.917
1/1c	TS 1,2-H	−550.56355	−550.66023	−550.62177	144.4	0.801
1b	$HC^+(=S){-}OH{-}CH_2^{\bullet}$	−550.60920	−550.70723	−550.66870	158.7	0.759
1/1b	TS 1,2-H	−550.53751	−550.63399	−550.60798	129.4	0.965
1b/1d	TS 1,3-H	−550.58653	−550.68916	−550.64555	140.6	0.778
1a	$S=C=O{-}CH_3^+ + H^{\bullet}$	−550.61391	−550.70904	−550.66324	134.0	0.750
1e	$CH_3OH^{\bullet+} + CS$	−550.52866	−550.62854	−550.60335	143.6	0.762
1f	$H_2COH^{\bullet} + HCS^+$	−550.59212	−550.69666	−550.65060	146.1	0.759
1g	$H_3CO^{\bullet} + HCS^+$	−550.57780	−550.67650	−550.64371	145.6	0.758
1/1a	TS H-loss	−550.58799	−550.68702	−550.65028	138.2	0.933
2	$HC(=O)SCH_3^{\bullet+}$	−550.67432	−550.77389	−550.73476	155.5	0.789
2d	$HC^+(OH)SCH_2^{\bullet}$	−550.67140	−550.77030	−550.73512	158.5	0.882
2/2d	TS 1,4-H	−550.61796	−550.71604	−550.68902	147.1	0.787
2c	$H_3C{-}SH{-}CO^{\bullet+}$	−550.68768	−550.79008	−550.74806	145.9	0.763
2/2c	TS 1,2-H	−550.63119	−550.73096	−550.68966	151.2	0.797
2b	$HC^+(=O)SH{-}CH_2^{\bullet}$	−550.63620	−550.73865	−550.69626	146.3	0.766
2/2b	TS 1,2-H	−550.59949	−550.70387	−550.65962	140.8	0.792
2a	$O=C=S{-}CH_3^+ + H^{\bullet}$	−550.62848	−550.72728	−550.67702	131.5	0.750
2e	$CH_3SH^{\bullet+} + CO$	−550.67602	−550.77969	−550.73772	141.9	0.763
2f	$H_2CSH^{\bullet} + HCO^+$	−550.59274	−550.69610	−550.64940	133.1	0.764
2g	$H_3CS^{\bullet} + HCO^+$	−550.61963	−550.71753	−550.67445	147.5	0.758
2h	$O=CHSCH_2^+ + H^{\bullet}$	−550.58699	−550.68560	−550.64426	128.7	0.750
2/2a	TS H loss	−550.60826	−550.71155	−550.66313	135.5	0.803
2i	$HCOH^{\bullet+} + CH_2=S$	−550.55746	−550.65370	−550.62095	144.3	0.760
2j	$HCOH + CH_2=S^{\bullet+}$	−550.52443	−550.62955	−550.60187	142.9	0.952

[a] Based on the (U)MP2/6-31G(d,p) geometries. [b] From (U)HF/6-31G(d,p) harmonic vibrational wavenumbers (non-scaled vales).

electric sector and collecting the ions in the fifth field-free region with an off-axis photomultiplier detector.

The low energy CA spectra were obtained in the following way. Mass-selected ions were decelerated to *ca.* 20–30 eV and focused into the quadrupole collision cell pressurized with argon (10^{-3} Torr estimated pressure); after reacceleration at 8 kV, the product ions were separated by scanning the field of the second magnet and collected on the last photomultiplier detector.

In the ion–molecule reactions, the mass-selected ions were decelerated to *ca.* 5 eV and reacted with nitric oxide in the quadrupole collision cell. The reaction products were then reaccelerated and separated as described above; after mass selection with the second magnet, a specific ion–molecule product was collisionally activated and the fragments recorded by scanning the field of the last electric sector.

The alkyl thioformates were prepared according to the literature methods.[8–16]

Results and discussion

Molecular orbital calculations of the $[CH_4OS]^{\bullet+}$ potential energy surface

Let us first describe the portions of the $[CH_4OS]^{\bullet+}$ potential energy surface related to the unimolecular rearrangement of both *O*-methyl and *S*-methyl thioformate ions. *Ab initio* molecular orbital calculations were performed with the aid of the Gaussian94 set of programs.[17] The stationary points were initially located using Hartree–Fock wavefunctions in conjunction with the 6-31G(d,p) basis set. The unrestricted formalism (UHF) was employed for doublet electronic structures. The nature of each stationary point was determined by harmonic vibrational analysis at the same level and, when necessary, the identity of each transition structure (TS) was established by intrinsic reaction coordinate (IRC) calculations. Geometric parameters of the relevant equilibrium and transition structures were then reoptimized at the second-order perturbation level [(U)MP2/6-31G(d,p)]. Subsequently, the schematic potential energy curves connecting various stationary points were constructed from single-point electronic energies calculated using the quadratic configuration interaction method, (U)QCISD(T), with the same basis set and the (U)MP2-optimized geometry. To improve the relative energies, the basis set effect was further considered from UMP2 calculations with the larger 6-311++G(d,p) basis set. Our best estimates were thus obtained from approximate QCISD(T)/6-311++G(d,p) values according to an additivity scheme [eqn. (1)] between the

$$\Delta E(\mathrm{QCISD(T)/L}) = \Delta E(\mathrm{QCISD(T)/S}) + \Delta E(\mathrm{MP2/L}) - \Delta E(\mathrm{MP2/S}) \quad (1)$$

effects of electron correlation and one-electron functions, where L is the larger 6-311++G(d,p) and S the smaller 6-31G(d,p) basis set.

Except for a few radical cation structures, mainly TSs, the UHF wavefunctions for doublet structures are not particularly contaminated by higher spin configurations. The expectation values for $\langle S^2 \rangle$ lie within an acceptable range, being in fact < 0.8. Of the level of theory employed, the accuracy on the relative energies is known to be only moderately high, being about ±12 kJ mol^{-1}. Therefore, we do not put much importance on the quantitative aspect of the energy surface but rather on the relative positions of stationary points that, we believe, are qualitatively correct.

While Table 1 records the total energies of the structures considered at different levels and zero-point energies, Table 2 summarizes the relative energies. Throughout this paper, bond lengths are given in Ångströms and bond angles in degrees, total energy in hartrees, zero-point and relative energies, unless otherwise stated, in kJ mol^{-1}. In general, there are two groups of structures: while the first is related to the *O*-methyl thioformate ion **1**, the second group is associated with the *S*-methyl thioformate ion **2**. Following convention, **X/Y** stands for a TS connecting both equilibrium structures **X** and **Y**.

Rearrangement of *O*-methyl thioformate ion 1. Fig. 1 displays selected UMP2/6-31G(d,p)-optimized geometries of the structures relevant to unimolecular reactions of **1**, whereas Fig. 2 illustrates the potential energy profiles. Parameters of the frag-

Table 2 Calculated relative energies (kJ mol^{-1}) of the $[C_2H_4OS]^{\bullet +}$ radical cations considered[a]

	Structures	UMP2/ 6-31G(d,p)	UMP2/ 6-311++G(d,p)	UQCISD(T)/ 6-31G(d,p)	UQCISD(T)/ 6-311++G(d,p)[b]
1	$HC(=S)OCH_3^{\bullet +}$	0.0	0.0	0.0	0.0
1d	$HC^+(SH)OCH_2^{\bullet}$	73.2	65.2	69.1	61.0
1/1d	TS 1,4-H	114.0	99.0	108.6	93.6
1c	H_3C–OH–$CS^{\bullet +}$	203.0	194.3	182.8	174.2
1/1c	TS 1,2-H	287.9	282.6	295.7	290.5
1b	$HC^+(=S)$–OH–$CH_2^{\bullet}$	180.9	172.1	185.4	176.6
1/1b	TS 1,2-H	342.8	338.0	318.4	313.7
1b/1d	TS 1,3-H	224.2	203.3	229.9	209.0
1a	$S=C=O$–$CH_3^+ + H^{\bullet}$	146.3	145.1	177.5	176.3
1e	$CH_3OH^{\bullet +} + CS$	378.8	365.1	343.4	329.7
1f	$H_2COH^{\bullet} + HCS^+$	214.4	188.5	221.6	195.7
1g	$H_3CO^{\bullet} + HCS^+$	251.6	241.0	239.2	228.6
1/1a	TS H-loss	218.2	206.7	215.3	203.9
2	$HC(=O)SCH_3^{\bullet +}$	7.1	−5.8	9.1	−3.8
2d	$HC^+(OH)SCH_2^{\bullet}$	17.4	6.3	10.8	0.3
2/2d	TS 1,4-H	147.5	138.5	121.6	112.7
2c	H_3C–SH–$CO^{\bullet +}$	−36.6	−56.9	−34.5	−54.8
2/2c	TS 1,2-H	116.4	103.1	123.6	110.2
2b	$HC^+(=O)SH$–$CH_2^{\bullet}$	98.9	78.5	101.9	81.5
2/2b	TS 1,2-H	190.3	164.8	193.1	167.6
2a	$O=C=S$–$CH_3^+ + H^{\bullet}$	105.8	95.0	139.1	128.2
2e	$CH_3SH^{\bullet +} + CO$	−9.6	−33.3	−10.9	−34.6
2f	$H_2CSH^{\bullet} + HCO^+$	201.1	178.3	213.0	190.2
2g	$H_3CS^{\bullet} + HCO^+$	143.5	135.0	160.2	151.7
2h	$O=CHSCH_2^+ + H^{\bullet}$	212.2	201.9	222.6	212.2
2/2a	TS H loss	162.5	139.9	179.1	156.5
2i	$HCOH^{\bullet +} + CH_2=S$	303.8	299.7	297.8	293.7
2j	$HCOH + CH_2=S^{\bullet +}$	389.3	361.9	346.6	319.2

[a] At the level indicated including ZPE corrections (scaled down by 0.9 from UHF values). [b] Using the additivity approximation of eqn. (1).

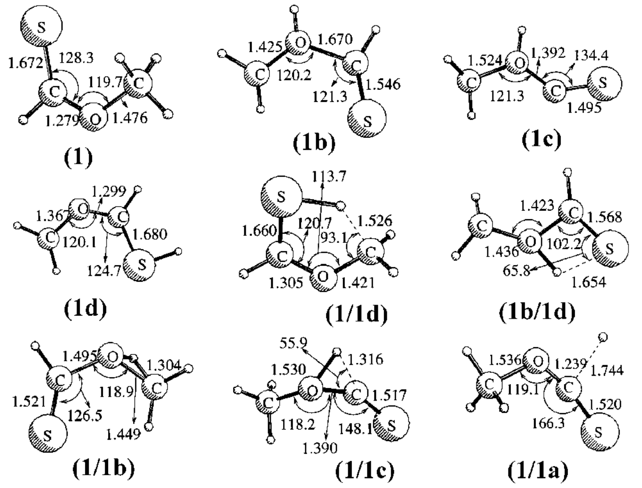


Fig. 1 Selected (U)MP2/6-31G(d,p) geometries of the structures related to *O*-methyl thioformate ion **1**. All structures are positively charged.

ments are omitted for the sake of simplification. Of the four isomeric structures located, the classical form **1** is by far the most stable, lying about 61 kJ mol^{-1} below the distonic ion **1d**. This is in clear contrast to the situation in the oxygen counterpart[7] where the distonic ion $HC^+(OH)OC^{\bullet}H_2$ has been found to be about 43 kJ mol^{-1} more stable than $HC(=O)OCH_3^{\bullet +}$. Both structures **1b** and **1c** result from 1,2-shifts of a hydrogen to oxygen in **1**. While **1b** is actually a distonic species, being a thioformyl derivative of $^{\bullet}CH_2$–OH_2^+, **1c** can best be regarded as an ion–molecule complex resulting from a strong stabilizing interaction between both CS and $CH_3OH^{\bullet +}$ fragments. In fact, the C–O bond which is formally a three-electron bond, turns out to be quite short, being 1.39 Å; that is even shorter than the distance of a single C–O bond (1.43 Å).

Direct fragmentation of **1** *via* an α-cleavage producing $HCS^+ + H_3CO^{\bullet}$ **1g** is rather a difficult process, which is somewhat less favoured than hydrogen loss along the C–H bond yielding $S=C=O^+$–$CH_3 + H^{\bullet}$ **1a**. For its part, the 1,4-H shift connecting **1** to **1d** is a rather facile process, whereas a further 1,3-H shift of **1d** through **1d/1b** is much more energetically demanding. Due to the higher energy of **1d/1b**, relative to the fragments **1f**, the distonic **1b** is, once formed, readily dissociated into $HCS^+ + {}^{\bullet}CH_2OH$ **1f** without additional activation energy.

It is equally remarkable that the one-step 1,2-H shift from C to O *via* **1/1b** is substantially more difficult to achieve than the two-step route consisting of a 1,4-H shift from C to S *via* **1/1d** and the reverse *via* a 1,3-H shift form S to O **1d/1b**. Similarly, the direct 1,2-H shift from C to O through **1/1c** is also a significant high-energy step. As mentioned above, **1c**, formally an ion–molecule complex, is quite stable with respect to bond cleavage, making the route **1**→**1c**→**1h** hardly operative.

Within the expected accuracy of our calculations, the three channels including α-cleavage **1**→**1g**, H-loss **1**→**1a** and **1**→**1d**→**1b**→**1f** could be regarded as competitive. Formation of H_2C–OH is probably somewhat favoured over that of its H_3C–O isomer.

Rearrangements of *S*-methyl thioformate ion 2. While Fig. 3 records the geometrical parameters, Fig. 4 shows the schematic energy profiles related to unimolecular isomerization and fragmentation of **2**. It turns out that *S*-methyl thioformate ion **2** is marginally more stable by 4 kJ mol^{-1} than its *O*-methyl counterpart **1**. In contrast, the distonic ion **2d** resulting also from a 1,4-H shift from **2** has a similar energetic content, being 4 kJ mol^{-1} higher than **2**. The corresponding TS **2/2d** is also higher in energy than **1/1d**.

Relative to the *O*-methyl counterpart **1b** and **1c**, the distonic ion **2b** and the ion–molecule complex **2c** are strongly stabilized, in particular **2c**. This is due to the higher stability of the CO molecule. While the complex **2c** is not at all stable with respect to fragmentation, the distonic **2b** lies now in a deeper potential well, suggesting a certain possibility for its observation. The C–S bond cleavage is also barrier-free producing $^{\bullet}CH_2SH + HCO^+$.

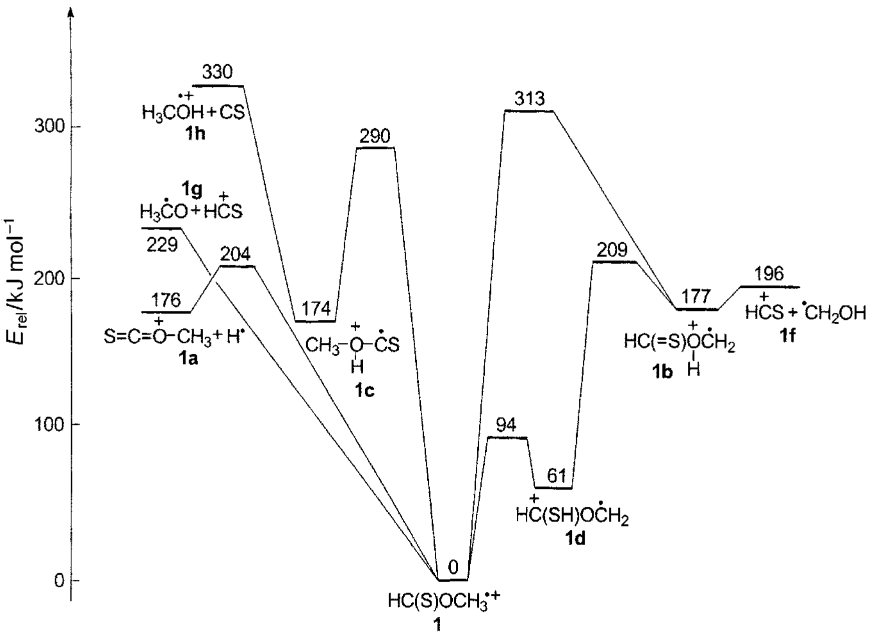


Fig. 2 Schematic energy profiles showing the unimolecular rearrangements of *O*-methyl thioformate ion **1**. Values are obtained from approximately UQCISD(T)/6-311++G(d,p) + ZPE calculations (kJ mol^{-1}).

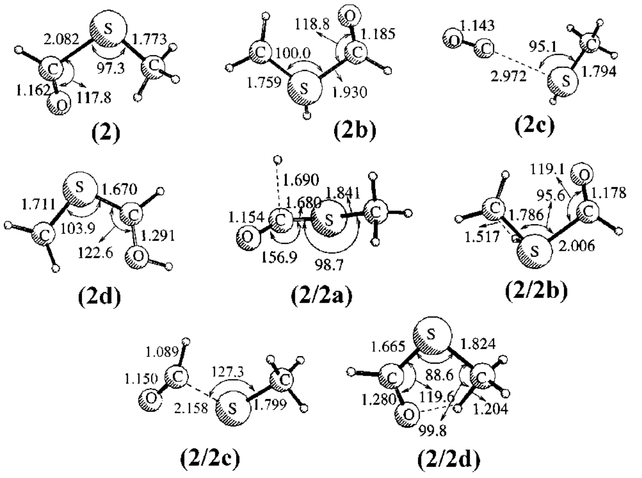


Fig. 3 Selected (U)MP2/6-31G(d,p) geometries of the structures related to *S*-methyl thioformate ion **2**. All structures are positively charged.

The H-loss along the C(=O)–H bond occurs through TS **2/2a**, but it is still much easier to achieve than that along the barrierless methyl C–H cleavage. In this case, a direct 1,2-H shift from C to S connecting **2** to **2b** becomes more reasonable in terms of barrier height. On the contrary, a 1,3-H shift connecting **2** and **2b** could not be found. We have not identified a simple rule governing the behaviour of hydrogen migrations in these ion species.

Overall, the CO elimination constitutes the most obvious fragmentation of the ion **2**. The low-energy ion–molecular complex **2c** is apparently involved in the process but is not stable at all. The distonic species **2d** is a low-energy isomer and should be stable with respect to unimolecular decompositions. To a lesser extent, the distonic ion **2b** is a high-energy but detectable isomer. The C–S distance in **2b** is also markedly short, being only 1.93 Å as compared with that of 2.08 Å in **2**.

Starting from **2**, the α-cleavage giving $CH_3S^•$ + HCO^+ **2g** appears to be barrier-free and less energetic than the whole process leading to the isomeric $^•CH_2SH$ + HCO^+ system **2h**. Thus, in this case, formation of $CH_3S^•$ is somewhat favoured over that of $^•CH_2SH$, in contrast with the situation in the pair $CH_3O^•$/$^•CH_2OH$ generated from **1** as discussed above.

Mass spectrometric results

We now turn to the experimental results recorded using different mass spectrometric techniques. The thioformates **I**–**IV** used to generate the *m*/*z* 76 ions are shown in Scheme 1, which also indicates the relative abundance in the 70 eV electron ionization mass spectra (values in parentheses). Based on the observation that an intense loss of propene occurs in the case of isobutyl formate,[6] it was hoped that similar behaviour should be observed for **III** and **IV**.

High energy collisional activation spectra. The high energy (8 keV) CA spectra of both molecular ions of **I** and **II** are compared in Fig. 5. While the base peak at *m*/*z* 45 (HCS^+, thioformyl ions) upon ionization of **I** is in agreement with the occurrence of stable ions **1**, the peak at *m*/*z* 29 and the cluster at *m*/*z* 48–46 require partial and/or post-collisional isomerization. In the case of **II**, the CA spectrum indicates extensive isomerization of the primary ion **2** as the major fragment ions correspond to $CH_3SH^{•+}$ (*m*/*z* 48) ions and the products of their consecutive fragmentations (*m*/*z* 47 and 45). *Ab initio* MO results discussed above are thus consistent with the predominant loss of CO from **2**.

Neutralization–reionization (NR) experiments. Consecutive collisions of the *m*/*z* 76 ions **1** and **2** with ammonia and oxygen afford the NR mass spectra shown in Fig. 6. An important difference between these spectra lies in the much stronger intensity of the recovery signal corresponding to survivor ions seen in the case of **1**. This recovery signal can be attributed to the stable *O*-methyl thioformate radical cations **1**. The situation is clearly different for the isomeric ion **2**: the recovery signal is of very low intensity and a new peak corresponding to the reionization of CO is seen at *m*/*z* 28. We suggest that the recovery signal is attributable to stable *S*-methyl thioformate ions **2**, while the peaks at *m*/*z* 48 and 28 could be due to the ion complex species **2c** which dissociates spontaneously upon neutralization.

Isobutyl thioformates III and IV. An intense loss of propene is manifested in the mass spectrum of **IV**; both CA and NR spectra of the resulting *m*/*z* 76 ions do not significantly differ from those of **II**.[18] Nevertheless a characteristic loss of 14 daltons (loss of CH_2, *m*/*z* 62) and the intensification of the charge stripping peak at *m*/*z* 38 in the CA spectrum are worthy of note. These features indicate that the loss of propene starting from **IV** has produced distonic ions **2d**, H–C^+(OH)SC$^•H_2$,

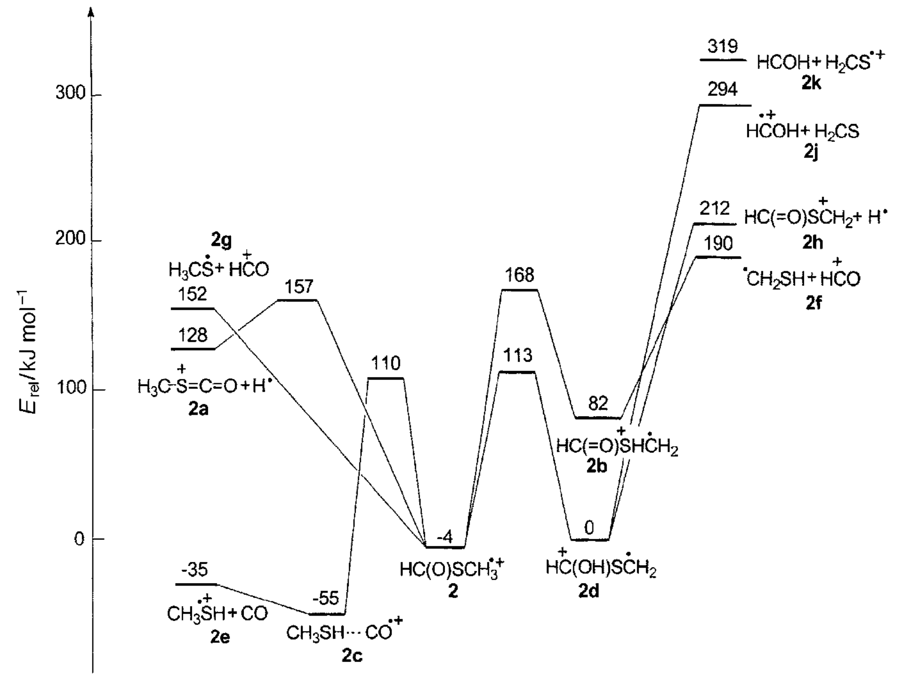


Fig. 4 Schematic energy profiles showing the unimolecular rearrangements of *S*-methyl thioformate ion **2**. Values are obtained from approximate UQCISD(T)/6-311++G(d,p) + ZPE calculations (kJ mol^{-1}).

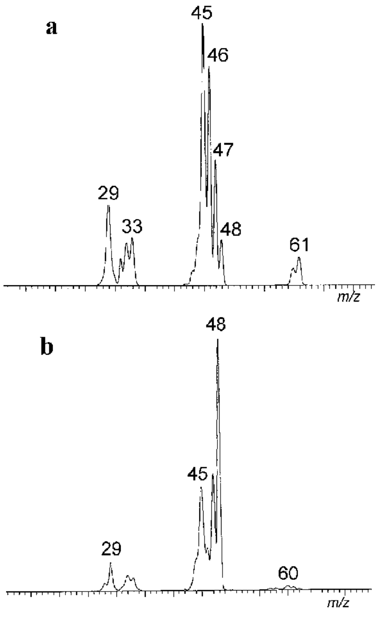
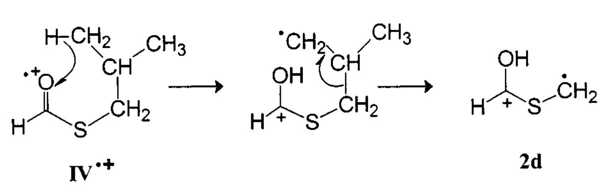


Fig. 5 CA (O_2) spectra of the *m*/*z* 76 ions generated by ionization of the isomeric methyl thioformates: (a) *O*-methyl thioformate **I** and (b) *S*-methyl thioformate **II**.



Scheme 2

probably generated according to the mechanism shown in Scheme 2.

Unfortunately, the loss of propene is of low abundance in the mass spectrum of the isomeric isobutyl thioformate **III** precluding the recording of 'pure' MS/MS data. This is probably due to the fact that the expected $H–C^+(SH)OCH_2CH(CH_3)CH_2^•$ intermediate ions are less stable than the isomeric distonic ions shown in Scheme 2. It is indeed known that OH bonds have a stabilizing effect on radical cations (as compared to CH bonds),[4] while SH bonds should have a destabilizing effect.

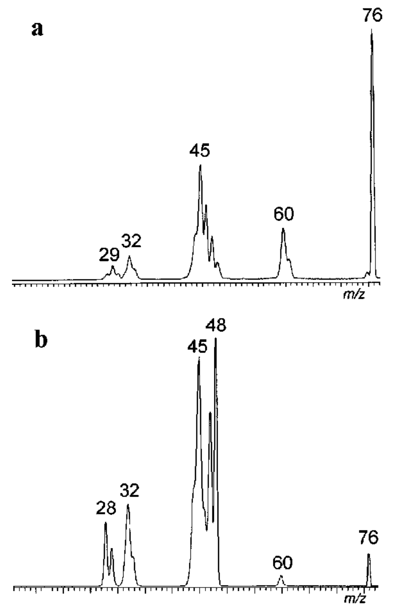


Fig. 6 NR (NH_3/O_2) spectra of the *m*/*z* 76 ions generated by ionization of the isomeric methyl thioformates: (a) *O*-methyl thioformate **I** and (b) *S*-methyl thioformate **II**.

Low energy collisional activation spectra. When beams of decelerated (*ca.* 20–30 eV) *m*/*z* 76 ions generated by ionization of *S*-methyl and *S*-isobutyl thioformates **II** and **IV** collide with argon in the radiofrequency only quadrupole collision cell, fragmentation occurs giving mainly intense peaks in the *m*/*z* 48–45 region in both cases. The spectra were nevertheless found to be different as the significant peak at *m*/*z* 29 (formyl ions) for $\mathbf{II}^{•+}$ is replaced by an intense peak at *m*/*z* 62 (loss of CH_2) for the $[\mathbf{IV} - C_3H_6]^{•+}$ ions.[18] This loss of carbene, already observed (but to a lesser extent) in the high energy CA spectra, strongly suggests that these last ions have the distonic structure **2d**, $HC^+(OH)SC^•H_2$. The peak at *m*/*z* 29 can be seen as arising from the 'classical' structure **2**, $HC(O)SCH_3^{•+}$, or from an ion–molecule complex such as $H_3CSH^{•+}/CO$ **2c**. Peaks at *m*/*z* 29 and 62 are not observed in the low energy CA spectrum of

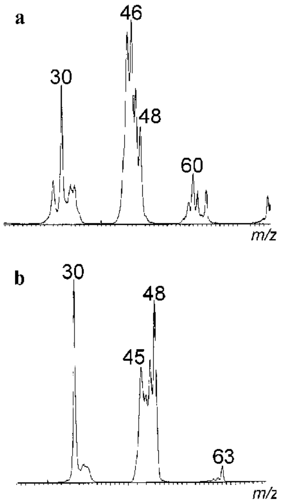


Fig. 7 High energy CA(N_2) spectrum of the *m*/*z* 78 ions generated by: (a) ion–molecule reaction of the *m*/*z* 76 ions of *S*-methyl thioformate **II** and nitric oxide, and (b) chemical ionization of a mixture of nitric oxide and methanethiol.

ions **1**; the loss of a methyl group corresponds in this case to an intense process (*m*/*z* 61).

Ion–molecule reactions with nitric oxide. The use of nitric oxide was envisaged because this reagent has proved to be valuable for the identification of ions presenting a distonic character. For instance, $^{\bullet}CH_2–X^+–CH_3$ (X = Cl, Br) distonic ions, unlike their conventional $CH_3CH_2X^{\bullet +}$ isomers, react with NO producing CH_2NO^+ cations.[19] Radical cations derived from 1,2-dipoles were also found to react efficiently with NO.[20–22]

Mass-isolated *m*/*z* 76 ions derived from **II** and **IV** react mainly with NO by charge exchange (*m*/*z* 30, NO^+); CH_2NO^+ ions are not observed but, instead, a weak peak is seen at *m*/*z* 78 corresponding formally to the replacement of CO by NO in the *m*/*z* 76 precursor ions; this process appears slightly more efficient for *S*-methyl thioformate **II** and sensitivity was found high enough in this case to allow the recording of a high energy CA spectrum of these peculiar *m*/*z* 78 ions [Fig. 7(a)]. The latter spectrum is characterized by an intense signal at *m*/*z* 30 for NO^+ ions and intense peaks at *m*/*z* 48–45 which can be ascribed to $CH_3SH^{\bullet +}$ ions and products of consecutive decompositions; this indicates that an ion–molecule complex such as $CH_3SH^{\bullet +}$/CO is actually produced in the experiment. The high intensity of the *m*/*z* 46 peak is, however, unexpected. As a matter of fact, when a mixture of nitric oxide and methanethiol is ionized in a chemical ionization source, *m*/*z* 78 ions are readily produced and their CA spectrum [depicted in Fig. 7(b)] is now in complete agreement with the production of the complex formed from interaction of $CH_3SH^{\bullet +}$ and NO. Due to the similar ionization energies of NO and CH_3SH, peaks associated with the corresponding ions are indeed produced in a competitive manner, following collisional activation.[23] Formation of *m*/*z* 46 ions is not a dominant process. It can therefore be proposed that the *m*/*z* 78 ions generated from **II** may either contain the ion–molecule complex mixed with isomeric ions or simply consist of another isomeric species such as $HO^+{=}N–SCH_3$. Whatever the actual structure of the *m*/*z* 78 ions could be, the fact that the NO radical undergoes a displacement against CO through an unknown complex leads us to believe that part of the *m*/*z* 76 ions generated by ionization of **II** are ion–molecule complexes connecting $CH_3SH^{\bullet +}$ radical cation to neutral CO molecule.

Concluding remarks

A combination of collisional activation, neutralization–reionization and ion–molecule reaction experiments has been used to characterize various $[C_2H_4OS]^{\bullet +}$ radical cations derived from *S*-alkyl thioformate precursors, and the results suggest the occurrence of distonic ions and ion–molecular complexes, in addition to the production of more classical structures. Concerning ionized *O*-methyl thioformate derivatives, although the corresponding distonic ion **1d** is actually less stable than its classical isomer **1**, it is likely to play the role of a key intermediate in the generation of $^{\bullet}CH_2OH$. For this system, H loss is a more competitive channel than HCS^+ elimination. Overall, results obtained from *ab initio* MO calculations are consistent with the experimental observations and thus lend further theoretical support. Calculations also point out the completely different gas phase ion chemistries of *O*-methyl **1** and *S*-methyl thioformate **2** radical cations.

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