

RCM

Letter to the Editor

To the Editor-in Chief
Sir,

The gas phase sulfur-containing distonic radical cation $\text{HC}^+(\text{OH})\text{SC}^-\text{H}_2$

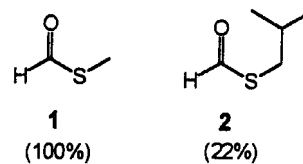
Many unimolecular fragmentations observed in the field-free regions of mass spectrometers do not occur directly from the initial ionized molecules, but involve several preliminary isomerizations to reactive intermediates as critical steps of the fragmentation mechanism. Two types of reactive intermediates are usually identified: distonic ions^{1,2} and ion/neutral complexes.³ Distonic ions are species where the charge and radical sites are centered at different atoms.⁴ Such radical ions are known in mass spectrometry and radiation chemistry.¹ In the last decade, these ions have gained considerable experimental interest^{1,2} due to the fact that calculations⁵ predicted that many exhibit thermodynamic stability equal to, if not larger than, the corresponding conventional isomers. In previous work,⁶ we have shown that the distonic radical cation $\text{HC}^+(\text{OH})\text{OC}^-\text{H}_2$, an isomer of ionized methyl formate $\text{HC}(\text{=O})\text{OCH}_3^+$, can be generated by fragmentation of ionized isobutyl formate upon loss of propene. Identification of the distonic structure was based on collisional activation (CA) and neutralization-reionization (NR) mass spectrometry and further supported by MO calculations.⁷ Evidence for the distonic species has also been found in the low energy CA spectrum featuring an intense loss of water, not observed for the classical species.⁸

Recently, we have prepared and studied a large series of alkyl thioformates, either *O*-alkyl or *S*-alkyl derivatives. Their behaviour upon electron impact was investigated by

using tandem mass spectrometry methodologies and several complex rearrangement reactions were identified and rationalized with the aid of molecular orbital calculations.^{9,10,11,12,13} In the present paper, the structural identification of m/z 76 ions having the $[\text{C}_2\text{H}_4\text{O}_2\text{S}]^+$ composition is reported. These are derived from direct electron ionization of *S*-methyl thioformate **1** and dissociative ionization (loss of propene) of *S*-isobutyl thioformate **2**. These latter ions correspond to the sulfur-containing distonic radical cation, $\text{HC}^+(\text{OH})\text{SC}^-\text{H}_2$.

The spectra were recorded on a large scale tandem mass spectrometer of EBEEBE geometry (E-electric sector and B-magnetic sector) fitted with five collision cells and, in its hybrid configuration, with an additional rf-only quadrupole collision cell. The characteristics of the mass spectrometer and general conditions of experiments are as presented in previous papers.^{14–16} Collisional activation (CA) and neutralization-reionization (NR) spectra were recorded by scanning the field of the third 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 (EBE) 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 to 8 kV, the product ions were separated by scanning the field of the second magnet and collected on the final photomultiplier detector. In our ion-molecule reaction studies, 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 **1** and **2** were prepared according to literature methods.^{10,17}

The thioformates used to generate the m/z 76 ions are shown in **1** and **2** along with the relative abundance of m/z 76 ions in the 70 eV electron ionization mass spectra (values in parentheses).



METASTABLE ION (MI) REACTIONS

The MI spectrum of ionized *S*-methyl thioformate **1** features an intense peak at m/z 48 corresponding to loss of CO. The daughter ions generated from metastable parent ions have therefore the elemental composition $[\text{C}_2\text{H}_4\text{S}]$. Theory and experiment have established that two distinguishable $[\text{C}_2\text{H}_4\text{S}]^+$ ions exist, namely, the conventional form CH_3SH^+ and the distonic species $\text{CH}_2\text{S}^+\text{H}_2$. The former was found to be the more stable isomer by 86 kJ/mol.⁵ The CA spectra of these two isomers have already been reported¹⁸ and found to be very similar. However, we have observed¹² that the $[\text{C}_2\text{H}_4\text{S}]^+$ ions generated by the loss of CO from metastable $\text{HC}(\text{O})\text{SCH}_3^+$ [**1**⁺] are CH_3SH^+ ions rather than the distonic isomers.

HIGH ENERGY COLLISIONAL ACTIVATION SPECTRA

In the high energy (8 keV) CA spectrum of **1**, the low-energy process corresponding to the formation of m/z 48 ions, is still very abundant, but other signals of high intensity are now seen at m/z 47–44 and m/z 29 (HCO^+). Minor peaks are observed at m/z 60–61 related to losses of CH_4 , CH_3 . The intensity distribution of the m/z 47–44 peaks is similar to that of ionized methanethiol itself (Fig. 1(a)). Although the data recorded for the m/z 76 ions generated from **2**⁺ do not very significantly differ from those of **1**⁺ (Fig. 1(b)), a closer inspection of the low intensity signals at m/z 63–56 and 39–27 emphasizes clearly that a different type of ion (or a mixture of ions) is in fact generated. In particular, the characteristic loss of 14 Da (loss of CH_2 , m/z 62), the increase of intensity of the charge stripping (CS) peak at m/z 38 and the peak at m/z 58, corresponding to the loss of water, are worthy of note. These features leave no doubt that the loss of propene starting with **2**⁺ has produced the distonic ions a H-

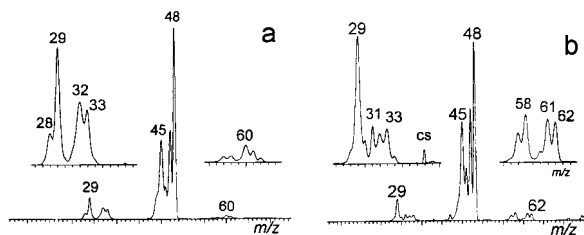
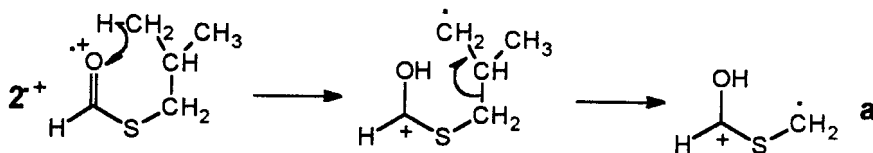


Figure 1. CA spectra of the m/z 76 ions generated by ionization of the *S*-methyl thioformate **1** (a) and dissociative ionization of *S*-isobutyl thioformate **2** (b). The insets show expanded views of the m/z 63–56 and 39–27 regions.



Scheme 1.

$C^+(OH)SCH_2^+$, rather than its isomer $HC(=O)SCH_3^+$. A plausible mechanism is depicted in Scheme 1.

NEUTRALIZATION-REIONIZATION EXPERIMENTS

The NR spectrum of 1^+ , obtained by neutralization with ammonia, followed by reionization of the intermediate neutral with oxygen, shows a recovery signal with a very low intensity and a new peak corre-

sponding to the reionization of CO lost in the metastable fragmentation is seen at m/z 28. It is proposed that the recovery signal is attributable to stable *S*-methyl thioformate ions 1^+ , while the peaks at m/z 48 and 28 are due to another species which dissociates spontaneously upon neutralization. To a good approximation, the NR spectra of the m/z 76 ions of 2^+ and 1^+ , shown in Fig. 2, present the same differences as those

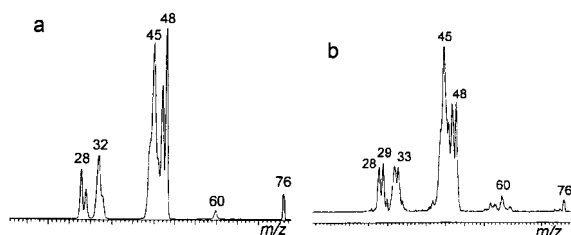


Figure 2. NR (NH_3/O_2) spectra of the m/z 76 ions generated by ionization of *S*-methyl thioformate **1** (a) and dissociative ionization of *S*-isobutyl thioformate **2** (b).

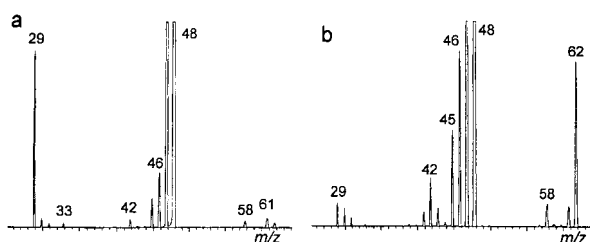


Figure 3. Low energy CA (Ar) spectra of the m/z 76 ions generated from **1** (a) and **2** (b). Peaks at m/z 48 and 47 are off scale.

observed in their CA spectra. However, the more significant differences between both NR spectra originate most probably from the neutralized distonic ion **a**, i.e. the diradical $HC^+(OH)SCH_2^+$, which is an unstable complex and ought to decompose into HCOH and SCH_2 . This may explain the appearance of the peak at m/z 30 ($HCOH^+$) and the increasing of intensity of the peak at m/z 46 (SCH_2^+) in the NR spectrum of m/z 76 ions of 2^+ .

LOW ENERGY COLLISIONAL ACTIVATION SPECTRA

Decelerated ions (*ca.* 20–30 eV) of m/z 76, generated by ionization of *S*-methyl **1** and *S*-isobutyl **2** thioformates, are allowed to collide with argon in the rf only quadrupole collision cell, and fragmentation is observed to occur giving intense peaks in the region m/z 48–45 both from **1** and **2** (Fig. 3). The spectra were nevertheless found to be different as the significant peak at m/z 29 (formyl ions) for 1^+ is replaced by an intense peak at m/z 62 (loss of CH_2) for the $[2-C_3H_6]^+$ ions. This loss of a carbene, already observed but to a lesser extent in the high energy CA spectra, strongly suggests that these latter ions have the distonic structure **a**, $HC^+(OH)SCH_2^+$. The peak at m/z 29 can be ascribed to the classical structure 1^+ , $HC(O)SCH_3^+$, and/or to an ion-molecule complex such as **b**, $[H_3CS^+H-CO]$.

ION-MOLECULE REACTION WITH NITRIC OXIDE

Ion-molecule reactions of both ions **a** and 1^+ with nitric oxide (NO) carried out in the quadrupole collision cell show that in the reaction of 1^+ , a peak is seen at m/z 78 corresponding formally to a replacement of CO for NO in the m/z 76 precursor ions. The CA spectrum of the peculiar m/z 78 ions is characterized by an intense signal at m/z 30 for NO^+ and intense peak at m/z 48–45 which can be ascribed to CH_3SH^+ ions and consecutive fragmentation products [Relative intensities of the major peaks (m/z , %): 48(72), 47(81), 46(100), 45(90), 30(91)]. These data strongly suggest that part of the m/z 76 ions generated upon ionization of **1** may correspond to the complexes **b**. In the reaction of **a**

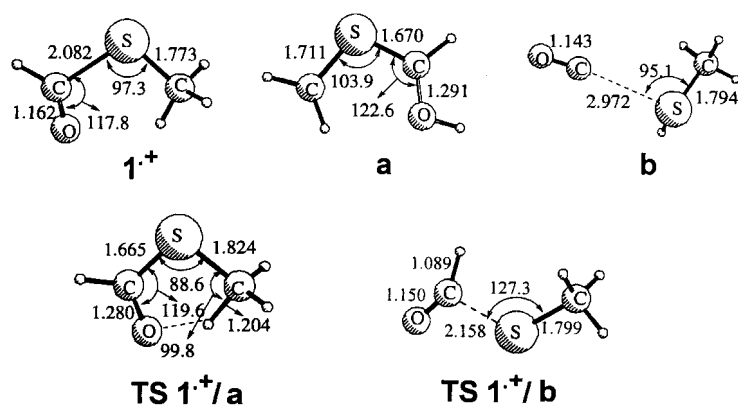


Figure 4. Selected (U)MP2/6-31G(d,p)-geometries of the structures of the *S*-methyl thioformate ion 1^+ , the distonic isomer **a**, the ion-molecule complex **b** and the transition structures TS $1^+/a$ and TS $1^+/b$.

with NO^\cdot , the m/z 78 ions are still formed but with a reduced efficiency. No peak corresponding to H_2CNO^+ was recorded.

AB INITIO MOLECULAR ORBITAL CALCULATIONS

In order to gain some quantitative information on the relative stability between the radical cations considered in this work, we conducted ab initio molecular orbital calculations using the Gaussian 94 set of programs.¹⁹ Initial geometry optimization and characterization by harmonic vibration analysis were done at the unrestricted Hartree-Fock level (UHF) with the 6-31 G(d,p) basis set. Geometries of the relevant structures were then reoptimized using second-order perturbation theory (UMP2) (Fig. 4). To improve relative energies, single-point electronic energies were obtained using quadratic configuration interaction methods, (U)QCISD(T), using the larger 6-311++G(d,p) basis set.

Relative energies of 1^{++} , **a**, **b** and both transition structures $1^+/a$ and $1^+/b$, together with those of fragmentation products, are collected in Table 1. The adiabatic ionization energy of *S*-methyl thioformate is estimated to be $\text{IE}_a(1) = 9.7$ eV, with a probable error of ± 0.3 eV on the basis of (U)QCISD(T) results along with an empirical correction.²⁰ Due to the fact that most of the MO methods consistently underestimate the IE_a 's, as compared with experimental values, the correction scheme simply consists of applying a systematic and appropriate correction to the calculated values. As far as the (U)QCISD(T)/6-311++G(d,p) level is concerned, we have found that a systematic correction of +0.3 eV needs to be added to the calculated IE_a 's in order to obtain realistic estimates for this quantity.

A few points can be noted when inspecting Table 1. The calculated results indicate that the distonic species **a** is slightly higher in energy than its classical isomer 1^+ , whereas

the complex **b** resulting formally from interaction of CH_3SH^+ and CO is more stable by 51 kJ/mol than 1^+ . Starting from 1^+ , when a CO-elimination occurs, a small fraction of the distonic species **a** is expected to be formed due to the small difference in energy between both transition structures $1^+/a$ and $1^+/b$. It is thus likely that a mixture of ions, including the classical 1^+ , the distonic **a** and the complex **b** are present upon ionization of **1**. Moreover, starting from the distonic species **a**, a partial isomerization can also give rise to 1^+ in a primary step. This is in line with the detection of a small amount of 1^+ upon direct production of **a**. Formation of **b** from **a** is also possible but needs to involve a two-step process via 1^+ . This may be more difficult to detect due to the small amount of 1^+ . These indications are not in conflict with experimental observations reported above, in particular with the reduced efficiency of a CO/NO exchange in the ion-molecule reaction of m/z 76 ion produced from **2** with NO^\cdot gas. Finally, a loss of hydrogen from 1^+ yielding methylated carbon oxysulfide, $\text{H}_3\text{C-S=C=O}^+$, m/z 75, is also competitive with the C-S bond cleavage producing formyl ions, HCO^+ (m/z 29), but both processes are more energy demanding.

In summary, the tandem mass spectrometric experiments suggest that the distonic species $\text{HC}^+(\text{OH})\text{SCH}_2^\cdot$ **a** (m/z 76) has been generated for the first time, upon ionization of *S*-isobutyl thioformate **2**. A minor amount of the ions observed are expected to be its more conventional isomer, ionized *S*-methyl thioformate, 1^+ . Inversely, upon ionization of **1**, the conventional isomer 1^+ also partially isomerizes not only to the distonic **a** but also to an ion-molecule complex $[\text{H}_3\text{CSH-CO}]^+$ **b**, which is an ultimate species, as observed in MI experiments.

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Table 1. Relative energies (kJ/mol) obtained from (U)QCISD(T)/6-311++G(d,p) // (U)MP2/6-31G(d,p) + ZPE calculations

Structures	Relative energies
$\text{H}_3\text{CS}^+\text{H}^\cdot\text{CO}$ (b)	-51
$\text{H}_3\text{CSH}^+ + \text{CO}$	-31
$\text{HC(=O)S}^+\text{CH}_3$ (1^+) ^a	0
$\text{HC}^+(\text{OH})\text{SC}^\cdot\text{H}_2$ (a)	4
TS $1^+/b$	114
TS $1^+/a$	117
$\text{O=C=S}^+\text{-CH}_3 + \text{H}^\cdot$	132 (TS 161)
$\text{CH}_3\text{S}^\cdot + \text{HC}^+=\text{O}$	156
$\text{HC(=O)SCH}_2^+ + \text{H}^\cdot$	216
$\text{HC}^+\text{OH} + \text{H}_2\text{C}=\text{S}$	298

^a Vertically ionized **1**: 33 kJ.mol⁻¹.

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