PERKIN 2

# Formation and characterization of methoxy isothiocyanate ($CH_3ON{=}C{=}S$) and methyl cyanate *N*-sulfide ($CH_3OC{\equiv}N^+{-}S^-$) as radical cations and neutrals in the gas phase

**Robert Flammang,**[*a] **Pascal Gerbaux,**[a] **Monique Barbieux-Flammang,**[a] **Carl Th. Pedersen,**[*b] **Allan T. Bech,**[b] **Eva H. Mørkved,**[c] **Ming Wah Wong**[d] **and Curt Wentrup**[*e]

[a] *Organic Chemistry Laboratory, University of Mons-Hainaut, B-7000 Mons, Belgium. E-mail: robert.flammang@umh.ac.be*
[b] *Department of Chemistry, Odense University, DK-5230 Odense, Denmark*
[c] *Department of Organic Chemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway*
[d] *Department of Chemistry, National University of Singapore, 119260 Kent Ridge, Singapore*
[e] *Department of Chemistry, The University of Queensland, Brisbane, QLD 4072, Australia. E-mail: wentrup@chemistry.uq.edu.au*

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Dissociative ionization of heterocyclic precursors has provided a convenient source of isomeric $[CH_3O,C,N,S]^{\cdot+}$ radical cations. Metastable ion (MI), collisional activation (CA), neutralization–reionization (NR) spectra, and ion–molecule reactions, performed in a hybrid tandem mass spectrometer of sectors–quadrupole–sectors configuration, have demonstrated the isothiocyanate, $CH_3ON{=}C{=}S^{\cdot+}$ **a**, and the nitrile *N*-sulfide, $CH_3OC{\equiv}N{-}S^{\cdot+}$ **b**, connectivities. For the sake of comparison, a potential precursor of the isocyanate, $CH_3SN{=}C{=}O^{\cdot+}$ **c**, was also investigated. The gas phase stability of the corresponding neutral molecules is indicated by the NR and NR/CA spectra. In addition, consecutive collisional activation processes (MS/MS/MS spectra) were used to characterize the structures of metastable ions which, in several cases, were found to be different from the corresponding ions generated in the ion source. Calculated ionization energies and enthalpies of reaction with $NO^{\cdot}$ (at the G2(MP2,SVP) level) support the experimental characterization of ions **a** and **b**.

## Introduction

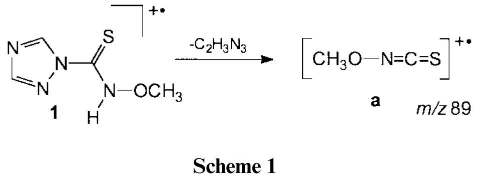
Alkoxy isothiocyanates, RO–N=C=S, have represented an unknown class of compounds until now. Whereas 5-aryl-1,2,3,4-thiatriazoles decompose thermally and photochemically to nitriles, $N_2$, and sulfur together with varying amounts of isothiocyanates, RNCS,[1,2] the same type of reaction is not observed for the 5-alkoxy- and 5-aryloxythiatriazoles. The latter compounds decompose at or near room temperature to afford cyanates, ROCN, $N_2$, and sulfur, and by performing this reaction in the gas phase, it was shown that the extremely unstable molecule $N_2S$ is formed first. $N_2S$ decomposes in a bimolecular process ($2\ N_2S \rightarrow 2N_2$ and $S_2$) even in the high vacuum conditions used in flash-vacuum pyrolysis.[2] No alkoxy isothiocyanates, RONCS, were detectable during the decomposition of 5-alkoxythiatriazoles, or on reaction of *O*-alkylhydroxylamines with thiophosgene.[3] However, it is to be expected that these compounds will be extremely unstable, and we have therefore undertaken an investigation using gas phase and matrix isolation techniques. We have succeeded in the identification of alkoxy isothiocyanates from different precursors by means of mass and IR spectroscopy.[4] In this paper we report the MS investigation of MeONCS radical cation as well as neutralization–reionization experiments which confirm the existence of the neutral species. The isomeric nitrile sulfide, MeOCNS, is also described. All the experiments reported here were performed in a single hybrid instrument of sectors–quadrupole–sectors configuration.

## Results and discussion

### Mass spectrometric experiments

The connectivities of nitrile *N*-sulfides (RCNS) and the isomeric isothiocyanates (RNCS) have been shown to be readily differentiated by collisional activation (CA) mass spectrometry.[5] Ion–molecule reactions using nitric oxide as the reagent have also been shown to be versatile for the identification of these isomers: the ionized *N*-sulfides react with the production of $ONS^+$ (*m*/*z* 62),[6] whereas the corresponding ionized isothiocyanates react mainly by charge exchange in reactions governed by the relative ionization energies.[7]

Radical cations of the composition $C_2H_3NOS$ can be prepared efficiently in the gas phase by dissociative ionization of the triazolide **1** (Scheme 1) and give rise to the base peak in the electron ionization mass spectrum. Based on the nature of this precursor molecule, it is tentatively proposed that these ions represent the hitherto unknown methoxy isothiocyanate structure, $CH_3ON{=}C{=}S^{\cdot+}$ **a**.



Scheme 1

**Table 1** MI, CA and NR spectra of the *m*/*z* 89 ions generated by dissociative ionization of **1**–**3**. Abundances (%) relative to the most intense peak (peaks less than 10% are not indicated)

| | | *m*/*z* (Relative abundances) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compounds | | **89** | **74** | **61** | **59** | **58** | **47** | **46** | **45** | **44** | **43** | **42** | **32** | **30** | **29** | **28** |
| **1** | MI | | 100 | | 79 | | | | | | | | | | | |
| | CA | | 52 | | 100 | 61 | | 16 | | 18 | | | 28 | 31 | 20 | |
| | NR | 32 | | | 30 | 100 | | | | 44 | | | 61 | 16 | 21 | |
| **2** | MI | | 43 | 100 | | | | | | | | | | | | |
| | CA | | 100 | 19 | | 20 | | 61 | | | | | 18 | | | |
| | NR | 18 | 33 | | | 27 | | 100 | | | | 22 | 87 | 10 | 14 | 11 |
| **3** | MI | | | 100 | | | 13 | 17 | | | | | | | | |
| | CA | | | | | | | 100 | 39 | 33 | 18 | | | | | |
| | NR | 8 | | | | | | 100 | 77 | 45 | 54 | 46 | 24 | | | 17 |

This proposal is supported by the metastable ion (MI) spectrum of the *m*/*z* 89 ions, featuring two peaks at *m*/*z* 74 and 59 (1.27 abundance ratio) corresponding to losses of a methyl radical and formaldehyde, respectively (Table 1). The former reaction appears (erroneously, as shown below) to be a simple cleavage fragmentation, while the loss of formaldehyde is the result of a rearrangement process not unexpected for an oxime methyl ether. However, MS/MS/MS analysis of the metastably produced *m*/*z* 59 ions indicates that they do not correspond to "pure" $HNCS^{\cdot+}$ ions, as the relative abundances of the *m*/*z* 46–45–44 peaks differ from those measured for $HNCS^{\cdot+}$ and $HCNS^{\cdot+}$ ions.[5b] Preliminary calculations (*vide infra*) suggest that the metastable reaction proceeds *via* a $[CH_2{=}O\cdots NC(S)H]^{\cdot+}$ complex with the production of thiazirine radical cations.

A similar MS/MS/MS experiment performed on metastable *m*/*z* 74 ions also indicates that they do not possess the expected ONCS connectivity, but instead the OCNS connectivity. Indeed, the base peak in the spectrum is due to $NS^+$ ions (loss of CO), and the loss of the methyl group must therefore be preceded by a rearrangement reaction.

Whatever the nature of the rearrangement mechanisms occurring in the low energy metastable ions, the MI spectrum firmly demonstrates the presence of a methyl group which can be further defined as a methoxy group given the observed competitive loss of formaldehyde.

In the collisional activation (CA) spectrum, new intense peaks are observed at *m*/*z* 58 ($CNS^+$), 32 ($S^{\cdot+}$), 30 ($CH_2O^{\cdot+}$) and 29 ($HC^+{=}O$) and, to a lesser extent, at *m*/*z* 44 ($CS^{\cdot+}$) and 46 ($NS^+$). The detection of *m*/*z* 58, 44 and 32 fragment ions is in agreement with the proposed isothiocyanate structure **a**, but the other fragments are difficult to reconcile with such a structure. It is possible that they arise from the above mentioned ion–molecule complex between formaldehyde and $CHNS^{\cdot+}$ contributing to the beam of stable *m*/*z* 89 ions.

Sequential reduction of the *m*/*z* 89 ions by collision with xenon and reionization by collision with oxygen generates the neutralization–reionization (NR)[8] spectrum (Table 1). This spectrum features an intense recovery signal corresponding to survivor ions and a very significant intensity decrease of the peaks corresponding to unimolecular (metastable) fragmentations (*m*/*z* 74 and 59). Such a behaviour is not unexpected as more internal energy can be deposited in the ions in NR than in CA resulting in an increased competitiveness of the higher energy processes. The three structurally significant peaks at *m*/*z* 58, 44 and 32 are also very intense. It appears, therefore, that the NR spectrum is much more characteristic of the methoxy isothiocyanate structure than the corresponding CA spectrum and that neutral methoxy isothiocyanate is also a viable molecule when isolated in the gas phase. Isomerization does not take place during the flight between the neutralization and the reionization cells. This was demonstrated by an NR/CA experiment, in which the survivor ions giving rise to the recovery signal are collisionally activated (Fig. 1); the close similarity of the CA and NR/CA spectra indicates that the atom connectivity remains unchanged during the various collisional events.

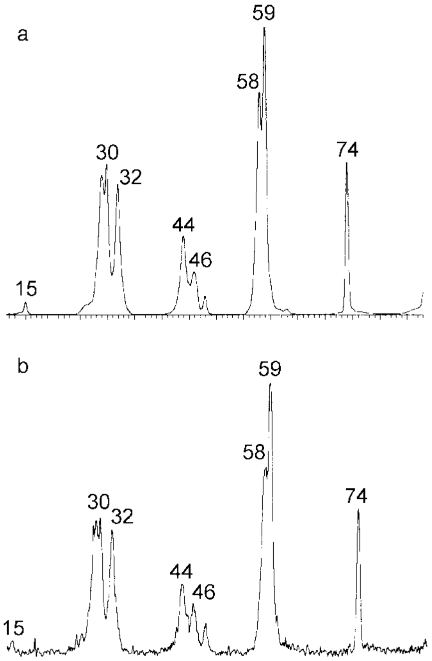


**Fig. 1** Comparison of the CA ($O_2$) spectrum (a) and the NR/CA (Xe/$O_2$/$O_2$) spectrum (b) of the *m*/*z* 89 ions generated from **1**.

When a beam of these *m*/*z* 89 ions, decelerated at near-thermal energies, is allowed to interact with nitric oxide in the RF-only quadrupole collision cell, the major ion–molecule reaction observed is charge exchange leading to the formation of $NO^+$ ions (*m*/*z* 30) (Fig. 2a). The ionization energy of methoxy isothiocyanate is therefore higher than (or close to) 9.25 eV, *viz.* the ionization energy of nitric oxide.[9] This behaviour is thus in perfect agreement with previous results on the ion–molecule reactions of isothiocyanates with nitric oxide.[7] It is also worthy of note that, in the reaction described in Scheme 1, the charge remains localized on the isothiocyanate, not on the triazole moiety; this observation fixes the ionization energy of methoxy isothiocyanate between 9.25 eV and 9.8 eV, the latter limit being defined by the ionization energy of 1,2,4-triazole.[9]

Further confirmation of the $CH_3ONCS$ connectivity arises from a study of the CA and NR spectra of the *m*/*z* 74 ions produced within the ion source of the mass spectrometer. The CA spectrum (Fig. 3) characterizes the occurrence of a mixture of SNCO and ONCS connectivities. While the former structure was also obtained for the long-living metastable ions (*vide supra*), the formation of the ONCS structure requires more internal energy, and such a situation is expected for a simple

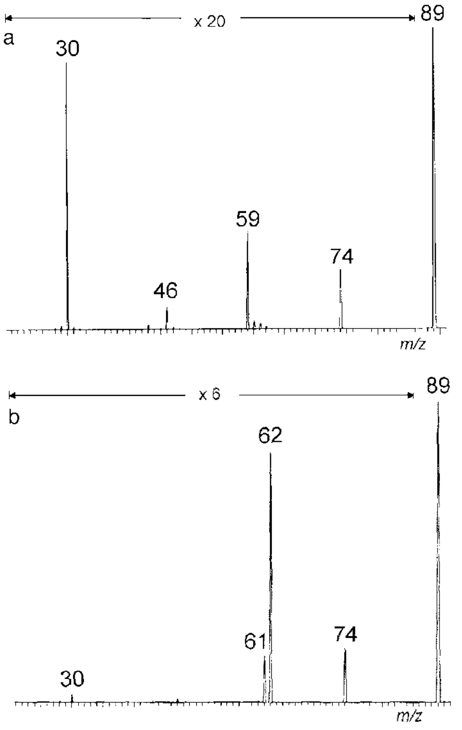


**Fig. 2** Ion–molecule reactions of ions **a** (a), and **b** (b) with nitric oxide in the quadrupole collision cell (magnet scan).

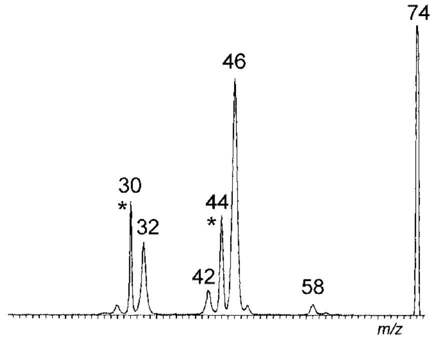
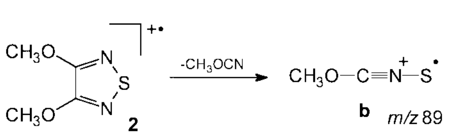


**Fig. 3** CA (He) spectrum of the *m*/*z* 74 ions generated by dissociative ionization of **1**. Labelled peaks (*) are ascribed to the simple cleavage reaction of $O{=}N^+{=}C{=}S$ ions.

cleavage reaction characterized by a high frequency factor. The products detected in the CA spectrum resulting from the ONCS connectivity are $NO^+$ and $CS^{\cdot+}$.[10]

In order to investigate the possibility of forming other $CH_3ONCS$ isomers, 3,4-dimethoxy-1,2,5-thiadiazole **2** was prepared. On the basis of previous literature,[11] it was expected that ionization could be followed by a cycloreversion reaction with the elimination of methyl cyanate (Scheme 2). Such a process should therefore produce the cyanate *N*-sulfide radical cations **b**, $CH_3O{-}C{\equiv}N^+{-}S^{\cdot}$.

Indeed, *m*/*z* 89 ions are readily formed in satisfactory yield (*ca.* 25%) upon electron ionization of **2**. The MI and CA data differ considerably from those of ions **a**. For instance, in the MI spectrum (Table 1), two reaction channels are in competition: the loss of a methyl group (*m*/*z* 74) and an unexpected loss of carbon monoxide (*m*/*z* 61). In this case, collision strongly favours the loss of a methyl group in favor of a simple cleavage reaction. This is supported by the identical CA spectra of the *m*/*z* 74 ions produced within the ion source and in a field-free region. These data indicate the OCNS connectivity also found in the fragmentation of metastable *m*/*z* 89 ions generated from **1**.



**Scheme 2**

The loss of CO from metastable *m*/*z* 89 ions generated from **2** requires rearrangement. Moreover, given the fact that the metastable $CH_3ONCS^{\cdot+}$ ions **a** do not lose CO, an isomerization **a**→**b** cannot be invoked to explain the formation of $S{=}N^+{=}C{=}O$ ions from metastable ions **a**.

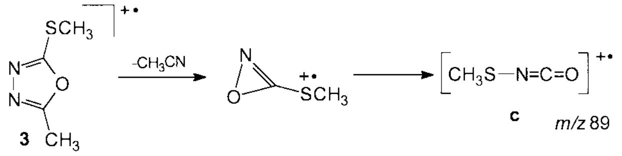
Beside the intense collision-induced loss of a methyl group (*m*/*z* 74), intense peaks are observed in the CA spectrum of ions **b** at *m*/*z* 58, 46 and 32 in agreement with the $CH_3OCNS$ connectivity.

The features of the CA spectrum are also found in the corresponding NR spectrum together with the presence of a recovery signal, thus demonstrating the stability of the neutral dipole molecule $CH_3ONCS$ when isolated in the gas phase (Table 1).

Very strong evidence for the formation of the nitrile *N*-sulfide ions **b** is provided by their reactivity towards nitric oxide. Contrasting with the behaviour of ions **a**, the isomeric ions **b** react mainly by transfer of $S^{\cdot+}$ to nitric oxide, generating an intense signal at *m*/*z* 62 for $ONS^+$ ions (Fig. 2b). Going from isothiocyanates to the isomeric *N*-sulfides usually reduces the ionization energy by *ca.* 0.8 eV.[9,11] It is therefore not unexpected that charge exchange is almost absent.

To summarize, the analysis of MI, CA and NR data together with the study of the reactions with nitric oxide provide good evidence for the production of stable $CH_3ONCS$ and $CH_3OCNS$ radical cations in the gas phase. The corresponding neutral molecules are also shown to be stable species. In contrast, metastable $CH_3ONCS$ radical cations undergo extensive, not yet well defined, isomerization reactions before cleavage.

Finally, 2-methyl-5-methylthio-1,3,4-oxadiazole **3** has also been studied as the molecular ions of this compound were expected to lose easily acetonitrile generating formally oxazirine or nitrene ions which could be isomerized into isocyanate ions **c** (Scheme 3).



**Scheme 3**

The EIMS of **3** features indeed a low intensity (4%) signal at *m*/*z* 89. In contrast, the same ion gives rise to the base peak in the MI spectrum of the molecular ion of **3**. Such a behaviour strongly suggests that the "slow" elimination of acetonitrile follows a rearrangement process, and this was confirmed by CA experiments performed on *m*/*z* 89 ions produced within the ion source or in a field-free region (Fig. 4). These spectra differ considerably from the spectra of **a** and **b** ions and therefore suggest that new isomeric species are formed in the dissociative ionization of **3**. The metastable *m*/*z* 89 ions predominantly lose carbon monoxide, but the actual structure of these *m*/*z* 61 ions differs from that of the isomeric ions produced from **2**.[12] The NR spectrum of the *m*/*z* 89 ions is not very different from the corresponding CA spectrum except for the increased intensity of the peak at *m*/*z* 42 (NCO). The weak recovery signal at *m*/*z* 89 supports the stability of a third isomeric species, not yet clearly defined, in the gas phase. The exact nature of ions **c** will be the subject of further research.

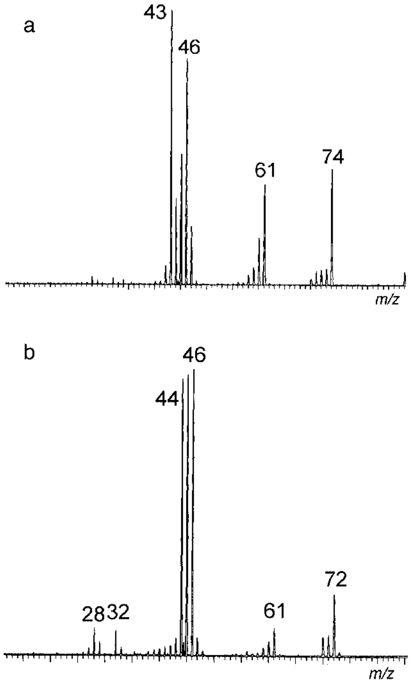


**Fig. 4** CA spectra of *m*/*z* 89 ions formed by dissociative ionization of the oxadiazole **3**: ion source generated ions (a) and metastably generated ions formed from *m*/*z* 130 molecular ions during the flight (b). Spectra recorded in the linked scan (E/B/E) mode.

## Molecular orbital calculations

Standard *ab initio* calculations were carried out using the GAUSSIAN 98 series of programs.[13] The structures and energies of $CH_3ONCS$ and $CH_3OCNS$ neutrals and radical cations and related fragments were examined at the G2(MP2,SVP) level of theory.[14] This corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* energies together with zero-point vibrational and isogyric corrections.

$CH_3OCNS$ is predicted to lie very close in energy to the isocyanate isomer, $CH_3ONCS$ (by just 2 kJ mol$^{-1}$). In sharp contrast, the parent thiofulminic acid (HCNS) is 122 kJ mol$^{-1}$ less stable than isothiocyanic acid (HNCS).[15] This dramatic change in relative energy may be attributed to the fact that the NCS fragment is significantly destabilized by the π effect of the methoxy group. The effects of a methoxy substituent on HCNS and HNCS may be determined by considering the isodesmic stabilization reactions (1) and (2). The calculated stabilization

$$CH_3OCNS + CH_4 \longrightarrow CH_3OCH_3 + HCNS \quad \Delta E = -0.3\ \mathrm{kJ\ mol^{-1}} \quad (1)$$

$$CH_3ONCS + CH_4 \longrightarrow CH_3OCH_3 + HNCS \quad \Delta E = -153.4\ \mathrm{kJ\ mol^{-1}} \quad (2)$$

energies for $CH_3OCNS$ and $CH_3ONCS$ are 0 and −153 kJ mol$^{-1}$, respectively.

We have calculated the ionization energies (IEs) of $CH_3ONCS$ and $CH_3OCNS$ using the G2(MP2,SVP) theory (Table 2). For the parent compound HNCS, the calculated G2(MP2,SVP) IE is 9.96 eV, in excellent agreement with the experimental value of 9.92 eV.[16] For $CH_3ONCS$, the calculated adiabatic ($IE_a$) and vertical ($IE_v$) ionization energies (9.0 and 9.2 eV, respectively) are in close agreement with the experimental estimate made above (≥9.25 eV). A significantly lower ionization energy is predicted for $CH_3OCNS$ ($IE_a = 8.1$ eV). The calculated difference in IE between $CH_3ONCS$ and $CH_3OCNS$ (0.8–0.9 eV) is consistent with the observed difference between isothiocyanates and the isomeric *N*-sulfides (~0.8 eV).[9,11,15]

**Table 2** Calculated ionization energies (eV) for $CH_3ONCS^{\cdot+}$ and $CH_3OCNS^{\cdot+\,a}$

| Ionization process | $CH_3OCNS$ | $CH_3ONCS$ |
|---|---|---|
| Adiabatic ($IE_a$) | 8.1 | 9.0 |
| Vertical ($IE_v$) | 8.4 | 9.2 |

[a] G2(MP2,SVP) level.

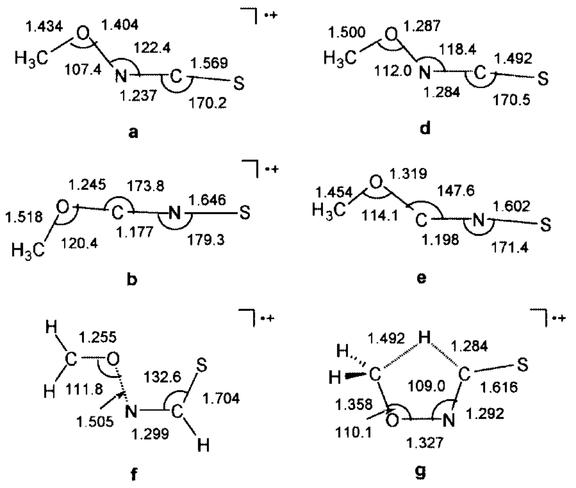


**Fig. 5** Optimized geometries (MP2/6-31G*) of $CH_3ONCS$, $CH_3OCNS$ neutrals and radical cations and related systems (bond lengths in angstroms and angles in degrees).

In distinct contrast to the neutral analogues, $CH_3OCNS^{\cdot+}$ (**b**) is predicted to be more stable than $CH_3ONCS^{\cdot+}$ (**a**), by 90 kJ mol$^{-1}$. Ion **b** has an almost linear OCNS skeleton. The short C–O bond length (1.245 Å, Fig. 5) suggests that the π electrons are delocalized into the CNS moiety. Similar findings have been reported for $RCNS^{\cdot+}$ ions with an electron donating group R (*e.g.* $NH_2$ and $SCH_3$).[11,15] Interestingly, the O–N bond length in $CH_3ONCS$ increases by 0.12 Å upon ionization (Fig. 5). The large structural changes upon ionization are consistent with the significant difference in calculated $IE_a$ and $IE_v$ values for both $CH_3ONCS$ and $CH_3OCNS$ (Table 2).

Calculated relative energies for the fragmentation of the $CH_3ONCS^{\cdot+}$ and $CH_3OCNS^{\cdot+}$ ions [G2(MP2,SVP) level] are given in Table 3. Both radical cations are calculated to be stable with respect to all possible unimolecular fragmentation processes. Previous studies have shown that calculated fragmentation energies are generally in reasonably good accord with the measured intensities in CAMS.[17] In the present case, the CAMS are significantly complicated by fragment ions resulting from a rearrangement of the molecular ions. As a consequence, there is little correlation between theory and experiment.

We have examined another plausible isomer of $CH_3ONCS^{\cdot+}$ (**a**), namely $CH_2ONC(S)H^{\cdot+}$ (**f**). **f** is slightly less stable than **a** by 23 kJ mol$^{-1}$. Rearrangement of **a** to **f**, *via* a 1,4-H shift transition structure **g** (Fig. 5), has a moderate barrier of 178 kJ mol$^{-1}$. **f** is characterized by a rather long N–O bond length of 1.505 Å (Fig. 5), and is, therefore, best considered as a complex between $CH_2O$ and $NC(S)H^{\cdot+}$. Fragmentation of **f** would lead to $CH_2O^{\cdot+}$ (*m*/*z* 30) and $[CHNS]^{\cdot+}$ (*m*/*z* 59) fragment ions, which are the additional peaks observed in the CAMS of $CH_3ONCS^{\cdot+}$ (Fig. 1 and Table 1). Hence, the isomerization of **a** to **f** may account for the observed complicated CA and MI spectra of **a** (Fig. 1 and Table 1).

Finally, we consider the energetics for the reactions of $CH_3ONCS^{\cdot+}$ and $CH_3OCNS^{\cdot+}$ ions with nitric oxide (Table 4). There are two possible channels for these reactions: (1) an $S^{\cdot+}$ ion transfer and (2) charge exchange to form $NO^+$ ion. The

**Table 3** Calculated fragmentation energies (kJ mol$^{-1}$) of $CH_3ONCS^{\bullet+}$ and $CH_3OCNS^{\bullet+}$ radical cations[a]

| | | | |
|---|---|---|---|
| $CH_3ONCS^{\bullet+}$ (*m*/*z* 89) | 0 | $CH_3OCNS^{\bullet+}$ (*m*/*z* 89) | 0 |
| $CH_3O^+ + NCS^\bullet$ (*m*/*z* 31)[b] | 112.5 | $CH_3O^+ + CNS^\bullet$ (*m*/*z* 31)[b] | 164.1 |
| $CH_3^\bullet + ONCS^+$ (*m*/*z* 74) | 259.9 | $CH_3OC^+ + NS^\bullet$ (*m*/*z* 43) | 219.5 |
| $CH_3^+ + ONCS^\bullet$ (*m*/*z* 15) | 332.1 | $CH_3^\bullet + OCNS^+$ (*m*/*z* 74) | 236.3 |
| $CH_3ON^{\bullet+} + CS$ (*m*/*z* 45) | 385.7 | $CH_3^+ + OCNS^\bullet$ (*m*/*z* 15) | 248.3 |
| $CH_3O^\bullet + NCS^+$ (*m*/*z* 58) | 536.6 | $CH_3OC^\bullet + NS^+$ (*m*/*z* 46) | 399.9 |
| $CH_3ONC + S^{\bullet+}$ (*m*/*z* 32) | 648.1 | $CH_3OCN + S^{\bullet+}$ (*m*/*z* 32) | 503.7 |
| $CH_3ONC^{\bullet+} + S$ (*m*/*z* 57) | 657.1 | $CH_3OCN^{\bullet+} + S$ (*m*/*z* 57) | 511.9 |
| $CH_3ON + CS^{\bullet+}$ (*m*/*z* 44) | 698.4 | $CH_3O^\bullet + CNS^+$ (*m*/*z* 58) | 543.4 |

[a] G2(MP2,SVP) level. [b] $CH_3O^+$ is not a stable species; it spontaneously rearranges to $CH_2OH^+$ upon geometry optimization.

**Table 4** Calculated reaction enthalpies (kJ mol$^{-1}$) for $CH_3ONCS^{\bullet+}$ (**a**) and $CH_3OCNS^{\bullet+}$ (**b**) reacting with $NO^\bullet$[a]

| Reaction | R = $CH_3ONC$ | R = $CH_3OCN$ |
|---|---|---|
| $RS^{\bullet+} + NO^\bullet$ | 0 | 0 |
| $R + SNO^+$ | 82.9 | −61.5 |
| $RS + NO^+$ | 20.5 | 111.8 |

[a] G2(MP2,SVP) level.

calculated energetics are in perfect agreement with the experimental findings. For $CH_3ONCS^{\bullet+}$, the charge exchange process is energetically more favorable than the corresponding ion transfer reaction. In contrast, for $CH_3OCNS^{\bullet+}$, the $S^{\bullet+}$ ion transfer is preferred over the charge exchange process (by 173 kJ mol$^{-1}$). The different chemical behaviour of the $CH_3ONCS^{\bullet+}$ (**a**) and $CH_3OCNS^{\bullet+}$ (**b**) ions in reacting with nitric oxide may be attributed to the fact that cleavage of the N–S bond in **b** to form $CH_3ONC + S^{\bullet+}$ is substantially weaker than the corresponding C–S bond cleavage in **a**. The calculated N–S and C–S bond dissociation energies are 504 and 648 kJ mol$^{-1}$, for **b** and **a**, respectively (Table 3).

## Experimental

All spectra were recorded on a large scale tandem mass spectrometer (Micromass AutoSpec 6F) combining six sectors of $E_1B_1©E_2©©E_3B_2©E_4$ geometry (E stands for electric sector, B for magnetic sector and © for the collision cells installed in various field-free regions).[18] In the hybrid mode, the neutralization cell is replaced by a demagnification lens and an RF-only quadrupole collision cell (q) fitted with deceleration and acceleration lenses is installed behind $E_2$ ($E_1B_1©E_2q©E_3B_2©E_4$ configuration).[19]

General conditions: 8 kV accelerating voltage, 200 μA trap current, 70 eV ionizing electron energy, and 200 °C ion source temperature. The solid samples **1** and **3** were introduced *via* a direct insertion probe, whereas sample **2** was injected into the ion source *via* a heated (180 °C) septum inlet.

Metastable ion (MI), collisional activation (CA; oxygen as the collision gas) and neutralization–reionization (NR; xenon/oxygen as collision gases) spectra were recorded by scanning the field of $E_3$ and collecting the ions in the fifth field-free region with an off-axis photomultiplier detector. In the NR/CA experiments, the survivor ions (recovery signals) were selected by a combination of $E_3$ and $B_2$ and collided in the last collision cell (oxygen collision gas), the fragments being analyzed by scanning $E_4$.

Details of the use of this instrument in the hybrid mode have been reported recently.[20] Briefly, the experiments consist of the selection of a beam of fast ions (8 keV) with $E_1B_1E_2$ (MS1), the retardation of these ions at near-thermal energies, and the reaction with nitric oxide (Praxair 2.0) at a pressure estimated to be around $10^{-3}$ Torr. After reacceleration to 8 keV, all the ions present in the quadrupole cell are separated and mass measured by scanning the field of the second magnet $B_2$. The high energy CA spectra of selected ions generated in the quadrupole can also be recorded by a linked scanning of the fields of the last three sectors $E_3B_2E_4$ (MS2) (resolved mode), or by conventional scanning of $E_4$ after mass selection in $B_2$.

The precursor molecules were prepared according to literature procedures: **1**,[21] **2**[22] and **3**.[23]

## Conclusions

Applications of tandem mass spectrometric methodologies (collisional activation, neutralization–reionization, MS/MS/MS experiments, and ion–molecule reactions) have allowed the characterization of new [$CH_3O$, C, N, S] radical cations in the gas phase. Collisional reduction of these ions demonstrates that the corresponding neutral molecules are also stable species when isolated in the gas phase, and they can therefore be expected to be detectable species in low temperature matrix IR experiments following flash vacuum pyrolysis of appropriate precursors. Extensive and unexpected rearrangements of some metastable ions have also been detected by means of MS/MS/MS experiments.

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