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Identification of singlet and triplet SCNO$^+$ cations in the gas phase: theory and experiment

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Abstract

Experimental evidence, based on collisional activation (CA) mass spectrometry, is provided for the existence in the gas phase of SCNO$^+$ singlet and triplet cations. The production of the triplet state is enhanced upon collisional activation with oxygen or nitric oxide as collision gas. The identification of the two spin states of SCNO$^+$ is strongly supported by ab initio calculations of their unimolecular fragmentation energies. Theory predicts SCNO$^+$ has a singlet ground state, with the triplet state lying close in energy (38 kJ mol^{-1}). The singlet state is best described as an ion–neutral complex (SC $\cdot\cdot$ NO$^+$) while the triplet state is a normal covalently bounded species (S=C=N$^+$=O). The CA mass spectrum of the isomeric SNCO$^+$ ions is also discussed. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

We have been interested in the production in the gas phase of a new class of isothiocyanates, namely alkoxyisothiocyanates, RO–N=C=S, making use of a combination of flash-vacuum pyrolysis, tandem mass spectrometry and low-temperature matrix isolation IR spectroscopy [1,2]. It was found that dissociative ionization of the heterocycles **1** and **2** generate in high yields CH$_3$ONCS (m/z 89) radical cations (Scheme 1).

The MIKE (mass-analyzed ion kinetic energy) spectrum of these m/z 89 ions features two peaks of nearly identical intensity corresponding to the formation of [CNOS]$^+$ cations (m/z 74, 56%; loss of a methyl group) and to the formation of [C,H,N,S]$^{\cdot+}$

radical cations (m/z 59, 44%; loss of CH$_2$O). If the first reaction can be considered (erroneously, see Section 2.1) as a simple cleavage reaction, the second process requires rearrangement.

In this Letter, we describe the structure of the [CNOS]$^+$ cations (m/z 74) making use of tandem mass spectrometry methodologies and high-level ab initio molecular orbital calculations. Both theory and experiment suggest that the different spin states of the SCNO$^+$ ion are experimentally accessible.
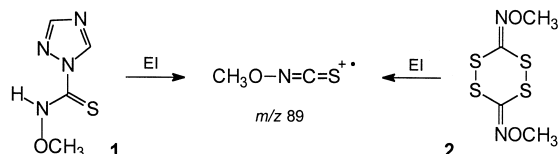
Scheme 1.

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2. Experimental results

2.1. Collisional activation mass spectra

Fig. 1a and b shows the collisional activation (CA) spectra of the m/z 74 ions produced in the ion source or during the flight in a field-free region. The collision gas was oxygen in the two cases and the accelerating voltage was modified in order to confer to the ions the same kinetic energy before collisional excitation. Although the two CA spectra present the same base peak at m/z 46 (NS^+), they differ considerably by the presence of peaks at m/z 44 and 30 ($CS^{\cdot +}$ and NO^+, respectively) for the ions produced
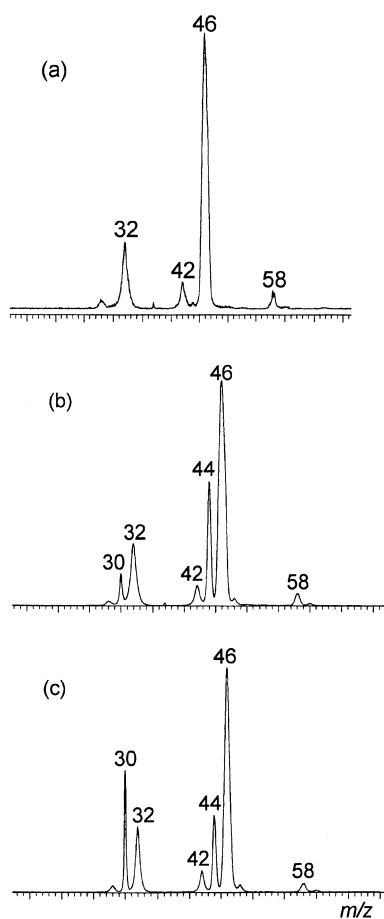

Fig. 1. CA (oxygen collision gas) of the m/z 74 ions produced by dissociation of metastable CH_3ONCS ions in the third field-free region of the AutoSpec 6F mass spectrometer (a), or by dissociative ionization in the ion source of **2** [oxygen collision gas (b) and helium collision (c)].

in the ion source. These spectra indicate therefore that the $[CNOS]^+$ species produced from long-living (~ 10 μs) m/z 89 ions differ from the species formed from short-living (< 1 μs) ions.

The CA spectrum of the m/z 74 ions produced in the field-free region (Fig. 1a) indicates that the major reaction channel leads to NS^+ plus CO. This reaction [together with the losses of either O (m/z 58) or S (m/z 42)] is expected for a S=N=C=O connectivity and requires therefore rearrangement of the precursor CH_3ONCS ions. That explains why the m/z 74 peak is so intense in the MIKE spectrum of the CH_3ONCS ions (intense metastable peak for the loss of a radical from a radical cation frequently diagnoses the occurrence of a pseudo-simple cleavage reaction [3]). The product ion is thus $S=N^+=C=O$ and, on the basis of thermochemical values [4], the less energy demanding fragmentation should effectively lead to NS^+ plus CO.

Further confirmation of the SNCO connectivity is provided by a recent work related to the preparation of thiazyl isocyanate, NSNCO, in the gas phase by reacting silver cyanide with NSCl in the ion source of a mass spectrometer [5]. The $NSNCO^{\cdot +}$ ions lose surprisingly very efficiently a nitrogen atom and the CA spectrum of the so-produced m/z 74 ions is identical with the spectrum depicted in Fig. 1a.

For the ions produced within the ion source, the $SNCO^+$ species is also present (base peak at m/z 46), but the new peaks at m/z 44 and 30 are consistent with the occurrence of ions presenting the SCNO connectivity, that is the connectivity predicted for a simple cleavage reaction of the CH_3–O bond in $CH_3ONCS^{\cdot +}$. On the basis of thermochemistry (relative ionization energies of NO and CS) [4], one should however predict an increased intensity of the peak at m/z 30 as compared to m/z 44, and that has induced the idea that the nature of the collision gas may be responsible for this peculiar behaviour.

Fig. 1c shows indeed the CA spectra of the m/z 74 (ion source produced) ions using helium as the target gas. Everything remaining nearly constant, the increasing intensity of the peak at m/z 30 for NO^+ ions is beyond doubt quite significant. The peculiar role of oxygen in collisional activation mass spectrometry has already been thoroughly investigated in our laboratory [6] and it appears that its unusual multiplicity can play an important role, the same for

doublet nitric oxide [7]. Branching m/z 44: m/z 30 ratios amount indeed to 3.8 (oxygen), 1.7 (nitric oxide) and 0.6 (helium).

We have recently shown that $SCCS_2^{\cdot+}$ and SCCSS$^{\cdot+}$ radical cations can be readily differentiated by associative ion–molecule reactions, not by collisional activation [8]. In particular, $SCCS_2^{\cdot+}$ radical cations react with nitric oxide by displacing inter alia CS_2 by NO$^{\cdot}$. The resulting species should therefore also present the SCNO connectivity. The CA spectra (helium and oxygen collision gas) of the corresponding ions are presented in Fig. 2. The SCNO is now free of the isomeric SNCO$^+$ ions and the effect of the nature of the collision gas is again clearly indicated.
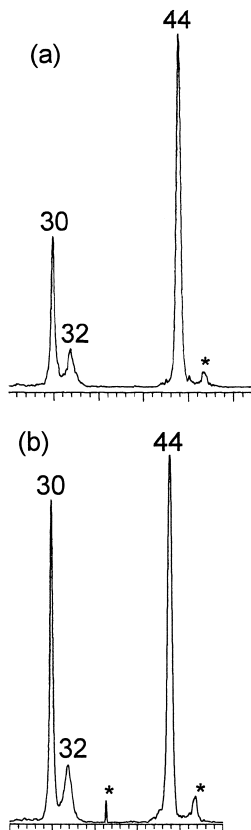

Fig. 2. CA spectra of the m/z 74 ions produced by ion–molecule reaction between $SCCS_2^{\cdot+}$ radical cations and nitric oxide in an r.f. only quadrupole collision cell: oxygen collision gas (a) and helium collision gas (b). ∗ Artefact peaks.

2.2. Experimental

The spectra were recorded on a large-scale tandem mass spectrometer of $E_1B_1E_2qE_3B_2E_4$ geometry (E stands for electric sector, B for magnetic sector and q for a radiofrequency (r.f.) only quadrupole collision cell) [9,10]. Typical conditions were 8 keV accelerating voltage (except otherwise stated), 70 eV electron energy and 200 μA trap current.

The CA spectra depicted in Fig. 1 have been recorded using the following procedure: a beam of m/z 89 ions generated by dissociative ionization of **2** (or **1**) was selected using E_1B_1 and the products of their spontaneous fragmentation (m/z 74) were transmitted by reducing the field of E_2 at 74/89 of its initial value. These metastably generated m/z 74 ions were then fragmented by collision with oxygen in a collision cell preceding E_3 and the fragments were collected by scanning the field of E_3 making use of an intermediate off-axis photomultiplier detector (Fig. 1a). Fig. 1b shows the CA (oxygen) spectrum for m/z 74 ions produced within the ion source, the accelerating voltage being reduced at 74/89 of its initial value. The same for the spectrum shown in Fig. 1c, the oxygen collision gas being replaced by helium.

In the ion–molecule experiments, the m/z 74 ions were generated by reacting a beam of decelerated $SCCS_2^{\cdot+}$ (m/z 120) radical cations with nitric oxide in the r.f. only quadrupole collision cell. After reacceleration at 8 keV, the ion–molecule products were mass selected by E_3B_2 and collided with oxygen or helium in a collision cell in front of the last electric sector (E_4). The fragments were then recorded by scanning the field of E_4, collecting the ions with the last photomultiplier detector.

3. Molecular orbital calculations

3.1. Computational methods

Standard ab initio calculations were carried out with the Gaussian 94 series of programs [11]. The structures and energies of SNCO$^+$ (**3**) and SCNO$^+$

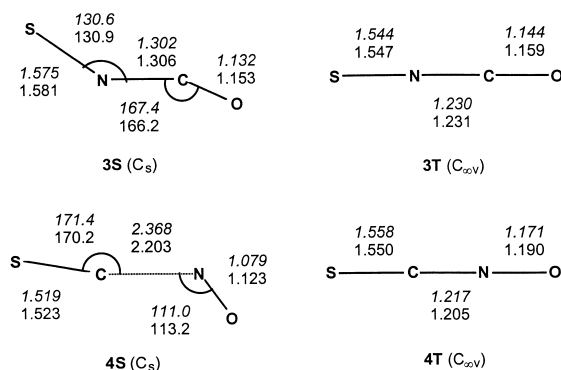Fig. 3. Optimized (MP2/6-31G*, with the QCISD/6-311G** values in italics) geometries for SNCO$^+$ (3) and SCNO$^+$ (4) cations (bond lengths in Å and angles in degrees).

3.2. Electronic structures of SNCO$^+$ and SCNO$^+$

The SNCO$^+$ cation (3) is predicted to have a singlet ground state ($^1A'$, 3S). The triplet state ($^3\Sigma^-$, 3T) is significantly less stable than the singlet state, by 142 kJ mol^{-1}. Thus, it is unlikely that the triplet state is experimentally observable in the CAMS. The singlet state (3S) has a bent structure and relatively long C=N bond length of 1.302 Å (Fig. 3). This bent geometry indicates the importance of the S$^+$–N=C=O resonance structure in the singlet state. The triplet state, on the other hand, has a linear geometry characterized by short cumulenic double bonds (Fig. 3). It is worth noting that the neutral cumulenic analogues RN=C=O [13] and RN=C=S [14] are also calculated to have a singlet ground state, while O=C=C=O [15,16], O=C=C=S [17] and S=C=C=S [15,18] prefer to have a triplet state.

As with SNCO$^+$, SCNO$^+$ is calculated to have a singlet ground state ($^1A'$, 4S). The triplet state ($^3\Sigma^-$, 4T) in this case lies very close in energy, 38 kJ mol^{-1} above 4S. Thus, given the right experimental conditions, we would expect both the singlet and triplet states to be experimentally observable. 4S and 4T are calculated to have quite different structures (Fig. 3). The singlet SCNO$^+$ ion has a unusually long C–N bond length (2.368 Å) and is best considered as an ion–molecule complex between CS and

(4) cations and related fragments were examined at the G2(MP2) level of theory [12]. This corresponds effectively to QCISD(T)/6-311 + G(3df, 2p)// MP2/6-31G* energies together with zero-point vibrational and isogyric corrections. For 3 and 4, higher-level geometry optimizations were performed at the QCISD/6-311G** level. Unless otherwise noted, this is the level referred to in the text. Spin-restricted calculations were used for closed-shell systems, and spin-unrestricted ones for open-shell systems.

Table 1
Calculated G2(MP2)[a] relative energies (kJ mol^{-1})

Species[b]	Relative energy	Species[b]	Relative energy
SNCO$^+$ (3S)	0.0	SCNO$^+$ (4S)	0.0
CO + NS$^+$ (m/z 46)	154.0	CS + NO$^+$ (m/z 30)	95.9
NS$^{\cdot+}$CO$^{\cdot+}$ (m/z 28)	677.0	NO$^{\cdot}$ + CS$^{\cdot+}$ (m/z 44)	305.3
NCO$^{\cdot}$ + S$^{\cdot+}$ (m/z 32)	730.5	CNO$^{\cdot}$ + S$^{\cdot+}$ (m/z 32)	686.1
S + NCO$^+$ (m/z 42)	937.6	O + SCN$^+$ (m/z 58)	765.2
O + SNC$^+$ (m/z 58)	1073.0	S + CNO$^+$ (m/z 42)	806.0
SNC$^{\cdot}$ + O$^{\cdot+}$ (m/z 16)	1339.3	SCN$^{\cdot}$ + O$^{\cdot+}$ (m/z 16)	1032.1
SNCO$^+$ (3T)	0.0	SCNO$^+$ (4T)	0.0
CO + NS$^+$(T) (m/z 46)	441.0	NO$^{\cdot}$ + CS$^{\cdot+}$ (m/z 44)	267.5
NS$^{\cdot}$ + CO$^{\cdot+}$ (m/z 28)	530.4	CS(T) + NO$^+$ (m/z 30)	410.2
NCO$^{\cdot}$ + S$^{\cdot+}$ (m/z 32)	583.9	O(T) + SCN$^+$ (m/z 58)	527.5
S + NCO$^+$(T) (m/z 42)	695.5	CNO$^{\cdot}$ + S$^{\cdot+}$ (m/z 32)	648.3
O(T) + SNC$^+$ (m/z 58)	726.5	S(T) + CNO$^+$ (m/z 42)	649.9
SNC$^{\cdot}$ + O$^{\cdot+}$ (m/z 16)	1192.8	SCN$^{\cdot}$ + O$^{\cdot+}$ (m/z 16)	994.3

[a] G2(MP2) E_0 energies include −565.25535 (3S), −565.19951 (3T), −565.13846 (4S) and −565.12407 (4T) hartree.
[b] T denotes triplet state.

NO^+. In sharp contrast, the triplet $SCNO^+$ is a covalently bounded species ($S=C=N^+=O$) characterized by short cumulenic double bonds. Although a singlet covalent-type structure, with a C–N bond length of 1.456 Å, could be found at the Hartree–Fock level, this species collapses to the ion–molecule complex (**4S**) when geometry optimization is carried out at the correlated level (MP2 or QCISD).

3.3. Unimolecular dissociations

Table 1 summarize the calculated energetics (G2(MP2) level) for the unimolecular fragmentation reactions of the singlet and triplet states of $SNCO^+$ and $SCNO^+$. Consistent with the experimental finding, the loss of CO represents the most favorable fragmentation process of the singlet $SNCO^+$ (**3S**). Homolytic C–N cleavage leading to $NS^{\cdot} + CO^{\cdot+}$ is significantly less favorable fragmentation. Overall, the calculated fragmentation energies agree well with the measured intensities of the CAMS (Fig. 1a) [4].

Both the singlet and triplet $SCNO^+$ are calculated to be stable with respect to all possible fragmentation processes (Table 1). Dissociation of the singlet (**4S**) to $CS + NO^+$ (m/z 30) is calculated to be a more energetically favorable process than fragmentation to $NO^{\cdot} + CS^{\cdot+}$. In contrast, the lowest spin-allowed fragmentation pathway for the triplet state (**4T**) corresponds to the loss of $NO^{\cdot}$, leading to the formation $CS^{\cdot+}$ (m/z 44), which is in disagreement with the so-called even–even electron rule [19]. Dissociation of **4T** to $CS (^3\Pi) + NO^+$ (m/z 30) is the next most favorable fragmentation process. Thus, one could readily differentiate the singlet and triplet states of $SCNO^+$ in the CA spectra based on the relative intensity of the ion peaks at m/z 30 and 44. This theoretical finding is in excellent accord with the observed CAMS (Figs. 1 and 2). The use of O_2 and $NO^{\cdot}$ collision gas increase the intensity of the m/z 44 ion peak, which indicates the increase contribution of the triplet state of the $SCNO^+$ cation. In summary, the calculated fragmentation energies of **4S** and **4T** confirmed the presence of singlet and triplet states in the CAMS of $SCNO^+$.

4. Conclusions

$SNCO^+$ and $SCNO^+$ cations can be produced by dissociative ionization or ion–molecule reactions of appropriate neutral/ionized precursors. The experimental data suggest that the singlet and triplet multiplicities of the $SCNO^+$ ions are observed and that collisional activation with gases like nitric oxide and mainly oxygen increases the contribution of the triplet state. The identification of the two states of $SCNO^+$ is strongly supported by the calculations of their fragmentation energies. Both singlet and triplet states of $SCNO^+$ are calculated to lie close in energy. The singlet state is best regarded as a $SC \cdot \cdot NO^+$ complex, while the triplet is normal covalently bounded species.

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