

New experiments on HNCSe and HCNSe radical cations[†]

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Dissociative ionization of the selenourea Se=C(NH₂)₂ (2) conveniently generates beams of pure isocyanoselenic acid radical cations. The HNCSe⁺ connectivity is established by collisional activation and by associative ion-molecule reactions with dimethyl sulfide or nitric oxide using a large-scale hybrid mass spectrometer. Copyright © 2005 John Wiley & Sons, Ltd.

In the context of an exhaustive mass spectrometry study of 1,3-dipoles derived from nitriles,¹ we reported the preparation and identification of isomeric HNCSe⁺ and HCNSe⁺ radical cations.² The dissociative ionization of 4-cyano-1,2,5-selenadiazole-3-carbothioamide (1) was demonstrated by (*inter alia*) collisional activation (CA) methodologies to predominantly generate ionized isoselenocyanic acid, HNCSe⁺. The isomeric HCNSe⁺ radical cation was prepared² by ionized selenium transfer to hydrogen cyanide under chemical ionization conditions starting with NCCNSe⁺ radical cations as the reagent ion (see Scheme 1). The connectivities of both ions were established by CA spectra that showed characteristic peaks at m/z 92 for the isocyanoselenic acid ion (HN loss, CSe⁺ ions) and m/z 94 for the *N*-selenide (HC loss, NSe⁺ cations). The observation in both CA spectra of both m/z 92 and 94 fragment ions was ascribed to a mixture of HNCSe⁺ and HCNSe⁺. The distinction between these isomers was nevertheless achieved on the basis of quite different branching ratios, i.e. m/z 92/ m/z 94 = 3.7 and 0.13 for HNCSe⁺ and HCNSe⁺ radical cations, respectively.²

As depicted in Scheme 1, theoretical calculations indicated the higher stability of HNCSe⁺ over HCNSe⁺. Ionized cyclic selenazirine, the potential intermediate in the interconversion process, was calculated to be the less stable isomer. It is interesting to note that, starting from both species, the fragmentation reaction requiring the least energy,² yielding ionized selenium in both cases, is higher in energy than the transition states linking HNCSe⁺ and HCNSe⁺ isomers (see Scheme 1). In other words, a post-collisional isomerization process is likely to be responsible for the occurrence of uncharacteristic fragment ions in the CA spectra, i.e. m/z 92 (94) ions from collisionally activated HCNSe⁺ (HNCSe⁺) ions.

In the present paper we report the specific preparation of hydrogen isocyanoselenide ions, HNCSe⁺, by dissociative ionization of selenourea (2) and its structural characterization by collisional activation methodologies as well as ion-molecule reaction processes.

EXPERIMENTAL

The mass spectrometric experiments were performed using Micromass AutoSpec 6F (UMH) and Micromass AutoSpec M (IICT) mass spectrometers, of c₁E₁B₁C₂E₂C₃C₄E₃B₂C₅E₄ and c₁E₁B₁C₂C₃E₂ geometries, respectively (E_i stands for electric sector, B_i for magnetic sector, and c_i for conventional collision cells). Detailed descriptions of these instruments have been reported previously.^{3,4}

Selenourea (2, for structure, see Scheme 2) was commercially available (Aldrich) and used without any further purification. 4-Cyano-1,2,5-selenadiazole-3-carbothioamide (1, for structure, see Scheme 2) and 3, 4-dicyano-1,2,5-selenadiazole (3, for structure, see Scheme 4) were prepared following procedures described in the literature.² The solid samples (1, 2 and 3) were introduced into the ion source using the direct insertion probe, and the liquid sample (hydrogen cyanide) via a heated septum inlet system (180°C)^{3,4} under the following conditions: source temperature 200°C; electron energy 70 eV; trap current 200 μA; emission current (in chemical ionization mode) 1 mA; acceleration potential 8 kV.

The collisional activation (CA) mass spectra of m/z 107 ions from 2 were recorded using the Autospec M by mass selecting the 8 keV beam of precursor ions using E₁B (MS-1), and allowing collisions with oxygen in the collision cell c₃; the resulting ions were analyzed by scanning E₂ (MS-2).

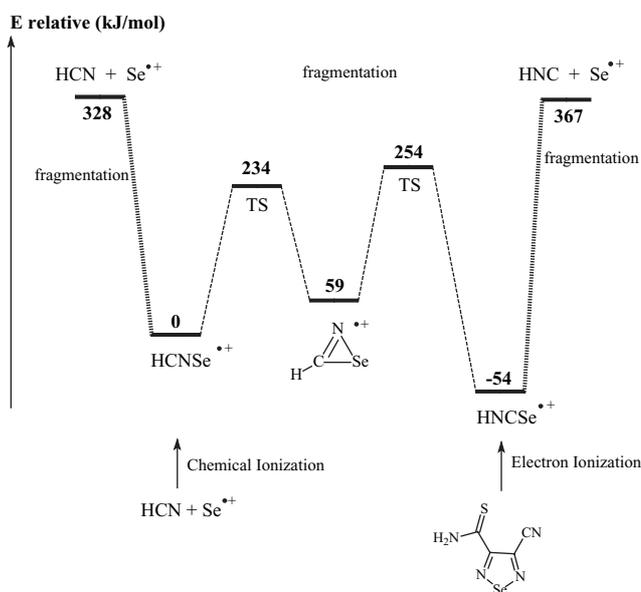
The Micromass AutoSpec 6F instrument has been modified by inserting a radio-frequency (rf)-only quadrupole collision cell (Q cell) between E₂ and E₃, as reported elsewhere.⁵ This modification allows the study of associative ion-molecule reactions of decelerated ions with about 5 eV kinetic energy. Briefly, the experiments using the quadrupole involve selection of a beam of fast ions (8000 eV) with the first three sectors and the deceleration of these ions to approximately 5 eV before entering the quadrupole in order to maximize the

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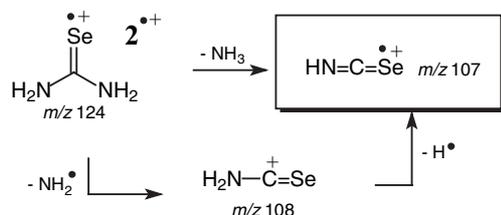
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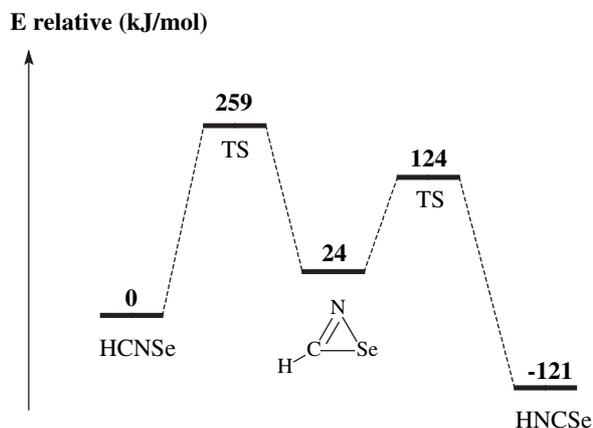


Scheme 1. Preparation methods and fragmentation energetics for the isomeric ions HCNSe^+ and HNCSe^+ .

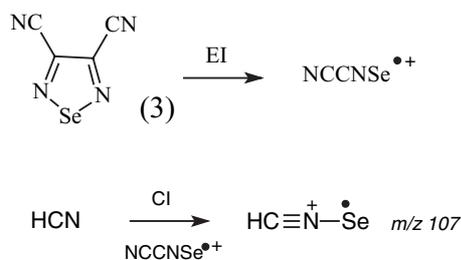


Scheme 2. Fragmentations of ionized selenourea (**2**).

yields of the associative ion-molecule reactions between the ions and the neutral reagent (pressure estimated to be ca. 10^{-3} Torr). After re-acceleration to 8000 eV, all the ions generated in the quadrupole cell are separated and mass-measured by scanning the field of the second magnet. The high-energy CA spectra of mass-selected ionic products of the ion-molecule reactions were recorded by scanning the field of the last electric sector (E_4) after mass-selection by the second magnet and collision with oxygen in the fifth (c_5) collision cell.



Scheme 3. Energetics for interconversion of neutral HCNSe and HNCSe .



Scheme 4. Formation of HCNSe^+ by chemical ionization.

Neutralization-reionization (NR) experiments were performed using both instruments. Briefly, such experiments involve two consecutive high-energy collision experiments, realized in two consecutive collision cells (c_3 and c_4 , and c_2 and c_3 , for the Autospec 6F and Autospec M instruments, respectively). The difference between the two arises from the fact that the Autospec 6F instrument is nothing other than a modified Autospec M instrument (a commercially available mass spectrometer), obtained by coupling two such three-sector machines.³ In the NRMS experiments, the collision-induced neutralization (xenon collision gas) of the mass-selected ions precedes the reionization (oxygen) of the resulting neutral species. Ions surviving the neutralization step are eliminated from the beam of fast neutrals; depending on the selected instrument, the deflection of the residual ions is achieved on the x -axis (Autospec 6F) or perpendicular to the x -axis (Autospec M).^{3,4} Nevertheless, the NR spectra obtained by scanning the field of E_2 (Autospec M) or E_3 (Autospec 6F) were found to be identical.

RESULTS AND DISCUSSION

Dissociative ionization of selenourea (**2**): structural characterization of the product ions

The 70 eV electron ionization mass spectrum of compound **2** features small but significant peaks at m/z 108 (3.5% relative to the m/z 124 base peak) and 107 (5%), corresponding to losses of NH_2 and NH_3 , respectively. Among the other peaks of importance are m/z 80 (6%) for selenium ions and m/z 43 (38%) for CN_2H_3^+ cations. As depicted in Scheme 2, the loss of ammonia from the molecular ions (m/z 124) of selenourea (**2**) could be a one- or a two-step process, as suggested by the CA spectra of the mass-selected m/z 124 and 108 ions (Figs. 1(a) and 1(b)), since both spectra feature a peak at m/z 107.

As expected from the connectivity of the starting compound **2**, the fragmentation pattern observed in the CA spectrum of the m/z 107 ions (Fig. 2(a)) could be explained on the basis of the proposed HNCSe connectivity. In particular, as explained previously² and discussed in the Introduction, the presence of the signal at m/z 92, corresponding to CSe^+ radical cations, is wholly in keeping with the fragmentation of HNCSe^+ ions. Moreover, the cleavage of the carbon-selenium bond leaving the charge on selenium (m/z 80) is expected on the basis of the respective ionization energies of selenium (9.75 eV) and HNC (12.5 eV);⁶ the peak at m/z 27 (ionized hydrogen isocyanide, HNC) is barely detectable at higher amplifier gain. The other observed peaks are readily attributed to NCCSe^+ ions (m/z 106) and HNCSe^{2+}

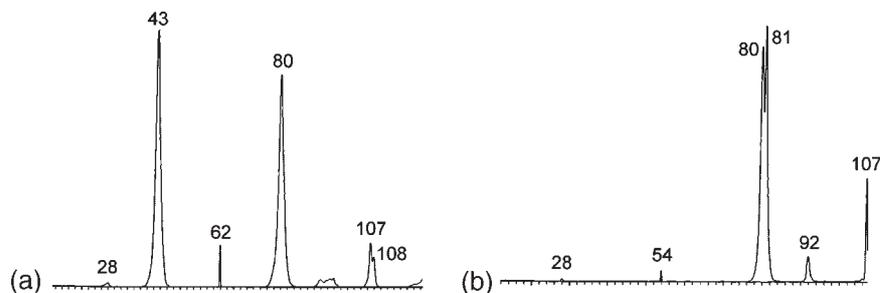


Figure 1. CA mass spectra of m/z 124 (a) and 108 (b) ions formed from EI of compound **2** (oxygen collision gas).

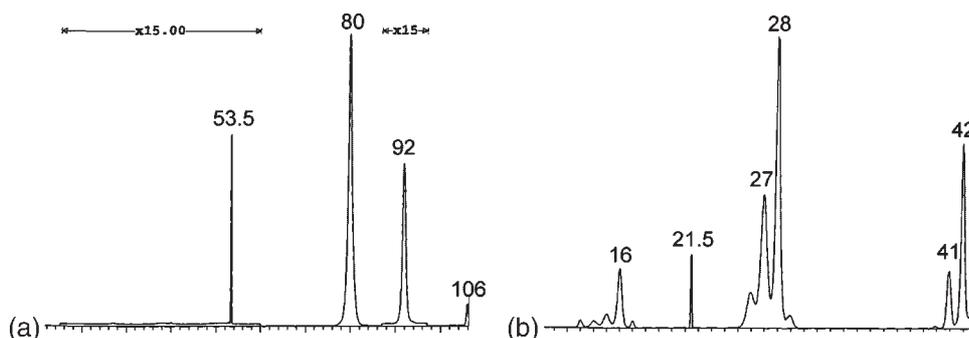


Figure 2. CA mass spectra of the m/z 107 ions (a) and the m/z 43 ions (b) from compound **2** (oxygen collision gas).

ions (m/z 53.5, formed via charge stripping). In contrast to the CA spectrum of the m/z 107 ions prepared from 4-cyano-1,2,5-selenadiazole-3-carbothioamide (**1**),² no signal at m/z 94, corresponding to NSe^+ cations and characteristic of the isomeric HCNSe^+ species, is observed in the spectrum shown in Fig. 2(a). The observation of this signal² was assumed to arise from the sampling of a mixture of both isomers or from post-collisional isomerization (*vide supra*). The present result confirms that the CA experiment does not induce partial isomerization of the HNCSe^+ ions prior to the decomposition, and also that the dissociative ionization of selenourea (**2**) specifically affords ionized isoselenocyanic acid.

Although not directly related to the main topic of the present report, it is of interest to analyze in some detail the dissociation chemistry of selenourea (**2**) under electron ionization (EI) conditions. The signal observed at m/z 43, representing the most abundant fragment ion peak in the EI-MS spectrum of (**2**), is of interest. In the same vein, the CA spectrum of the m/z 124 (2^+) ions (Fig. 1(a)) reveals that collisionally activated 2^+ ions mainly expel a SeH^\cdot radical to yields protonated carbodiimide ($\text{HN}=\text{C}=\text{N}^+\text{H}_2$) at m/z 43, as confirmed by the CA spectrum presented in Fig. 2(b).

NR experiments: probing the gas-phase stability of neutral HNCSe

The NR spectrum of the m/z 107 ions, obtained using xenon and oxygen in sequence, is shown in Fig. 3. This spectrum features a moderate but significant recovery signal at m/z 107, and fragments at m/z 106, 92 and 80 already identified in the CA spectrum (Fig. 2(a)). Charge-stripped ions are not sig-

nificant in the NR spectrum, probably reflecting a lower probability for the $m \rightarrow m^{2+}$ ionization process compared to the $m^+ \rightarrow m^{2+}$ process.⁷ Calculations on neutral HNCSe previously² indicated that this neutral species is stable with respect to all possible unimolecular fragmentation processes, e.g. although the Se and H atom losses represent the most favorable dissociation pathways, they require respectively 354 and 340 kJ/mol. The potential energy surface of the neutral CHNSe system is quite similar to that calculated for its ionic counterpart (see Scheme 1) except that the energy difference between HNCSe and HCNSe is calculated to be larger in the neutral state, amounting to 121 kJ/mol (see Scheme 3). These experimental and theoretical results emphasize the stability of neutral isocyanoselenide, HNCSe, in the gas phase.

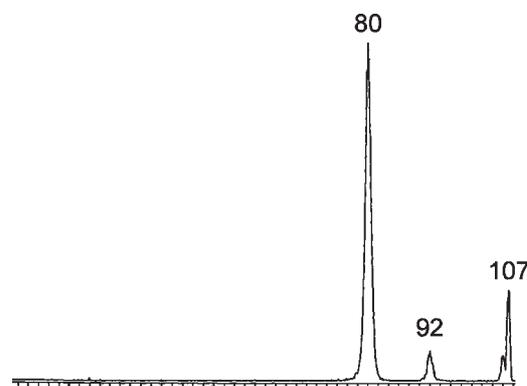


Figure 3. NR mass spectrum of the m/z 107 ions (xenon-oxygen).

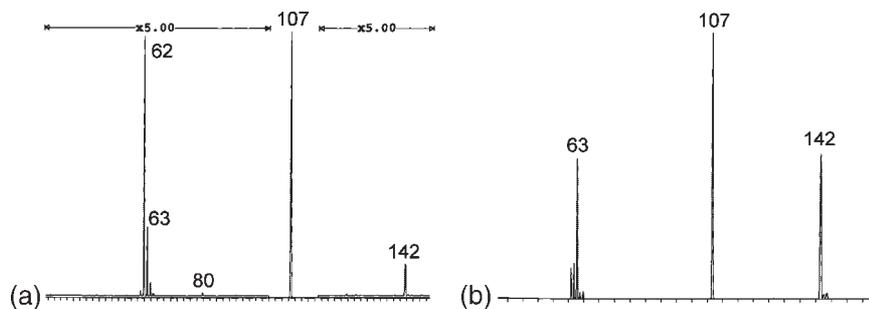
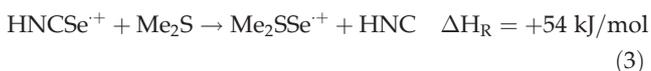
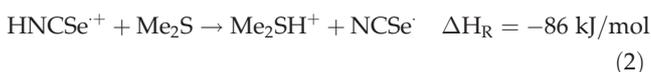
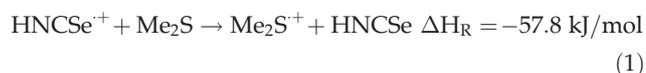


Figure 4. Ion products of ion-molecule reactions between dimethyl sulfide and decelerated HNCSe^+ ions (m/z 107) (a) or HCNSe^+ ions (m/z 107) (b) in the quadrupole collision cell.

Study of the associative ion-molecule reactions: gas-phase bimolecular chemistry of HNCSe^+ and HCNSe^+ ions

Although isomeric recognition is readily achieved by CA experiments, we decided to analyze the bimolecular chemistry of both isomeric ions with several different neutral reagents, such as dimethyl sulfide (Me_2S) and nitric oxide. Indeed, differentiation of isomeric ions can frequently be realized by examination of their associative ion-molecule reactions. If performed using a hybrid sector-quadrupole-sector mass spectrometer, product identification can be realized by high-energy collisional activation.⁸

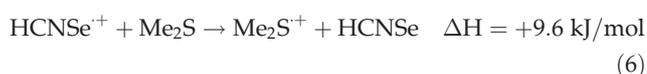
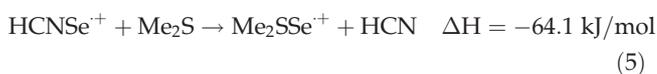
Charge exchange generates the most abundant interaction product (m/z 62 ions) when HNCSe^+ ions (obtained from 2) react with Me_2S (Fig. 4(a)). Although the mass-selected ions are not thermalized in the experimental set-up, the occurrence of a fast charge exchange process is consistent with the known ionization energies of both species, i.e. 8.69 eV for Me_2S ⁶ and 9.29 eV for HNCSe .⁹ The second process of importance is the proton transfer reaction giving a sulfonium ion (m/z 63) plus a NCSe radical. Finally, the peak at m/z 142 corresponds to ions produced by transfer of an ionized selenium atom to Me_2S . The weak signal detected at m/z 80, corresponding to ionized selenium, can originate from collision-induced dissociation (CID) or from spontaneous unimolecular dissociation of the mass-selected ions, given the fact that a thermalization step does not precede the reactions in the quadrupole cell. On the basis of the available thermochemical data,^{2,6} the energetics of the observed ion-molecule reactions can be calculated:



The ionization energy difference fixes the exothermicity of the charge exchange process (Eqn. (1)) at 57.8 kJ/mol. The exothermicity (86 kJ/mol) of the proton transfer to dimethyl sulfide (Eqn. (2)) is obtained from the proton affinity of Me_2S (839 kJ/mol)⁶ and the theoretically estimated heat of deprotonation of HNCSe^+ ions.² The third reaction involves the

transfer of an ionized selenium atom to Me_2S yielding dimethyl sulfide *S*-selenide ions, Me_2SSe^+ . Using the theoretically estimated heats of formation of Me_2SSe^+ ions (738.1 kJ/mol, B3LYP/6-311++G(d,p), this work) and HNCSe^+ ions (920.7 kJ/mol),² this reaction is surprisingly found to be endothermic by about 54 kJ/mol. This result is unexpected in view of observation of the products of reaction (3), but nevertheless is in keeping with the non-thermalization of the mass-selected ions prior to the reaction. Moreover, the detection of the weak signal at m/z 80 can help to determine the maximum internal energy excess. Indeed, the decomposition reaction yielding these ions from HNCSe^+ requires 440.8 kJ/mol.² This value is large enough to overcome the endothermicity of the ionized selenium transfer reaction, and is also large enough to overcome the isomerization energy barriers between HNCSe^+ and HCNSe^+ . In several preceding reports, we have shown that the NCCNSe^+ ion is very efficient in transferring Se^+ to several neutral molecules, such as other nitriles² and pyridine.¹⁰ Consequently, we could not rule out the intervention of HCNSe^+ in the case of the Se^+ transfer to Me_2S . The isomeric species, HCNSe^+ , can be prepared by chemical ionization of hydrogen cyanide using 3,4-dicyanoselenadiazole (3) as the reagent gas.² These ions have been demonstrated to arise from the reaction between cyanogen *N*-selenide ions (NCCNSe^+) and HCN (Scheme 4).

When reacting HCNSe^+ with Me_2S in the quadrupole cell, the yields of product ions are quite different from those observed with HNCSe^+ , as shown in the spectrum in Fig. 4(b). The first observation is the higher efficiency of the reactions; compared to the peak at m/z 107 (unreacted mass-selected ions), no amplification factor was required to detect the products at m/z 142 and 63 (cf. Fig. 4(a)). The main reactions are thus proton transfer (m/z 63) and ionized selenium transfer (m/z 142). Reaction enthalpies for the observed reactions are again calculated from the available thermochemical data.^{2,6}



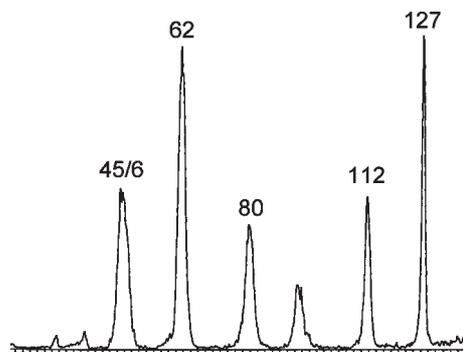


Figure 5. CA spectrum of the m/z 142 radical cations obtained following the interaction between HCNSe^+ ions and neutral dimethyl sulfide.

Processes (4) and (5) are thus calculated to be exothermic by 36 and 64 kJ/mol, respectively, consistent with observation of accordingly Me_2SH^+ and Me_2SSe^+ as the major ionic products. A signal at m/z 62 is also detected, corresponding to molecular ions of dimethyl sulfide that could originate from a slightly endothermic charge exchange process, given the lack of thermalization of the ionic reactant. The connectivities of the m/z 63 and 142 ions thus obtained can be readily accessed by subsequent high-energy CA experiments. As observed in the high collision energy CA spectrum (Fig. 5), the dimethyl sulfide *S*-selenide connectivity of the m/z 142 ions can be deduced from the collision-induced fragments detected at m/z 127 (loss of CH_3), 112 (SSe^+ ions), 80 (Se^+ ions) and 62 (Me_2S^+ ions). The propensity of HCNSe^+ radical cations to easily transfer ionized selenium to different nucleophilic species such as dimethyl sulfide is quite consistent with the distonic character of these ions,¹¹ exemplified in the mesomeric structure presented in Scheme 4. The observation of the ionized selenium atom transfer reaction to dimethyl sulfide starting from HCNSe^+ does not allow us to conclude that dissociative ionization of **2** specifically affords HCNSe^+ , as concluded from the CA experiments summarized above.

In this context nitric oxide (NO^\bullet) has been described on several occasions as an efficient trapping reagent for distonic radical cations.¹² Because of its relatively high ionization energy (9.26 eV),⁶ charge exchange is usually less competitive than in reactions with other neutral reagents such as dimethyl sulfide, and consequently other structurally significant

reactions are often operative. Representative examples of ion-molecule reactions are attachment of NO^\bullet ; trapping of small radical cations by NO^\bullet ; or displacement of neutral molecules by NO^\bullet .¹² We found that nitric oxide reacts in the quadrupole cell with mass-selected HNCSe^+ ions to produce in good yield ionized nitric oxide (m/z 30) and ionized selenium (m/z 80) (see Fig. 6(a)). The m/z 80 peak probably arises, as previously discussed, from CID or spontaneous fragmentation of the mass-selected ions. On the other hand, charge exchange is the major observed ion-molecule reaction since the m/z 30 peak corresponding to ionized nitric oxide is by far the most intense signal. The efficiency of the charge exchange process is completely consistent with the similar ionization energies of nitric oxide (9.26 eV) and isoselenocyanic acid (9.29 eV). Ionized selenium atom transfer to nitric oxide was not significantly observed, and this confirms that the contribution of HCNSe^+ radical cations to the mass-selected m/z 107 ion beam from **2** is negligible, if any. Indeed, when reacting CI-prepared HCNSe^+ radical cations with nitric oxide in the quadrupole cell, ionized selenium is readily transferred from the reacting ions to the neutral target yielding SeNO^+ ions, detected at m/z 110 (Fig. 6(b)).

The charge exchange reaction (Eqn. (7)) is calculated to be almost thermoneutral, explaining the large intensity of the peak at m/z 30 for NO^+ . The Se^+ transfer reaction (Eqn. (8)) is found to be endothermic by ca. 23 kJ/mol and the corresponding peak is barely detected, and can probably be attributed to the presence of a minute amount of the HCNSe^+ isomer. As far as the HCNSe^+ ions are concerned, thermochemical estimates yield a large exothermicity for the Se^+ transfer to nitric oxide (reaction (10), -97.5 kJ/mol, calculated from data of Refs. 2 and ¹³), and a large endothermicity of the charge exchange reaction (9).

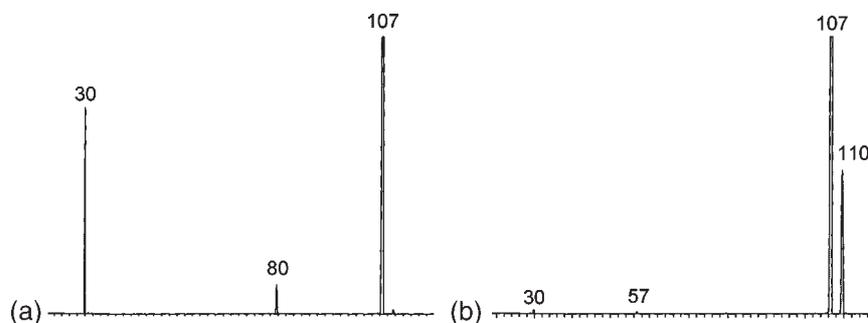
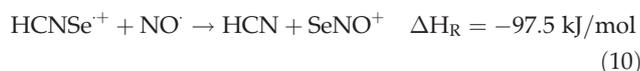
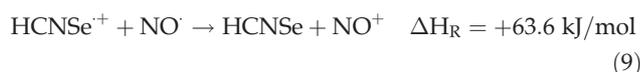
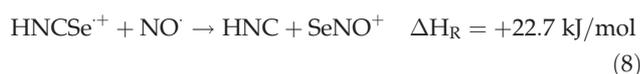
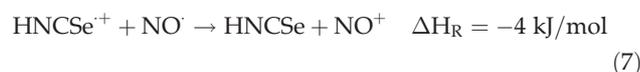
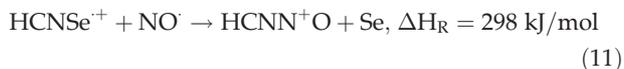


Figure 6. Product ions from ion-molecule reactions between nitric oxide and HNCSe^+ ions (a) or HCNSe^+ ions (b) in the quadrupole collision cell. The peaks at m/z 107 are off-scale (intensities $\div 6$).

The small peak observed at m/z 30 cannot result from a consecutive dissociation of the SeNO^+ generated in reaction (10) because such a cleavage requires about 470 kJ/mol. This peak is thus ascribed to a slight contamination with HNCSe^+ isomers or to the non-thermalization of the mass-selected reactive ions.

Finally, the weak signal detected at m/z 57 in Fig. 6(b), which formally corresponds to the substitution of selenium by nitric oxide:



is presently not properly characterized. Moreover, the intensity of this peak is too low to allow structural characterization by a subsequent CA experiment.

CONCLUSIONS

In a previous report we demonstrated that, after electron ionization (EI), 4-cyano-1,2,5-selenadiazole-3-carbothioamide (**1**) decomposes leading to ionized isoselenocyanic acid (HNCSe^+) in good yield. Nevertheless, based on collisional activation (CA) experiments, we were not able at that time to unambiguously conclude that the ions thus obtained could not be a mixture of two different isomeric species, HNCSe^+ and HCNSe^+ . In the present work related to the EI-MS behavior of selenourea (**2**), we propose, on the basis of both CA and ion-molecule reaction studies, that the dissociative ionization of **2** specifically affords ionized isoselenocyanic acid, HNCSe^+ . Indeed, the recorded CA spectra do not reveal the presence of even minute amounts of HCNSe^+ ions. Moreover, the different reactivities of HNCSe^+ and HCNSe^+ ions toward dimethyl sulfide and nitric oxide were investigated using a hybrid tandem mass spectrometer, and allowed a clear-cut distinction between these two connectivities.

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