Pergamon

Tetrahedron Letters 39 (1998) 533-536

TETRAHEDRON
LETTERS

Generation of Nitrile *N*-Selenides, RC≡NSe, as Neutrals and Radical Cations in the Gas Phase

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Received 16 July 1997; accepted 25 September 1997

Abstract: Cyanogen *N*-selenide radical cation, NCCNSe$^{\bullet+}$, is prepared by dissociative ionization of 3,4-dicyano-1,2,5-selenadiazole [**1**]. It reacts readily with nitriles in the gas phase to produce nitrile *N*-selenide ions, RCNSe$^{\bullet+}$. The stability of the corresponding neutral dipoles is confirmed by neutralization-reionization mass spectrometric experiments.

Whereas nitrile *N*-oxides are well-known compounds showing 1,3-dipolar reactivity,[1] the corresponding *N*-sulfides are short-lived species under usual reaction conditions.[2,3] Recently, we have found that nitrile *N*-sulfide radical cations can be generated efficiently in the gas phase.[4,5] Consequently, collision-induced neutralization, the first step of the neutralization-reionization methodology (NRMS),[6] has allowed the production of a series of neutral *N*-sulfides in the gas phase of a mass spectrometer.[4]

Much less is known about nitrile *N*-selenides (R-C≡N$^+$-Se$^-$). There is good evidence[7,8] for the existence of benzonitrile *N*-selenide (C_6H_5-C≡N$^+$-Se$^-$) at low temperature but trapping experiments have failed so far.

In the present work, we report on the first generation of cyanogen *N*-selenide radical cations and neutrals in the gas phase starting from 3,4-dicyano-1,2,5-selenadiazole [1]. The NCCNSe$^{\bullet+}$ ion is an unknown member of the NCCNX family.[9] Westwood *et al.* have extensively described the generation and the characterization of the cyanogen *N*-oxide molecule[10-12] while we have recently reported the production of the corresponding *N*-sulfide molecule.[4]

It is also shown that the interaction, in a chemical ionization (CI) source or in a quadrupolar collision cell, between NCCNSe$^{\bullet+}$ and neutral nitriles leads to an efficient Se$^{\bullet+}$ transfer, producing nitrile *N*-selenides radical cations. The stability of the corresponding neutral dipoles has been evaluated by the NRMS methodology.[6]

Dissociative ionization of 3,4-dicyano-1,2,5-selenadiazole [1]: Following 70eV electron impact, the molecular ions of 3,4-dicyano-1,2,5-selenadiazole **1**$^{\bullet+}$ [*m/z* 184 (molecular ions containing the most abundant ^{80}Se isotope), 70%] predominantly lose cyanogen, yielding *m/z* 132 ions (100%) (Scheme 1). Other intense peaks in the mass spectrum of **1** are ascribed to Se$^{\bullet+}$ (*m/z* 80, 92%), NCCN$^{\bullet+}$ (*m/z* 52, 78%) and NCC$^+$ (*m/z* 38, 30%).

The collisional activation (CA) spectrum of the *m/z* 132 radical cations indicates the NCCNSe connectivity **2**$^{\bullet+}$ as evidenced by the collision induced fragmentations: the loss of CN$^\bullet$ (*m/z* 106), the loss of CCN$^\bullet$ (*m/z* 94) and the production of cyanogen ions (*m/z* 52) (Fig.1a). Compared to the CA spectrum of the cyanogen *N*-sulfide ions,[4] the Se$^{\bullet+}$ ions are now forming the base peak of the spectrum. That may be readily interpreted as resulting from the difference in ionizing energy between selenium and sulfur [IE (Se) = 9.75eV *vs.* IE (S) = 10.36eV].[13] The small peak at *m/z* 92 (formation of CSe$^{\bullet+}$ ions) probably results from a post-collisional isomerization process.[14] Note also that the doubly charged NCCNSe^{2+} ions are also accessible in the collision experiment, the charge stripping peak (CS) being present at *m/z* 66.

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PII: S0040-4039(97)10228-3

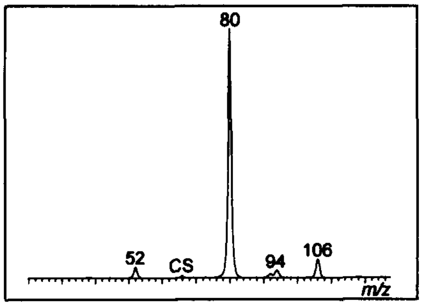
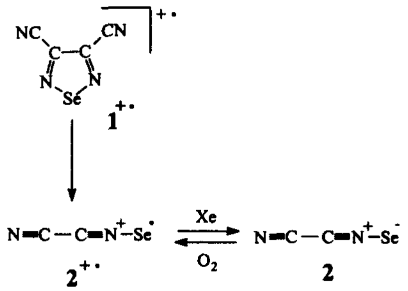
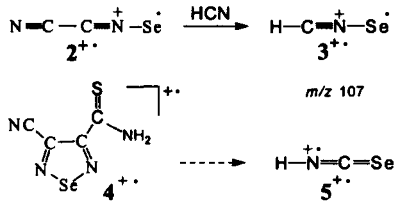


Fig.1a CA(O_2) mass spectrum of the $[NCCNSe]^{\bullet+}$ radical cations (*m/z* 132).[15]



Scheme 1[16]



Scheme 2[16]

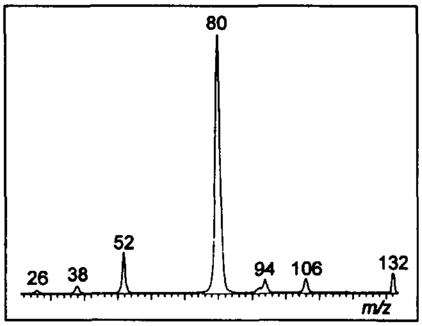


Fig.1b NR(Xe/O_2) mass spectrum of the $[NCCNSe]^{\bullet+}$ radical cations (*m/z* 132).[15]

The NR spectrum (Fig.1b) of the $NCCNSe^{\bullet+}$ radical cations, obtained by consecutive collisions with xenon and oxygen, features a weak but significant recovery signal at *m/z* 132 corresponding to survivor ions (Scheme 1). The fragmentations are also very similar to those observed in the CA spectrum, with small intensity differences already noticed when comparing CA to NR spectra. For instance, the increased intensity of the NR peak at *m/z* 52 may be due to reionization of neutral cyanogen produced in the neutralization cell and the absence of a charge stripping peak may result from a low probability for the NCCNSe → $NCCNSe^{2+}$ double ionization reaction.[17,18] The decreasing intensity of the recovery signal in the NCCNX series (X=O,[19] S,[4] Se) is in keeping with theoretical calculations showing that the energy requirement for the dissociation into NCCN + X decreases with the electronegativity of X, although the process remains endothermic in the three cases. It is indeed found, at the G2(MP2,SVP) level of theory, that the endothermicities of the reaction NCCNX→ NCCN + X follow the sequence O>S>Se, being respectively 415, 244 and 187 kJ/mol.[20]

CI experiments: $Se^{\bullet+}$ transfer to nitriles: Ionization of a mixture of HCN and 1 in a CI source leads to the formation of $[HCN,Se]^{\bullet+}$ radical cations (*m/z* 107) and also to protonated HCN as the major ion-molecule products. The CA spectrum of the $[HCN,Se]^{\bullet+}$ ions (Fig.2) is indicative of the HCNSe connectivity 3 , the most intense peak induced by collision (beside the formation of selenium ions) corresponding to the loss of $HC^{\bullet}$ (NSe^+ ions, *m/z* 94). Further support for the HCNSe connectivity 3 has been found in the study of another selenadiazole 4 which, after electron impact ionization, also generates $[C,H,N,Se]^{\bullet+}$ ions (*m/z* 107) through a complex reaction sequence probably involving a [1,4] hydrogen transfer on the ring nitrogen and losses of HNCS and C_2N_2. Also dominated by a very intense peak for selenium ions (*m/z* 80), the loss of $HC^{\bullet}$ observed in the case of $\mathbf{3}^{\bullet+}$ is now replaced by a loss of HN (*m/z* 92) indicative of the isoselenocyanate structure $\mathbf{5}^{\bullet+}$ (Fig.2).

The NR spectra of the $HCNSe^{\bullet+}$ and $HNCSe^{\bullet+}$ ions feature in both cases significant recovery signals and fragmentations in keeping with those observed in their corresponding CA spectra. The neutral HCNSe and HNCSe are therefore stable and distinct molecules in the gas phase (Scheme 2).

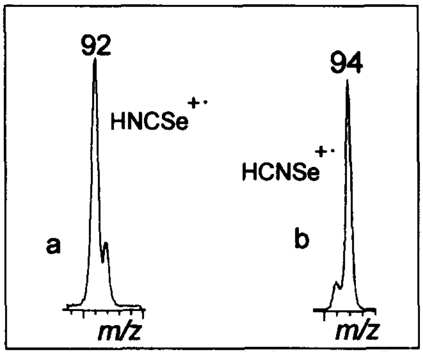
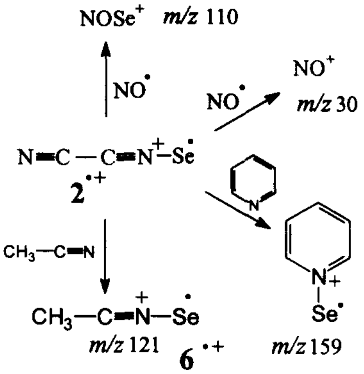


Fig.2 CA spectra (region 92-94) of the [HNCSe] (a) and [HCNSe] (b) radical cations (*m/z* 107).[15]



Scheme 3

Chemical ionization (dicyanoselenadiazole as reagent gas) of CH_3CN and PhCN generates $CH_3CNSe^{\bullet+}$ (*m/z* 121) $\mathbf{6}^{\bullet+}$ and $PhCNSe^{\bullet+}$ (*m/z* 183) $\mathbf{7}^{\bullet+}$ ions, respectively. In both cases, the CA spectra characterize the RCNSe connectivity. For R=Ph, the CA spectrum presents a base peak corresponding to the formation of $RCN^{\bullet+}$ ions (loss of Se) while for R=H or CH_3 the production of $Se^{\bullet+}$ ions (loss of RCN) is the dominant fragmentation. This different behaviour follows the trend in the ionization energies [IE(Se) = 9.75; IE(HCN) = 13.6; IE(acetonitrile) = 12.2 and IE(PhCN) = 9.62 eV].[13] Weak recovery signals are present in the NR spectra while a somewhat higher abundance of the $Se^{\bullet+}$ ions (*m/z* 80) in the NR spectrum of $PhCNSe^{\bullet+}$ ions is due to reionization of Se atoms generated in the neutralization cell.

Ion-molecule reactions in the quadrupole collision cell: In its hybrid configuration,[21] the AutoSpec 6F mass spectrometer[15] is a unique arrangement which allows the study of ion-molecule reactions between neutral reagents and mass-selected ions decelerated at near thermal energies. Compared to the ion-molecule reactions performed in the chemical ion source, this new hybrid arrangement presents the advantages of the absence of ambiguities concerning the actual nature of the precursor ions retaining the access to high energy CA spectra of mass-selected ion-molecule products.

For preliminary experiments, three different neutral targets have been selected: acetonitrile, pyridine and nitric oxide. The first target was chosen in order to confirm the results of the experiments performed in the CI source, the second to investigate the possibility of synthesis of the elusive pyridine *N*-selenide in the gas phase and the third target to indicate the distonic character of the $\mathbf{2}^{\bullet+}$ ions.

The reaction between decelerated $NCCNSe^{\bullet+}$ ions prepared in the EI source by electron impact of **1** and $NO^{\bullet}$ leads to charge exchange (NO^+, *m/z* 30) in competition with selenium transfer ($SeNO^+$ cations, *m/z* 110). SNO^+ formation was also a prominent process when $NCCNS^{\bullet+}$ ions were allowed to react with nitric oxide, whereas NO^+ is the major product in the case of $NCCNO^{\bullet+}$ ions.[19]

NCCNSe$^{\bullet+}$ ions also react very efficiently with pyridine producing *m/z* 159 ions. The interpretation of the CA spectrum of these ions is however not straightforward and additional experiments are required in order to confirm the supposed pyridine *N*-selenide structure.

Finally, reaction of **2**$^{\bullet+}$ with acetonitrile fully confirms the results of the experiments performed in the CI source: the precursor ions are NCCNSe$^{\bullet+}$ radical cation and the product ions are $CH_3CNSe^{\bullet+}$ ions as shown by their CA spectra which is identical with the spectrum of the corresponding ions when produced in the CI source. The ion-molecule reaction results are summarized in Scheme 3.

Acknowledgments: The Mons laboratory thanks the Fonds National de la Recherche Scientifique (FNRS) for its contribution in the acquisition of the large scale tandem mass spectrometer, Micromass AutoSpec 6F, and for financial support (PG).

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