

# Ion–molecule reactions between ionized nitrile oxides and neutral nitrile

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Dedicated to Yannik Hoppilliard on the occasion of her sixtieth birthday.

## Abstract

The ion–molecule reactions of ionized nitrile oxide,  $R-C\equiv N^+-O^\bullet$ , with several neutral nitriles have been studied using both tandem mass spectrometric techniques and ab initio molecular orbital calculations. Ionized oxygen atom transfer as well as a formal substitution of nitric oxide by the neutral reagent in the radical cation were the main processes. Whereas the former reaction yields the corresponding ionized nitrile oxide, the second process gives an even electron species tentatively ascribed, following high-kinetic energy collisional activation experiments, to an aromatic aziriny cation. All the experimental data point to a two-step reaction sequence where the primarily formed intermediate ions competitively dissociate by the loss of nitrile or of nitric oxide respectively giving nitrile oxide ions and aziriny ions. From a theoretical point of view, the mechanism of the simplest reaction  $HCNO^{\bullet+} + HCN \rightarrow \text{cyclo-HCCHN}^+ + NO^\bullet$  has been explored at the MP2/6-31G(d) level of theory. The most favorable reaction profile involves the formation of a C–N bond between the positively charged carbon atom of  $HCNO^{\bullet+}$  and the nitrogen atom of cyanhydric acid giving an  $HCNO^{\bullet+}/HCN$  intermediate which isomerizes into an ionized nitrosoazirine before losing  $NO^\bullet$ . (Int J Mass Spectrom 219 (2002) 643–658)

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## 1. Introduction

Three-membered rings represent the smallest potentially aromatic or antiaromatic systems. Most of these highly strained compounds are expected to be short-lived. However, some have been detected or postulated as reaction intermediates. The cyclopropenyl cation with two  $\pi$  electrons is, according to Hückel

theory, an aromatic system and is thus expected to be a relatively stable species. Indeed,  $c-C_3H_3^+$  cation is a well-studied stable gas-phase ion [1]. Moreover, such a cation has been prepared in the condensed phase as stable salts [2]. As far as the aza-analogs are concerned, it has been recently demonstrated that the resonance stabilization (or aromaticity) is still occurring when the CH group is replaced by a nitrogen atom as for the aziriny cation ( $C_2H_2N^+$ ) [3], and that a comparable situation is expected for diaziriny cations [3,4]. Moreover, several theoretical studies, performed at different levels of theory, revealed

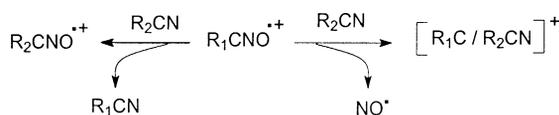
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that the lowest-energy form, amongst the  $C_2H_2N^+$  species, is the cyclic isomer with, the two linear forms,  $^+CH_2CN$  and  $^+CH_2NC$  being higher in energy [5]. The calculated isomerization barriers indicate that the three isomeric structures, once formed, would exist as stable, non-interconverting species in the absence of external influence [5d]. From all these theoretical works, it was concluded that the azirinylium cation could be observable in a non-nucleophilic medium. The low pressure which prevails in a mass spectrometer represents one of the most suitable environments for a direct observation of such a species. Indeed, the  $C_2H_2N^+$  ion ( $m/z$  40) is observed as a fragmentation product in the mass spectra of various nitrogen-containing compounds [6]. The cyclic isomer,  $c-C_2H_2N^+$ , has been suggested to account for the collision-induced spectra of the  $C_2H_2N^+$  ions generated from a series of  $C_2H_3N^+$  isomers, such as acetonitrile and methyl isocyanide [7]. Actually, the CA spectra of  $C_2H_2N^+$  ions generated from ionized  $CH_3CN$  and  $CH_3NC$ , are identical. The similarity of both spectra was interpreted in terms of identical structures. A cyclic aromatic structure was suggested as it would be in accord with the evidence that identical structures are formed from both stable ions,  $CH_3CN^{\bullet+}$  and  $CH_3NC^{\bullet+}$ , which initially have different CCN and CNC connectivities [7]. This problem was reconsidered by Holmes and Mayer [8]. They showed, by mass spectrometry, that dissociative ionization of  $CH_3CN$ ,  $CH_3NC$  or 1-*H*-1,2,3-triazole produced the lowest energy azirinylium cation. The linear  $^+CH_2CN$  cation could only be prepared starting with  $ICH_2CN$  [8].

During the last 5 years, we have thoroughly investigated the gas-phase behavior of ionized and neutral  $R-C\equiv N-X$  molecules ( $X = O$  [9],  $S$  [10], and  $Se$  [11]) making use of tandem mass spectrometry techniques. The preparation, characterization by collisional activation and collision-induced neutralization of the  $RCNX^{\bullet+}$  radical cations were the considered topics [12]. In order to achieve the structural characterization of the  $RCNX^{\bullet+}$  radical cations and to investigate the bimolecular reactivity of these ions, we also performed associative ion–molecule reactions between  $RCNX^{\bullet+}$  radical cations and some neutral reagents



Scheme 1.

[13]. For instance, whereas ionized nitrile sulfides and selenides readily react with nitric oxide by generating, respectively  $SN^+O$  and  $SeN^+O$  cations, such a reaction is by far less efficient in the case of ionized nitrile oxides [13]. Following molecular orbital calculations performed on the  $NCCNX^{\bullet+}$  system, these contrasting chemical behaviors can be attributed to the higher double-bond character of the  $NO$  bond in  $NCCNO^{\bullet+}$  ions as compared to the  $NS$  and  $NSe$  bonds in the corresponding radical cations [9].

In the present work, we report on the gas-phase reaction between several ionized nitrile *N*-oxides and neutral nitriles in the rf-only quadrupole collision cell of a hybrid mass spectrometer of sector-quadrupole-sector geometry. Competitively to the  $O^{\bullet+}$  transfer reaction, a formal substitution of  $NO^{\bullet}$  by the neutral nitrile reagent in the radical cation is always observed (Scheme 1). Note that these reactions between ionized nitrile oxides and neutral nitriles are a priori at variance with the condensed-phase reaction involving the neutral molecules. Indeed, nitrile oxides undergo 1,3-dipolar cycloaddition with nitriles, such a reaction yielding the corresponding 1,2,4-oxadiazole [14].

Considering the  $NO^{\bullet}$  loss route, the produced  $[R_1C/R_2CN]^+$  cations may possess structures such as  $R_1R_2C^+-CN$ ,  $R_1R_2C^+-NC$ , or  $R_1-\bullet C=N^+=C^{\bullet}-R_2$  but an attractive possibility could be the production of aromatic azirinylium cations. In such a case, this work would constitute the first direct observation of *substituted* azirinylium cations. For the sake of information, such cations have been proposed to intervene in the isomerization of 3-chloro-1-azirines [15].

## 2. Experimental section

The spectra were recorded on a large scale tandem mass spectrometer (Micromass AutoSpec 6F,

Manchester) combining six sectors of  $E_1B_1E_2qc_1E_3-B_2c_2E_4$  geometry (E stands for electric sector, B for magnetic sector, c for the collision cells used in the present work and q for the rf-only quadrupole collision cell) [16]. General conditions were 8 kV accelerating voltage, 200  $\mu$ A trap current (in the electron ionization mode, EI), 70 eV ionizing electron energy and 200 °C ion source temperature. The solid samples were introduced with a direct insertion probe, while the liquid samples were injected in the ion source via a heated (180 °C) septum inlet.

Collisional activation ( $O_2$ ) experiments of fast (8 keV kinetic energy) mass selected source ions were performed in the cell preceding  $E_3$  and the CA 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. The metastable decomposition (MIKE) of the source ions in the third field-free region were recorded at the first off-axis detector after scanning the second electric sector.

The study of associative ion–molecule reactions can be realized in the quadrupole collision cell [16b]. Briefly, such experiments consist of the selection of a beam of fast ions (8 keV) with the three first sectors ( $E_1B_1E_2$ ) and the deceleration of these ions to approximately 5 eV (to maximize ion–molecule reactions) before entering the quadrupole cell. The interaction between the ions and the reagent gas (the pressure of the gas is estimated to be about  $10^{-3}$  Torr) was thereafter realized in the quadrupole and, after reacceleration at 8 keV, all the generated ions were separated and mass measured by scanning the field of the second magnet. The high-energy CA spectra of mass-selected ions generated in the quadrupole cell were recorded by a linked scanning of the fields of the last three sectors after collisional activation with oxygen in  $c_1$  or by a conventional scanning of the field of the last electric sector if the ions were collided with nitrogen in the  $c_2$  collision cell.

The samples were commercially available (Aldrich) and used without further purification, except for 1,2,5-oxadiazole [17a], 3,4-dimethyl-1,2,5-oxadiazole [17b], 3,4-dicyano-1,2,5-oxadiazole [17c], dibromoformaldoxime [17d], cyanhydric acid [17e], 2-chloro-

2,3-dimethyl azirine [17f,g], which were prepared according to the procedures described in the literature. 3-Cyano-5-methyl-1,2,4-oxadiazole was prepared by 1,3-dipolar cycloaddition of cyanogen *N*-oxide with acetonitrile. The reactive dipole was generated by flash-vacuum pyrolysis (500 °C) of 3,4-dicyanofuroxan [17h] and trapped in acetonitrile. Afterwards, the crude reaction mixture was introduced in the septum inlet without further purification and the ions of interest, namely the molecular ions of 3-cyano-5-methyl-1,2,4-oxadiazole ( $m/z$  95), were analyzed by collisional activation (vide infra).

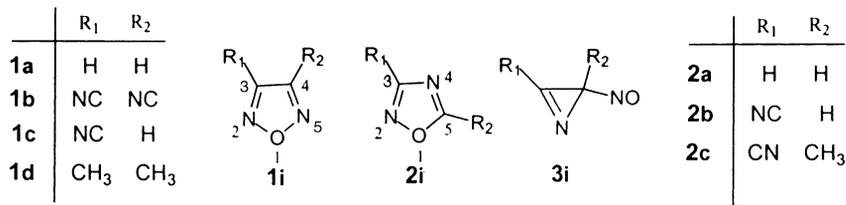
### 3. Results and discussion

#### 3.1. Reactions between ionized cyanhydric acid oxide, $HCNO^{\bullet+}$ , and hydrogen cyanide

After electron ionization, 1,2,5-oxadiazole (furan, **1a**, Scheme 2) readily expels a molecule of cyanhydric acid yielding  $HCNO^{\bullet+}$  radical cations ( $m/z$  43), the molecular ions of fulminic acid, as demonstrated by an earlier collisional activation study [13,18]. The  $HCNO^{\bullet+}$  radical cations can also be prepared starting from chlorooximinoacetic acid [18].

Mass-selected  $HCNO^{\bullet+}$  radical cations react with cyanhydric acid in the quadrupole collision cell by producing several different ionic species:  $m/z$  30 ( $NO^+$  cations),  $m/z$  28 ( $HCNH^+$  cations) and  $m/z$  40 ( $C_2H_2N^+$  cations) (Table 1 and Scheme 3).

The structural identification of the  $m/z$  28,  $HCN^+H$ , and 30,  $NO^+$ , product ions is readily achieved by high kinetic energy collisional activation experiments subsequent to their formation in the quadrupole. By contrast, it is less straightforward to establish the structure of the  $m/z$  40  $C_2H_2N^+$  cations. The CA spectrum of the ions generated during the  $HCNO^{\bullet+}/HCN$  reaction is found very similar to the CA spectra of the ions prepared from acetonitrile and 1,2,3-triazole ( $c-C_2H_2N^+$ ) but slightly different from the CA spectrum of the cations generated from iodoacetonitrile ( $^+CH_2CN$ ). In particular, the  $m/z$  13/ $m/z$  14 branching ratio ( $CH^+$  vs.  $CH_2^{\bullet+}$ ) can be used to differentiate the

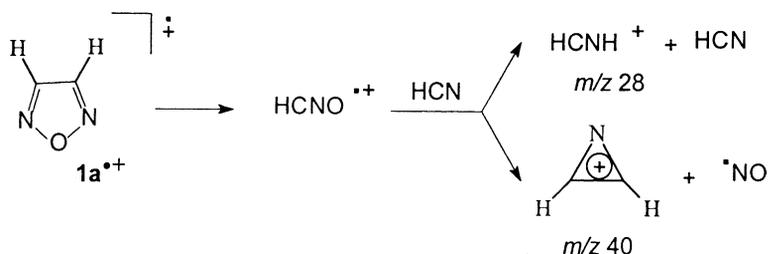


Scheme 2.

Table 1  
Products of associative ion–molecule reactions between ionized nitrile oxides and neutral nitriles

Reagents	Ionic products	Reactions	<i>I</i> <sup>a</sup>
HCNO <sup>•+</sup>			
HCN	HCN <sup>+</sup> H— <i>m/z</i> 28 <i>c</i> -C <sub>2</sub> H <sub>2</sub> N <sup>+</sup> — <i>m/z</i> 40	Protonation NO <sup>•</sup> /RCN substitution	16 3
CH <sub>3</sub> CN	CH <sub>3</sub> CN <sup>+</sup> H— <i>m/z</i> 42 <i>c</i> -C <sub>2</sub> H(CH <sub>3</sub> )N <sup>+</sup> — <i>m/z</i> 54	Protonation NO <sup>•</sup> /RCN substitution	37 0.3
ClCN	ClCN <sup>+</sup> H— <i>m/z</i> 62/64 <i>c</i> -C <sub>2</sub> H(Cl)N <sup>+</sup> — <i>m/z</i> 74/76 ClCNO <sup>•+</sup> — <i>m/z</i> 77/79	Protonation NO <sup>•</sup> /RCN substitution Ionized oxygen transfer	50 2 0.01
CH <sub>3</sub> CNO <sup>•+</sup>			
HCN	CH <sub>3</sub> CN <sup>+</sup> H— <i>m/z</i> 42 <i>c</i> -C <sub>2</sub> H(CH <sub>3</sub> )N <sup>+</sup> — <i>m/z</i> 54	Protonation NO <sup>•</sup> /RCN substitution	2 0.01
CH <sub>3</sub> CN	CH <sub>3</sub> CN <sup>+</sup> H— <i>m/z</i> 42 <i>c</i> -C <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> N <sup>+</sup> — <i>m/z</i> 68	Protonation NO <sup>•</sup> /RCN substitution	4 0.003
ClCN	CH <sub>3</sub> CN <sup>+</sup> H— <i>m/z</i> 42 ClCN <sup>+</sup> H— <i>m/z</i> 62/64 <i>c</i> -C <sub>2</sub> (CH <sub>3</sub> )(Cl)N <sup>+</sup> — <i>m/z</i> 88/89	Protonation Protonation NO <sup>•</sup> /RCN substitution	0.04 6 0.04
NCCNO <sup>•+</sup>			
HCN	HCNO <sup>•+</sup> — <i>m/z</i> 43 <i>c</i> -C <sub>2</sub> H(CN)N <sup>+</sup> — <i>m/z</i> 65 C <sub>3</sub> HN <sub>3</sub> O <sup>•+</sup> — <i>m/z</i> 95 C <sub>3</sub> HN <sub>3</sub> <sup>•+</sup> — <i>m/z</i> 79	Ionized oxygen transfer NO <sup>•</sup> /RCN substitution Intact adduct Loss of oxygen from the intact adduct	4 20 2.5 2.5
CH <sub>3</sub> CN	CH <sub>3</sub> CN <sup>+</sup> H— <i>m/z</i> 42 CH <sub>3</sub> CNO <sup>•+</sup> — <i>m/z</i> 57 <i>c</i> -C <sub>2</sub> (CH <sub>3</sub> )(CN)N <sup>+</sup> — <i>m/z</i> 79	? Ionized oxygen transfer NO <sup>•</sup> /RCN substitution	1 0.8 10
ClCN	ClCO <sup>+</sup> — <i>m/z</i> 63/65 ClCNO <sup>•+</sup> — <i>m/z</i> 77/79 <i>c</i> -C <sub>2</sub> (Cl)(CN)N <sup>+</sup> — <i>m/z</i> 99/101 <i>c</i> -C <sub>2</sub> (Cl)(Cl)N <sup>+</sup> — <i>m/z</i> 108/110/112	Ionized oxygen transfer NO <sup>•</sup> /RCN substitution Consecutive NO <sup>•</sup> /RCN substitution	1.5 6 71 5
BrCNO <sup>•+</sup>			
HCN	<i>c</i> -C <sub>2</sub> H(Br)N <sup>+</sup> — <i>m/z</i> 118	NO <sup>•</sup> /RCN substitution	0.3
CH <sub>3</sub> CN	<i>c</i> -C <sub>2</sub> (CH <sub>3</sub> )(Br)N <sup>+</sup> — <i>m/z</i> 83 <i>c</i> -C <sub>2</sub> (CH <sub>3</sub> )(NO)N <sup>+</sup> — <i>m/z</i> 132	NO <sup>•</sup> /RCN substitution NO <sup>•</sup> /RCN substitution	21 1
ClCN	ClCO <sup>+</sup> — <i>m/z</i> 63/65 <i>c</i> -C <sub>2</sub> (Cl)(NO)N <sup>+</sup> — <i>m/z</i> 103/105 <i>c</i> -C <sub>2</sub> (Cl)(Br)N <sup>+</sup> — <i>m/z</i> 152/154	NO <sup>•</sup> /RCN substitution NO <sup>•</sup> /RCN substitution NO <sup>•</sup> /RCN substitution	5 0.5 3

<sup>a</sup> Intensities relative to the main beam of reactant ions which was normalized to 100 units.



Scheme 3.

$^+\text{CH}_2\text{CN}$  ion from the  $c\text{-C}_2\text{H}_2\text{N}^+$  cation. This ratio amounts to 9.5, 1.9 and 1.9 in the CA spectra of the  $\text{C}_2\text{H}_2\text{N}^+$  cations prepared by the  $\text{HCNO}^{\bullet+}/\text{HCN}$  reaction and from acetonitrile and triazole, respectively (Fig. 1). This ratio is significantly lower (1.2) in the case of the iodoacetonitrile-generated cations. It may be recalled that Holmes and Mayer [8] proposed that  $\text{CH}_2\text{CN}^+$  cations are produced in the latter case while acetonitrile and triazole are precursors of the azirinyli

cation. Our data, show that the  $\text{HCNO}^{\bullet+}/\text{HCN}$  reaction generates a structure characterized by the largest  $m/z$  13/ $m/z$  14 ratio. Given the magnitude of this ratio, it is tempting to attribute the corresponding CA spectrum to the azirinyli structure since it is obviously prone to the direct formation of a  $\text{CH}^+$  group. At the opposite, the low  $m/z$  13/ $m/z$  14 ratio observed for the  $\text{C}_2\text{H}_2\text{N}^+$  ions coming from iodoacetonitrile is in keeping with the  $\text{CH}_2\text{CN}^+$  structure. The intermediate situation observed for acetonitrile and triazole may be interpreted by the presence of a mixture of both isomers.

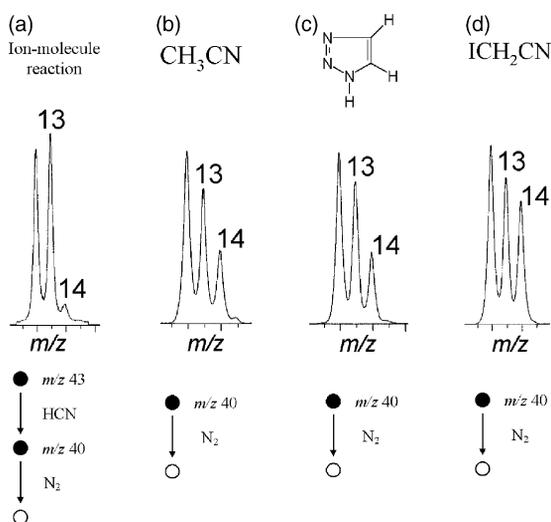


Fig. 1. CA spectra of  $\text{C}_2\text{H}_2\text{N}^+$  ions ( $m/z$  40) ( $m/z$  12/14 regions) obtained by (a) ion–molecule reactions between  $\text{HCNO}^{\bullet+}$  ions and HCN, (b) hydrogen-loss from ionized acetonitrile, (c) hydrogen- and nitrogen-losses from ionized  $v$ -triazole and (d) iodine atom-loss from ionized iodoacetonitrile. The terminology used to schematize the ion–molecule reactions is that introduced by Schwartz et al.: a filled circle represents a fixed (or selected) mass; an open circle, a variable (or scanned) mass, whereas the neutral reagent that causes the mass transition is shown between the circles [29].

Beside the structural assignment suggested by the experiments, it is also important to emphasize that, amongst all the  $\text{C}_2\text{H}_2\text{N}^+$  isomeric cations, the cyclic azirinyli structure is the global minimum on the potential energy surface [5]. Thus, in order to complete this study, we decide to explore the reactions presented in Scheme 3 by means of molecular orbital calculations.

Since the thermochemistry of the studied system was not fully documented, we first calculated the heats of formation of the reactants and expected products by using the atomization energies estimated by the G2 method [19].<sup>3</sup> The mean deviation observed at this level of theory, if no significant spin contamination occurs, is ca.  $7\text{ kJ mol}^{-1}$  [20]. As observed in Table 2, an excellent agreement is found between theory and experiment for HCN,  $\text{HCNH}^+$  and  $\text{NO}^{\bullet}$ . Severe discrepancies are however observed when G2 results are compared with the estimated heats of formation of  $\text{HCNO}^{\bullet+}$  and azirinyli cation (deviation:

<sup>3</sup> All the calculations have been done using the Gaussian 98 suite of programs.

Table 2  
Calculated and experimental heats of formation related to the  $\text{HCNO}^{\bullet+}/\text{HCN}$  system ( $\text{kJ mol}^{-1}$ )

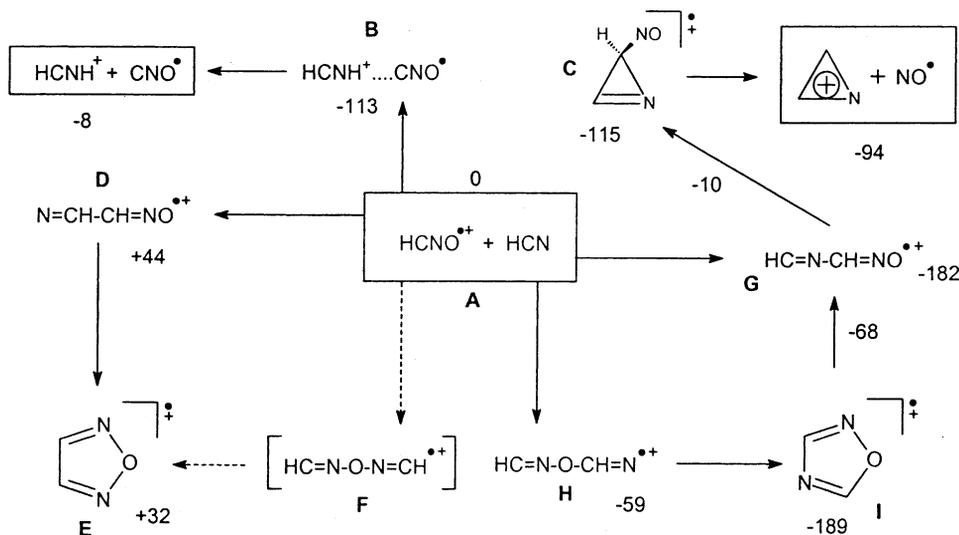
Species	$\Delta H_{f,298}^{\circ}$ ( $\text{kJ mol}^{-1}$ )	
	G2	Experimental
$\text{HCNO}^{\bullet+}$	1230.6	(1263)
HCN	131.8	135.1
$\text{CNO}^{\bullet}$	388.9	–
$\text{HCNH}^+$	949.6	952.2
$\text{cyclo-C}_2\text{H}_2\text{N}^+$	1198.6	(1138)
$\text{NO}^{\bullet}$	90.4	91.3

33 and  $60 \text{ kJ mol}^{-1}$ , respectively). Identical observation has been made for the latter ion by Radom and co-workers [5f], who attribute part of the discrepancy to an erroneous  $\Delta H_{f,298}^{\circ}$  value of the molecule used in the experimental study. Furthermore, a recent study by Lau et al. is in perfect agreement with our result [5g].

In the case of  $\text{HCNO}^{\bullet+}$ , the tabulated value of  $1263 \text{ kJ mol}^{-1}$  [21] has been obtained by combining the experimental ionization energy of HCN (10.83 eV) [22] to its estimated heat of formation. This latter value ( $228 \text{ kJ mol}^{-1}$ ) was derived from the experimental  $\Delta H_{f,298}^{\circ}(\text{HNCO})$  and the difference in total electronic energy calculated between HNCO and

HCNO at the HF/6-31G\*\*//HF/4-31G level [23]. No doubt that this difference is subject to a large uncertainty which is probably at the origin of the deviation noted in Table 2. Therefore, we feel confident that our G2 results are very likely to be more accurate estimates.

The reaction enthalpies for the proton transfer reaction:  $\text{HCNO}^{\bullet+} + \text{HCN} \rightarrow \text{HCNH}^+ + \text{CNO}^{\bullet}$ ; and for the azirinylation:  $\text{HCNO}^{\bullet+} + \text{HCN} \rightarrow \text{cyclo-HCCHN}^+ + \text{NO}^{\bullet}$  can be estimated by the G2 heats of formation. It is found that both reactions are exothermic, by 24 and  $74 \text{ kJ mol}^{-1}$ , respectively. The mechanism of the reactions has been explored theoretically at the MP2/6-31G(d) level of theory, the results are summarized in Scheme 4. The relative potential energies (in  $\text{kJ mol}^{-1}$ ) are indicated below the relevant stable structures and beside the arrows for the localized transitions structures. It may be first noted that, by comparison with the G2 results, the reaction exothermicity is correctly accounted for at the MP2/6-31G(d) level and thus a good, semi-quantitative description of the potential energy profile is expected. The  $\text{HCNO}^{\bullet+}$  radical cation may be seen as a distonic species where the radical is located on the oxygen atom and the charge in the



Scheme 4.

carbon atom. The approach of this ion toward neutral hydrogen cyanide may result in several reaction paths.

The proton transfer reaction occurs from a collinear approach of both reactants leading, without energy barrier, to a proton bound complex **B** stabilized by ca.  $100 \text{ kJ mol}^{-1}$  with respect to its components (Scheme 4). It is worthy to note that, in structure **B**, the transferred proton is covalently bonded to the nitrogen atom of the HCN moiety ( $d_{\text{NH}} = 1.110 \text{ \AA}$ ) while the  $\text{H} \cdots \text{CNO}$  distance is elongated to  $1.636 \text{ \AA}$ , as expected for a typical proton bonding. The overall reaction:  $\text{HCNO}^{\bullet+} + \text{HCN} \rightarrow \mathbf{B} \rightarrow \text{HCNH}^+ + \text{CNO}^{\bullet}$ , is in fact a typical example of a single well potential energy process since the second step, the stretching of the intermolecular proton bond, is continuously endothermic. This type of potential energy profile is generally associated with a fast (collision) rate in the exothermic direction. It probably explains the observation of a high yield of  $\text{HCNH}^+$  cations under our experimental conditions.

In order to explain the  $\text{NO}^{\bullet}$  loss, a number of reaction routes have been explored. No concerted cycloaddition reactions leading to radical cations **C**, **E** or **I** could be found, only stepwise processes were identified as depicted in Scheme 4. However, we were unable to locate a stable structure **F** at the MP2/6-31G(d) level, all tentatives leads to high energy intermediates which invariably collapse to either **A** or **E**. Clearly, the formation of ionized 1,2,5-oxadiazole, **E**, or its open forms **D** and **F**, is excluded since it corresponds to endothermic processes. By contrast, the formation of ionized 1,2,4-oxadiazole, **I**, is allowed through its open forms **G** and **H**. The large difference in energy between the two heterocyclic radical cations is not unexpected since a comparable contrast exists between ionized oxazole and isoxazole (the enthalpy difference amounts for  $130 \text{ kJ mol}^{-1}$  in that case).

In fact, the most favorable reaction between ionized fulminic acid and neutral hydrogen cyanide is the formation of a C–N bond between the positively charged carbon atom of  $\text{HCNO}^{\bullet+}$  and the nitrogen atom of HCN. The product ion, **G**, is situated  $182 \text{ kJ mol}^{-1}$  below the reactants and may isomerize either to ionized 1,2,4-oxadiazole, **I**, or ionized nitrosoazirine, **C**,



Scheme 5.

by ring closure. Starting from **G**, the closure of the CNC angle ( $180^\circ$  in **G**) leads to both cyclic products, depending upon the initial orientation of the NO group. Isomer **G<sub>a</sub>** leads to **I** while isomer **G<sub>b</sub>** gives rise to ion **C**, see Scheme 5.

The critical structures for both reactions, respectively leading to **I** and **C**, are situated at ca.  $-70$  and  $-10 \text{ kJ mol}^{-1}$  with respect to the reactants **A**, both reactions can thus be observed under our experimental conditions. Elimination of  $\text{NO}^{\bullet}$  has been simulated by C–N bond elongation from **G** and **C**. The former reaction rapidly becomes endothermic and is consequently excluded. By contrast, the dissociation of **C** leading to azirinylium cation occurs without a significant reverse activation barrier. The present calculations consequently indicate that the minimum energy reaction path leading to  $\text{NO}^{\bullet}$  loss passes through the two intermediate structures **G** and **C**. The reaction is thus characterized by a double well potential energy profile. Moreover, the isomerization step  $\mathbf{G} \rightarrow \mathbf{C}$  involves a tight transition structure close in energy to the reactants. In such a situation, a slow down effect upon the reaction rate is expected. This explains why the  $\text{NO}^{\bullet}$  loss, even being the most exothermic process, is the less efficient reaction.

### 3.2. Reactions between cyanhydrinic acid oxide, $\text{HCNO}^{\bullet+}$ , and acetonitrile or cyanogen chloride

The associative interaction between  $\text{HCNO}^{\bullet+}$  radical cations and neutral acetonitrile (or cyanogen chloride,  $\text{ClCN}$ ) was also investigated using the quadrupole cell and again the main reactions were the protonation of the neutral reagent and the formal substitution of  $\text{NO}^{\bullet}$  by acetonitrile (or cyanogen chloride) in the mass selected reactive ions, see Table 1. In the case of the cyanogen chloride neutral reagent, an additional process leads to the transfer of ionized

oxygen atom to C1CN, probably yielding C1CNO<sup>•+</sup> radical cations. As far as the NO<sup>•</sup>/RCN substitution reaction is concerned, the CA spectra of the cations were recorded and the fragment ions are gathered in Table 4 (vide infra for the discussion).

### 3.3. Reactions between ionized cyanogen oxide, NCCNO<sup>•+</sup>, and hydrogen cyanide

The dissociative ionization of 3,4-dicyano-1,2,5-oxadiazole (**1b**) readily leads to the production of NCCNO<sup>•+</sup> radical cations ( $m/z$  68) as demonstrated by an earlier collisional activation study [9]. Mass-selected NCCNO<sup>•+</sup> radical cations react with cyanhydric acid in the quadrupole collision cell by producing several different ionic species:  $m/z$  30 (NO<sup>+</sup> cations),  $m/z$  43 (HCNO<sup>•+</sup> radical cations),  $m/z$  65 (C<sub>3</sub>HN<sub>2</sub><sup>+</sup> cations) and  $m/z$  95 (adduct radical cations), see Fig. 2a and Table 1.

The peak at  $m/z$  54, corresponding to C<sub>2</sub>NO<sup>+</sup> cations, originates from the metastable decomposition of the  $m/z$  68 mass-selected ions [9]. The structural identification of  $m/z$  30 and 43 ions is readily achieved by high kinetic energy collisional activation experiments subsequent to their formation in the quadrupole. Tale-tell peaks at  $m/z$  13 (HC<sup>+</sup> cations),  $m/z$  27 (HCN<sup>•+</sup> radical cations) and  $m/z$  30 (NO<sup>+</sup> cations) unambiguously identify the HCNO connectivity [18]. It is quite interesting to emphasize that this *trans*-oxygenation process, NCCNO<sup>•+</sup> + HCN → NCCN + HCNO<sup>•+</sup>, seems to be less efficient than the corresponding ionized sulfur and selenium transfers from NCCNS(Se)<sup>•+</sup> radical cations to HCN. This phenomenon has been already recalled in the introduction [9].

The identification of the  $m/z$  65 cations, presenting the C<sub>3</sub>N<sub>2</sub>H composition, is less straightforward (Fig. 2b). Nevertheless, based on the structure of the reacting species and on the presence of some characteristic collision-induced fragmentations such as the losses of a CH group ( $m/z$  52), of a nitrogen atom ( $m/z$  51), of a CN<sup>•</sup> radical ( $m/z$  39) and of HCN ( $m/z$  38) the formation of a  $m/z$  65 ion of azirinyll structure may be suggested (Scheme 6).

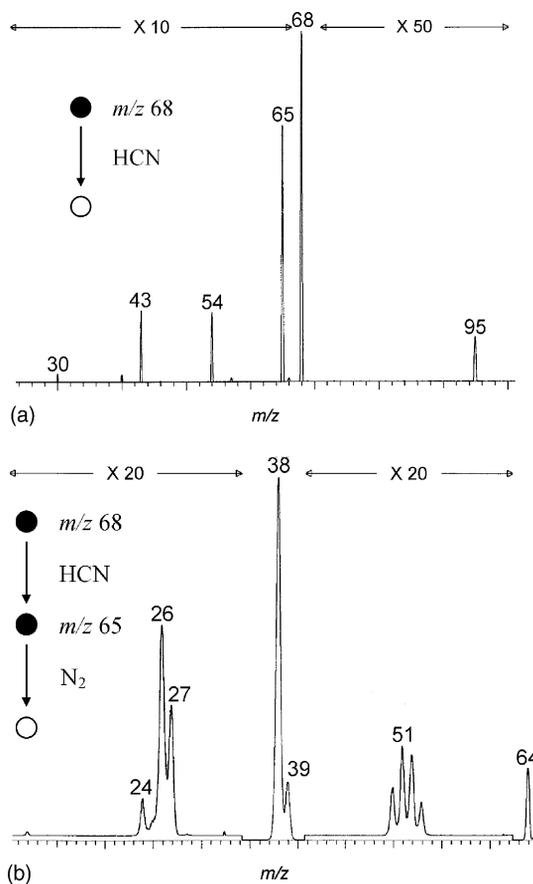
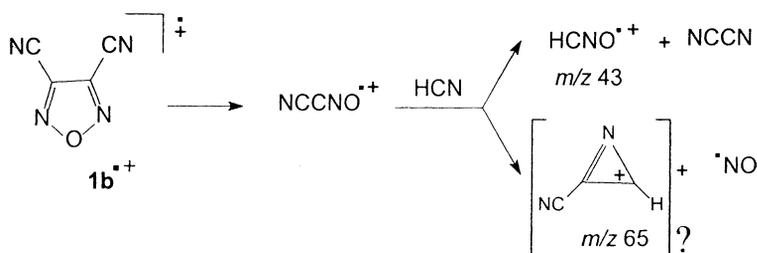


Fig. 2. Ion–molecule reactions between ionized cyanogen oxide ( $m/z$  68) and cyanhydric acid: (a) mass spectrum of the ion–molecule reaction products, and (b) CA spectrum (8 keV, E scan, nitrogen) of the  $m/z$  65 ions. The  $m/z$  54 signal, observed in all the mass spectra when  $m/z$  68 ions are the reactant species, originates from the unimolecular dissociation of the  $m/z$  68 ions.

Molecular orbital calculations, at the MP2/6-31G(d) level, shed also some lights on the possible formation of an azirinyll ion by reaction of NCCNO<sup>•+</sup> with HCN. The first argument is that, again, the azirinyll structure is predicted to be more stable than its isomeric forms. At the MP2/6-31G(d) level, ions HC(CN)<sub>2</sub><sup>+</sup>, HC(CN)(NC)<sup>+</sup>, HC(NC)<sub>2</sub><sup>+</sup>, HCNCN<sup>+</sup> and HCNCC<sup>+</sup> are situated 25, 73, 127, 153 and 419 kJ mol<sup>-1</sup>, respectively above the cyanoazirinyll cation (the 298 K heat of formation of the latter ion, calculated at the G2 level using the atomization reaction, is



equal to  $1425 \text{ kJ mol}^{-1}$ ). The second point is that, as in the case of the parent  $\text{HCNO}^{\bullet+}$  ion, ionized cyanogen oxide is a distonic ion where the lone electron is localized on the oxygen atom and the positive charge on the carbon atom of the CNO moiety. Consequently, its reactivity toward hydrogen cyanide is expected to be comparable to that summarized in Scheme 4. In these circumstances, the primary adducts should be  $\text{N}=\text{C}-\text{C}=\text{N}-\text{O}-\text{CH}=\text{N}^{\bullet+}$  and  $\text{HC}=\text{N}-\text{C}(\text{CN})=\text{NO}^{\bullet+}$  whose isomerization by ring closure would lead to ionized 3-cyano-1,2,4-oxadiazole (**2b**) and 2,2-cyano-nitroso azirine, the latter being the precursor of the cyanoaziriny cation by  $\text{NO}^{\bullet}$  loss.

A mean to test the possible structures of the intermediate adducts is to thermalize the collision complex  $m/z$  95. When the partial pressure in HCN inside the quadrupole is increased (ion transmission reduced from 50 to 30%), the intensity of the  $m/z$  95 signal grows. This increase can be related to the collisional stabilization of these ions after their production in the quadrupole. The collisional activation spectrum of these  $m/z$  95 ions is of interest since it gives some pieces of information related to the mechanism of the observed reactions. As shown in Fig. 3, the CA spectrum of these ions features inter alia all the ion–molecule reaction products observed during the  $\text{NCCNO}^{\bullet+}/\text{HCN}$  interaction, namely  $m/z$  30, 43 and 65. The other peaks are likely to originate from fragmentations of these three ions together with the  $m/z$  68 ions (as for example the  $m/z$  38 ions which correspond to the  $\text{NO}^{\bullet}$  loss from  $m/z$  68). As mentioned in the preceding paragraph, potential structures for the  $m/z$  95 adduct radical cations are  $\text{N}=\text{C}-\text{C}=\text{N}-\text{O}-\text{CH}=\text{N}^{\bullet+}$ ,  $\text{HC}=\text{N}-\text{C}(\text{CN})=\text{NO}^{\bullet+}$ , 3-cyano-1,2,4-oxadiazole (**2b**)

and 2,2-cyano-nitroso azirine, but other candidates such as 3-cyano-1,2,5-oxadiazoles (**1c**) is also possible.

The loss of HCN is the predominant fragmentation of the collision-excited  $m/z$  95 ions (Fig. 3), and the corresponding signal at  $m/z$  68 ( $\text{NCCNO}^{\bullet+}$  ions) is the base peak of the CA spectrum. On a simple structural ground, this elimination may occur from the four putative structures. However, it may be noted that ionized 3-cyano-1,2,5-oxadiazole should lead to a major production of  $\text{HCNO}^{\bullet+}$  ( $m/z$  43) rather than  $\text{NCCNO}^{\bullet+}$  ( $m/z$  68) since the sum of the heats of formation,  $\sum \Delta H_f(\text{NCCNO}^{\bullet+} + \text{HCN}) = 1605 \text{ kJ mol}^{-1}$  is larger than  $\sum \Delta H_f(\text{HCNO}^{\bullet+} + \text{NCCN}) = 1570 \text{ kJ mol}^{-1}$  (Tables 2 and 3). This observation could indicate that the produced ions, if *penta*-cyclic, would possess the 1,2,4-oxadiazole structure rather than the isomeric 1,2,5-oxadiazole structure but it cannot completely

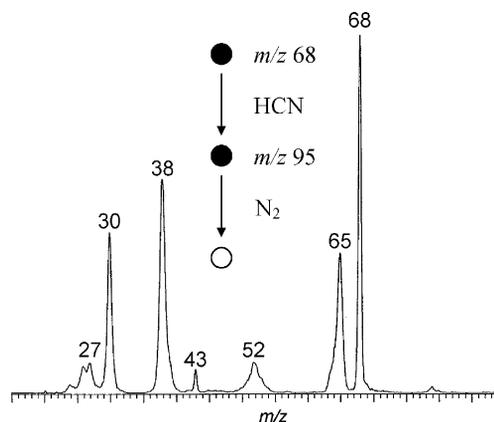


Fig. 3. Ion–molecule reaction between ionized cyanogen oxide ( $m/z$  68) and cyanohydrin acid: CA spectrum (8 keV, E scan, nitrogen) of the  $m/z$  95 adduct ions.

Table 3  
Selected experimental heats of formation of ionized nitrile oxides and neutral nitriles

	$\Delta H_f$ (kJ mol <sup>-1</sup> )
CH <sub>3</sub> CNO <sup>•+</sup>	1095 [27]
NCCNO <sup>•+</sup>	1470 [28]
CH <sub>3</sub> CN	74 [21]
NCCN	307 [21]

exclude a marginal contribution of this structure in the mixture of the thermalized  $m/z$  95 ions.

### 3.4. Reactions between ionized cyanogen oxide, NCCNO<sup>•+</sup>, and acetonitrile

The interaction in the quadrupole between ionized cyanogen oxide and acetonitrile also leads to several ionic species:  $m/z$  27 (CHN<sup>•+</sup> or C<sub>2</sub>H<sub>3</sub><sup>+</sup>),  $m/z$  42 (protonated acetonitrile),  $m/z$  53 (C<sub>2</sub>N<sub>2</sub>H<sup>+</sup> cations),  $m/z$  57 (CH<sub>3</sub>CNO<sup>•+</sup> ions) and  $m/z$  79 (C<sub>4</sub>H<sub>3</sub>N<sub>2</sub><sup>+</sup> cations), see Fig. 4a and Table 1. The adduct ion, that would be detected at  $m/z$  109, is never observed whatever the pressure in acetonitrile is. The structures or at least the compositions of the ion–molecule reaction products are probed by collisional activation. The  $m/z$  27 ions are confirmed to be C<sub>2</sub>H<sub>3</sub><sup>+</sup> cations (not HCN<sup>•+</sup> radical cations), whereas ionized acetonitrile oxide ( $m/z$  57) and protonated acetonitrile are readily identified by comparison with the collisional activation behaviors of authentic samples. A closer analysis of the collisional activation spectrum of the  $m/z$  79 is quite interesting (Fig. 4b): the  $m/z$  64 signal confirms the presence of a methyl group and the signals at  $m/z$  53, 52, 38, 27, 26, respectively correspond to the losses of NC<sup>•</sup> radical or C<sub>2</sub>H<sub>2</sub> (vide infra), to the formation of ionized cyanogen and NCC<sup>+</sup> cations and to the formation of C<sub>2</sub>H<sub>3</sub><sup>+</sup> cations and NC<sup>+</sup> cations. The use of perdeuterated acetonitrile as the neutral reagent confirms the previous conclusions as far as the compositions of the ion–molecule reaction products are concerned: the peaks at  $m/z$  27 (C<sub>2</sub>H<sub>3</sub><sup>+</sup> cations),  $m/z$  42 (protonated acetonitrile),  $m/z$  53 (C<sub>2</sub>N<sub>2</sub>H<sup>+</sup> cations),  $m/z$  57 (CH<sub>3</sub>CNO<sup>•+</sup> ions) and  $m/z$  79 (C<sub>4</sub>H<sub>3</sub>N<sub>2</sub><sup>+</sup> cations) are now observed respectively

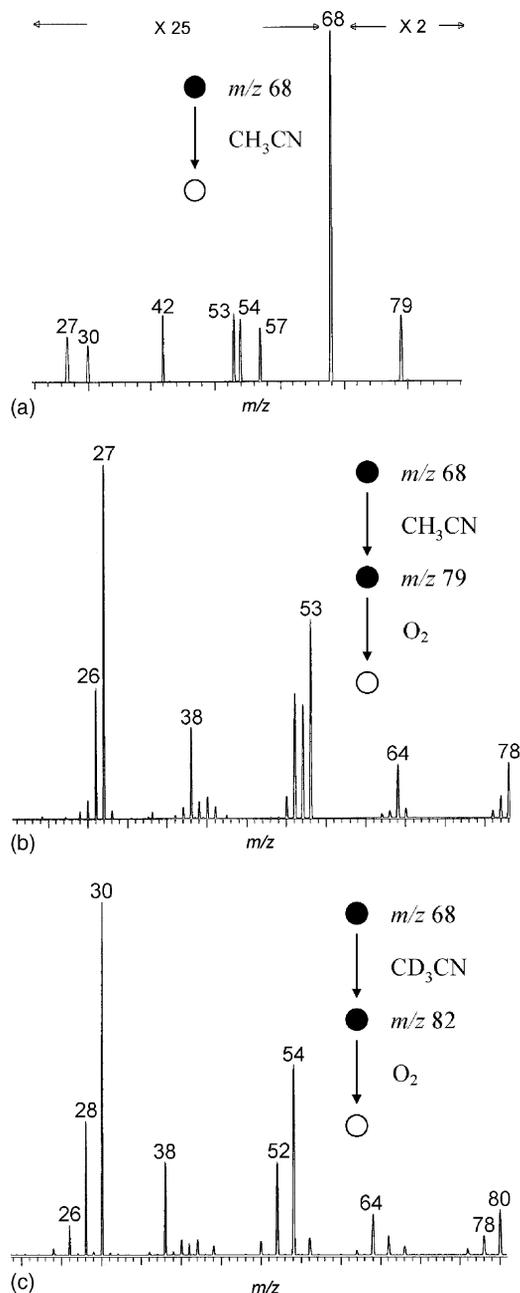
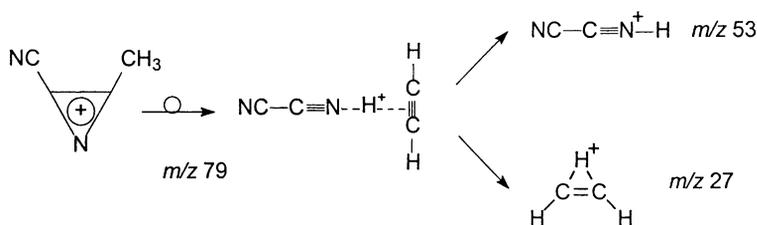


Fig. 4. Ion–molecule reactions between ionized cyanogen oxide ( $m/z$  68) and acetonitrile: (a) mass spectrum of the ion–molecule reaction products, and (b) CA spectrum (8 keV, linked scan, oxygen) of the  $m/z$  79 ions, (c) CA spectrum (8 keV, linked scan, oxygen) of  $m/z$  82 ions produced by ion–molecule reaction between ionized cyanogen oxide ( $m/z$  68) and CD<sub>3</sub>CN.

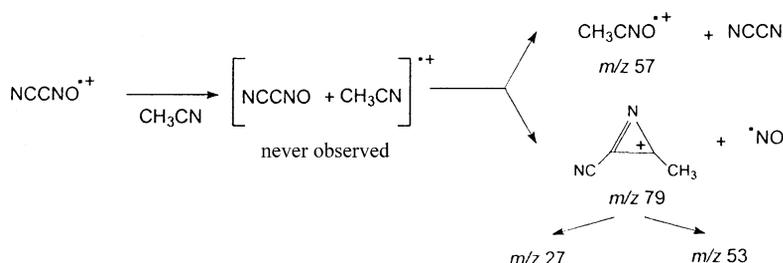


Scheme 7.

at  $m/z$  30 ( $C_2D_3^+$ ),  $m/z$  45 (protonated acetonitrile),  $m/z$  54 ( $C_2N_2D^+$  cations),  $m/z$  60 ( $CD_3CNO^{\bullet+}$  ions) and  $m/z$  82 ( $C_4D_3N_2^+$  cations). Furthermore, the CA spectrum of the  $m/z$  82 cations (Fig. 4c) reveals that the main reactions are the loss of  $C_2D_2$  ( $m/z$  54 signal) and the production of  $C_2D_3^+$  cations ( $m/z$  30), likely to be the vinyl cations (i.e.,  $\pi$ -protonated ethyne). On the basis of the azirinyll structure, both these decompositions require a rearrangement of the ionic structure on the way to the fragmentation. It is therefore expected that these processes correspond to metastable reactions and this is confirmed by the MIKE spectrum of the  $m/z$  79 cations featuring two signals at  $m/z$  27 (41%) and  $m/z$  53 (59%) (protonated ethyne and protonated cyanogen). It is tentatively proposed that the decomposing species is a proton-bridged dimer connecting cyanogen and ethyne as shown in Scheme 7. This is not unprecedented since, in the context of ionic rearrangements, proton-bridged ions are frequently proposed as intermediates to rationalize the dissociation behavior of low-energy ions [24]. Anyway, both processes being the less energy requirement reactions of the  $m/z$  79 ions, we can conclude that the  $m/z$  79 ions, formed by ion–molecule reaction, partly disso-

ciate in the quadrupole yielding  $m/z$  27 and 53 ions, see Scheme 8.

As already mentioned, no adduct ions are observed during the  $NCCNO^{\bullet+}/CH_3CN$  reaction and this is obviously at variance with the  $NCCNO^{\bullet+}/HCN$  interaction. Nevertheless, we decided to examine the chemistry of ionized 3-cyano-5-methyl-1,2,4-oxadiazole (**2c**) that could be a plausible intermediate. The study of the unimolecular and collision-induced decompositions of this ion confirms the previous conclusions. The metastable ions of this 1,2,4-oxadiazole only expel a molecule of nitric oxide, yielding  $m/z$  79 cations. This fragmentation remains the main collision-induced decomposition of the molecular ions, but, in addition, the RCA reactions appear in the CA spectrum. As previously observed in the case of the intact adduct ( $NCCNO^{\bullet+}/HCN$  interaction), the process leading to  $NCCNO^{\bullet+}$  ions is more pronounced than the competitive formation of  $CH_3CNO^{\bullet+}$  radical cations, although following the thermodynamical predictions—see Table 3—the reversed situation was expected— $\sum \Delta H_f(NCCNO^{\bullet+}/CH_3CN) = 1544 \text{ kJ mol}^{-1} > \sum \Delta H_f(CH_3CNO^{\bullet+}/NCCN) = 1402 \text{ kJ mol}^{-1}$ . The



Scheme 8.

structure of the metastably-generated  $m/z$  79 cations is probed by collisional activation and the recorded spectrum is found very similar to the CA spectrum of the  $m/z$  79 ions obtained in the quadrupole cell during the interaction between  $\text{NCCNO}^{\bullet+}$  and acetonitrile.

### 3.5. Reactions between ionized cyanogen oxide, $\text{NCCNO}^{\bullet+}$ , and cyanogen chloride

Finally, the interaction between  $\text{NCCNO}^{\bullet+}$  radical cations and cyanogen chloride (CICN) is studied and presented in Fig. 5a. Several ion–molecule reaction products are detected and readily identified as  $\text{CIC}^{\bullet+}$  ( $m/z$ , 47/49),  $\text{Cl-C}^+=\text{O}$  ( $m/z$ , 63/65),  $\text{CICNO}^{\bullet+}$  ( $m/z$ , 77/79),  $\text{C}_3\text{N}_2\text{Cl}^+$  ( $m/z$ , 99/101) and  $\text{C}_2\text{NCl}_2^+$  ( $m/z$ , 108/110/112), see Scheme 9 and Table 1. The occurrence of the  $\text{CIC}^+=\text{O}$  acylium ion could be related to the production of an 1,2,4-oxadiazole intermediate [25]. The ion–molecule reaction product ions are identified by collisional activation. The CA spectrum (Fig. 5b) of the  $\text{C}_3\text{N}_2\text{Cl}^+$  ( $m/z$ , 99/101) cations features some interesting signals, such as  $m/z$  85 (loss of nitrogen atom),  $m/z$  73 (loss of  $\text{NC}^{\bullet}$  radical),  $m/z$  64 (loss of chlorine),  $m/z$  61 ( $\text{CICN}^{\bullet+}$  ions),  $m/z$  52 ( $\text{NCCN}^{\bullet+}$  ions),  $m/z$  47 ( $\text{CIC}^+$  cations),  $m/z$  38 ( $\text{NCC}^+$  ions),  $m/z$  35 ( $\text{Cl}^+$  cations) and  $m/z$  26 ( $\text{NC}^+$  cations). These fragmentations can again be rationalized starting from an azirinyll structure.

In the same vein, the heavier product ion, detected at  $m/z$  108/110/112, is likely to be the dichloroazirinyll cation, probably generated in a consecutive interaction of  $\text{CICNO}^{\bullet+}$  ions with the neutral reagent (Scheme 9). This indicates that  $\text{CICNO}^{\bullet+}$  ion is also a very efficient reagent for the azirinyll cation production. The CA spectrum of these dichloroazirinyll cations, see Fig. 5c, features characteristic fragmentations:  $m/z$  94 (loss of nitrogen atom),  $m/z$  73 (loss of  $\text{Cl}^{\bullet}$  radical),  $m/z$  61 ( $\text{CICN}^{\bullet+}$  ions),  $m/z$  47 ( $\text{CIC}^+$  cations),  $m/z$  38 ( $\text{NCC}^+$  ions) and  $m/z$  35 ( $\text{Cl}^+$  cations).

In conclusion, ionized cyanogen oxide readily reacts with neutral nitriles by a *trans*-oxygenation reaction, giving an ionized nitrile oxide, and by a competitive elimination of nitric oxide from the collision complex probably generating azirinyll cations.

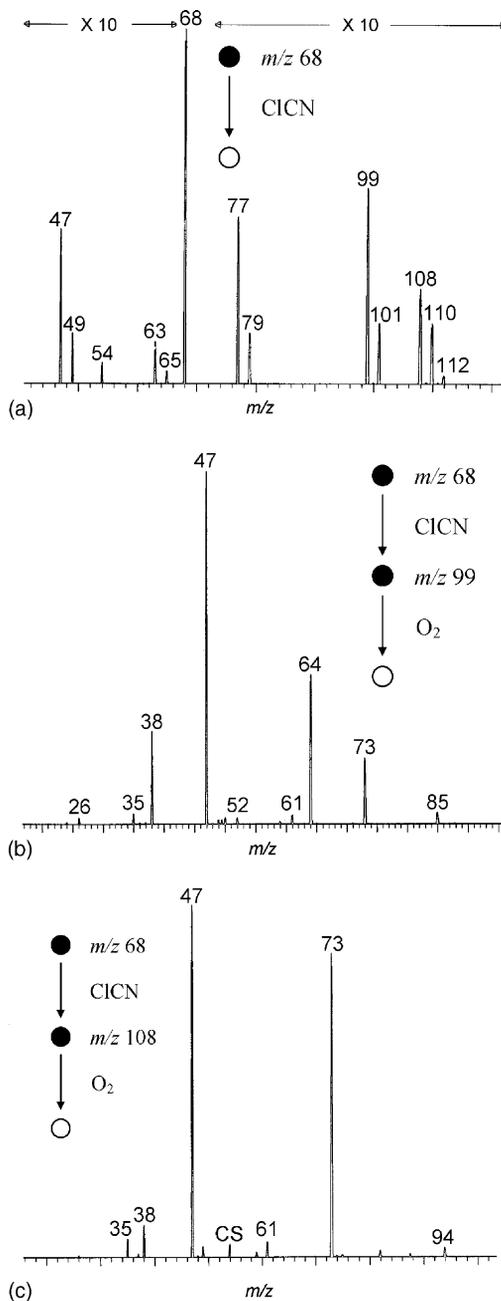
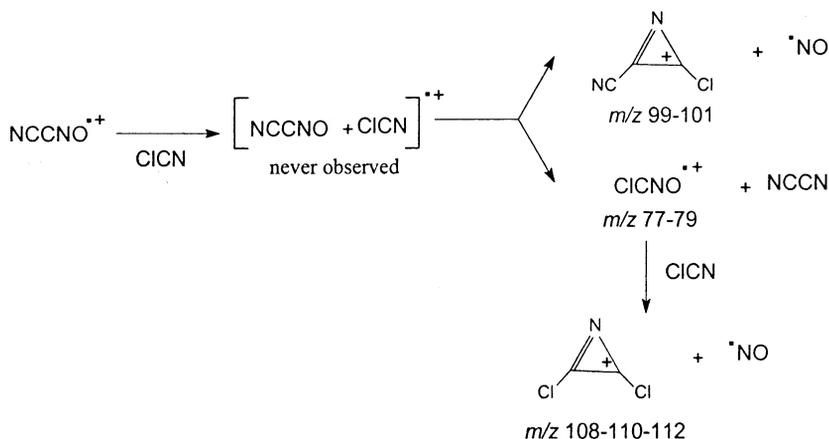


Fig. 5. Ion–molecule reactions between ionized cyanogen oxide ( $m/z$  68) and cyanogen chloride: (a) mass spectrum of the ion–molecule reaction products, (b) CA spectrum (8 keV, linked scan, oxygen) of the  $m/z$  99 ions, and (c) CA spectrum (8 keV, linked scan, oxygen) of the  $m/z$  108 ions.



Scheme 9.

The obtained experimental data suggest that ionized 1,2,4-oxadiazole (**2**) could be the transient structure in the *trans*-oxygenation reaction and on the way to the azirinylium cations. However, some other ionized species, such as ionized nitrosoazirines or opened structures, must also be held into account, see [Scheme 2](#).

### 3.6. Associative interactions of ionized nitrile oxides with nitriles

After having thoroughly investigated the bimolecular reactivity of  $\text{HCNO}^{\bullet+}$  and  $\text{NCCNO}^{\bullet+}$  toward neutral nitriles, we decided to examine the chemistry of other ionized nitrile oxides in order to know whether the observed azirinylium cation production can be regarded as a general reaction between both kind of reacting species.

The selected  $\text{RCNO}^{\bullet+}$  radical cations were the molecular ions of acetonitrile oxide ( $\text{CH}_3\text{CNO}^{\bullet+}$ ) and cyanogen bromide oxide ( $\text{BrCNO}^{\bullet+}$ ). The first radical cations were produced by dissociative ionization of 3,4-dimethyl-1,2,5-oxadiazoles (**1d**). The preparation of the bromine derivative was achieved by dissociative ionization of dibromoformaldoxime (loss of  $\text{HBr}$ ) [26]. The interaction between all these radical cations and several neutral nitriles ( $\text{HCN}$ ,  $\text{CH}_3\text{CN}$  and  $\text{ClCN}$ ) was then performed in the quadrupole collision cell.

The ion/molecule products for reactions between the mass-selected nitrile oxide ions and the nitriles

are indicated in [Table 1](#). The  $\text{NO}^{\bullet}/\text{RCN}$  substitution reaction is found to be very general and occurs for all the investigated ionized nitrile oxide/neutral nitrile pairs, regardless the nature of the substituents. However, the yield of this reaction is highly substituent-dependent. All together, the best yields are obtained with the cyano-containing ion, whereas ionized acetonitrile oxide is the less efficient reagent.

With regard to the results of [Table 1](#), the following must be noted: (i)  $\text{HCNO}^{\bullet+}$  radical cation (ionized fulminic acid) mainly reacts as an acid since the protonation reaction is always dominant; (ii) the protonation reaction also constitutes an efficient process starting from acetonitrile oxide ions; (iii) the interaction between  $\text{BrCNO}^{\bullet+}$  radical cation and acetonitrile leads to the expected formal substitution of nitric oxide by the neutral reagent in the ion to yield  $m/z$  132 cations. But, in addition and in opposition to the other reactions, the  $m/z$  83 cations formally arise from the competitive substitution of the bromine atom by acetonitrile in the reactive radical cation. The same behavior is observed when the  $\text{BrCNO}^{\bullet+}$  radical cation interacts with cyanogen chloride; (iv) chloro acylium cations,  $\text{Cl-C}^+=\text{O}$ , are generated during the reaction between  $\text{BrCNO}^{\bullet+}$  and  $\text{ClCN}$ . The observation of these acylium ions is again in keeping with the occurrence of an ionized 1,2,4-oxadiazole intermediate (**2**).

Table 4  
CA spectra (selected fragmentations) of the azirinium cations

R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub> C <sup>+</sup>	R <sub>2</sub> C <sup>+</sup>	-R <sub>1</sub>	-R <sub>2</sub>	R <sub>1</sub> <sup>+</sup>	R <sub>2</sub> <sup>+</sup>	-C <sub>2</sub> H <sub>2</sub>	N
H	H	2.5 <sup>a</sup>	2.5	100	100	–	–		7
H	CH <sub>3</sub>	–	100 <sup>b</sup>	18	23	–	2	50	10
H	Cl	–	100	13	13	–	6		2
H	Br	–	100	–	25	–	30		4
H	NC	–	100	17	18	–	3		3
CH <sub>3</sub>	CH <sub>3</sub>	32	32	5	5	3	3	100	1
CH <sub>3</sub>	Cl	28	39	6	29	–	11	100	1
CH <sub>3</sub>	Br	6	38	5	9	–	38	100	1
CH <sub>3</sub>	NC	100	26	15	56 <sup>a</sup>	1	10 <sup>b</sup>	55	2
CH <sub>3</sub>	NO	22	4	2	100	1	74	–	1
Cl	Cl	100	100	85	85	8	8		4
Cl	Br	44	100	44	62	–	26		2
Cl	NC	100	26	42	18	4	2		6
Cl	NO	24	6	4	100	8	22		–
NC	NC	100	100	26	26	2	2		4

<sup>a</sup> Intensities relative to the main beam of mass-selected ions which was normalized to 100 units.

<sup>b</sup> The intensities of those peaks were modified on the basis of experiments with CD<sub>3</sub>CN in order to remove isobaric interferences.

### 3.7. Collisional activation of the NO<sup>•</sup>/RCN substitution reaction products

All the ionized products, gathered in Table 1, were subjected to a collisional activation experiment and the main collision-induced dissociations are summarized in Table 4.

The CA spectrum of the parent C<sub>2</sub>H<sub>2</sub>N<sup>+</sup> cations (HCNO<sup>•+</sup>/HCN interaction) has already been analyzed and we have suggested the presence of a cyclic azirinylium structure, see Scheme 3.

The mass spectrum of 3-chloro-2,3-dimethyl-1-azirine (**4**) features an intense signal at *m/z* 68 (loss of chlorine) that could correspond to dimethylazirinium cations. The CA spectrum of the so-produced cations (Fig. 6) is found very similar to the CA spectrum of the ions generated during the CH<sub>3</sub>CNO<sup>•+</sup>/CH<sub>3</sub>CN interaction. The base peak of this spectrum corresponds to the loss of C<sub>2</sub>H<sub>2</sub> which is also a metastable decomposition of the mass-selected ions.

For the other ions, important fragmentations lead to (i) the formation of XC<sup>+</sup> cations (X = Cl, CN or Br), (ii) the loss of X (X = H, NO, Cl, Br); (iii) to the production of X<sup>+</sup> (X = Br) and (iv) the loss of C<sub>2</sub>H<sub>2</sub> if the ion bears at least one methyl group (Table 4).

Based on these collisional activation data, together with the theoretical results, it is thus proposed that all the investigated ion–molecule reactions afford azirinium cations whatever the nature of the R<sub>1</sub>CNO<sup>•+</sup>/R<sub>2</sub>CN partners is.

### 3.8. Trans-oxygenation reaction

As already mentioned, the interaction between NCCNO<sup>•+</sup> and the three neutral reagents also results

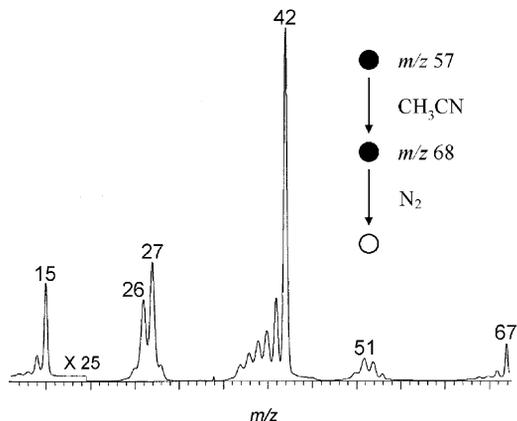


Fig. 6. Ion–molecule reaction between ionized acetonitrile oxide (*m/z* 57) and acetonitrile: CA spectrum (8 keV, E scan, nitrogen) of the *m/z* 68 ions.

formally in an ionized oxygen transfer from the radical cation to the neutral molecule. This process “ $\text{NCCNO}^{\bullet+} + \text{RCN} \rightarrow \text{NCCN} + \text{RCNO}^{\bullet+}$ ” can be considered as a *trans*-oxygenation reaction. Similarly,  $\text{HCNO}^{\bullet+}$  reacts with  $\text{ClCN}$  giving  $\text{ClCNO}^{\bullet+}$  (Table 1). Analogous processes were observed during the interaction of ionized nitrile sulfides or selenides and neutral nitriles [9,10].

On the basis of the available heats of formation of ionized nitrile oxides—see Table 3—and nitriles, it is possible to estimate the energy requirements of some of these processes. For instance, the *trans*-oxygenation reaction is calculated exothermic, and therefore thermodynamically favorable, for the  $\text{NCCNO}^{\bullet+}/\text{HCN}$  ( $-34 \text{ kJ mol}^{-1}$ ) and  $\text{NCCNO}^{\bullet+}/\text{CH}_3\text{CN}$  ( $-141 \text{ kJ mol}^{-1}$ ) interactions.

As far as the mechanism is concerned, an heterocyclic intermediate can also be considered, since the RCA reaction would lead to the *trans*-oxygenation products, directly in the case of a 1,2,5-oxadiazole species or via an ionized acylnitrene starting with an ionized 1,2,4-oxadiazole (vide supra).

#### 4. Conclusion

Tandem mass spectrometry studies, together with high level ab initio calculations, reveal that the associative bimolecular chemistry of ionized nitrile oxides toward neutral nitriles leads to azirinylium cations in competition with a *trans*-oxygenation process. Both reactions probably occur via cyclic intermediates such as ionized 1,2,4-oxadiazoles and ionized nitrosoazirines, as indicated by experimental and theoretical data. It is worthy of note that this work represents the first experimental observation of substituted azirinium ions.

#### Acknowledgements

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#### References

- [1] (a) M.L. Gross, *J. Am. Chem. Soc.* 94 (1972) 3744; (b) F.P. Lossing, *Can. J. Chem.* 50 (1972) 3973.
- [2] (a) R. Breslow, *J. Am. Chem. Soc.* 79 (1957) 5318; (b) R. Breslow, C.J. Yuan, *J. Am. Chem. Soc.* 80 (1958) 5991; (c) R. Breslow, H. Hover, H.W. Chang, *J. Am. Chem. Soc.* 84 (1962) 3168; (d) S.W. Tobey, R.J. West, *J. Am. Chem. Soc.* 86 (1964) 1459; (e) Z. Yoshida, Y. Tawara, *J. Am. Chem. Soc.* 93 (1971) 2573; (f) R. Breslow, J.T. Groves, *J. Am. Chem. Soc.* 92 (1970) 984.
- [3] I. Cernusak, P.W. Fowler, E. Steiner, *Mol. Phys.* 91 (1997) 401.
- [4] (a) X. Creary, A.F. Sky, *J. Am. Chem. Soc.* 112 (1990) 368; (b) R.A. Moss, S. Xue, W. Liu, *J. Am. Chem. Soc.* 116 (1994) 10821.
- [5] (a) K. Krogh-Jespersen, *Tetrahedron Lett.* 21 (1980) 4553; (b) C.U. Pittman, A. Kress, T.B. Patterson, P. Walton, L.D. Kispert, *J. Org. Chem.* 39 (1974) 373; (c) D.J. Swanton, G.B. Bacsakay, G.D. Willett, N.S. Hush, *J. Mol. Struct., THEOCHEM* 91 (1983) 313; (d) P.W. Harland, R.G.A.R. Maclagan, H.F. Schaefer, *J. Chem. Soc. Faraday Trans. 2* 85 (1989) 187; (e) Y.-G. Byun, S. Saebo, C.U. Pittman Jr., *J. Am. Chem. Soc.* 113 (1991) 3689; (f) P.M. Mayer, M.S. Taylor, M.W. Wong, L. Radom, *J. Phys. Chem. A* 102 (1998) 7074; (g) K.-C. Lau, W.-K. Li, C.Y. Ng, S.-W. Chiu, *J. Phys. Chem. A* 103 (1999) 3330.
- [6] (a) J. van Thuijl, J.J. van Houste, A. Maquestiau, R. Flammang, C. De Meyer, *Org. Mass Spectrom.* 12 (1977) 196; (b) H. Budzikiewicz, C. Djerassi, D.H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco, 1967; (c) G.D. Willett, T. Baer, *J. Am. Chem. Soc.* 102 (1980) 6774.
- [7] E.K. Chess, R.L. Lapp, M.L. Gross, *Org. Mass Spectrom.* 17 (1982) 475.
- [8] J.L. Holmes, P.M. Mayer, *J. Phys. Chem.* 99 (1995) 1366.
- [9] R. Flammang, M. Barbieux-Flammang, P. Gerbaux, C. Wentrup, M.W. Wong, *Bull. Soc. Chim. Belg.* 106 (1997) 545.
- [10] (a) R. Flammang, P. Gerbaux, E.H. Mørkved, M.W. Wong, C. Wentrup, *J. Phys. Chem.* 100 (1996) 17452; (b) P. Gerbaux, Y. Van Haverbeke, R. Flammang, M.W. Wong, C. Wentrup, *J. Phys. Chem. A* 101 (1997) 6970; (c) R. Flammang, P. Gerbaux, M. Barbieux-Flammang, C.T. Pedersen, A.T. Bech, E.H. Mørkved, M.W. Wong, C. Wentrup, *J. Chem. Soc., Perkin Trans. 2* (1999) 1683.
- [11] (a) P. Gerbaux, R. Flammang, E.H. Mørkved, M.W. Wong, C. Wentrup, *Tetrahedron Lett.* 39 (1998) 533; (b) P. Gerbaux, R. Flammang, E.H. Mørkved, M.W. Wong, C. Wentrup, *J. Phys. Chem. A* 102 (1998) 9021.
- [12] P. Gerbaux, C. Wentrup, R. Flammang, *Mass Spectrom. Rev.* 19 (2000) 367.

- [13] P. Gerbaux, PhD Thesis, University of Mons-Hainaut, 1999.
- [14] C. Grundmann, P. Grünanger, *The Nitrile Oxides*, Springer, New York, 1971.
- [15] J. Ciabattini, M. Cabell Jr., *J. Am. Chem. Soc.* 93 (1971) 1482.
- [16] (a) R.H. Bateman, J. Brown, M. Lefevre, R. Flammang, Y. Van Haverbeke, *Int. J. Mass Spectrom. Ion Processes* 115 (1992) 205;  
(b) R. Flammang, Y. Van Haverbeke, C. Braybrook, J. Brown, *Rapid Commun. Mass Spectrom.* 9 (1995) 795.
- [17] (a) R.A. Olofson, J.S. Michelman, *J. Org. Chem.* 30 (1965) 1854;  
(b) L.C. Behr, J.T. Brent, *Org. Synth., Coll.* 4 (1963) 352;  
(c) C. Grundmann, *Chem. Ber.* 97 (1964) 575;  
(d) P.A. Wade, J.F. Berezna, B.A. Palfey, P.J. Carroll, W.P. Dailey, S. Sivasubramanian, *J. Org. Chem.* 55 (1990) 3045;  
(e) K. Ziegler, *Org. Synth. Coll.* 1 (1932) 314;  
(f) F.W. Fowler, A. Hassner, L.A. Levy, *J. Am. Chem. Soc.* 89 (1967) 2077;  
(g) A. Hassner, F.W. Fowler, *J. Am. Chem. Soc.* 90 (1968) 2869;  
(h) E.C. Lupton, G. Hess, *J. Chem. Eng. Data* 20 (1975) 135.
- [18] C.E.C.A. Hop, K.-J. van den Berg, J.L. Holmes, J.K. Terlouw, *J. Am. Chem. Soc.* 111 (1989) 72.
- [19] (a) L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, *J. Chem. Phys.* 106 (1977) 1063;  
(b) Gaussian 98, Revision A.6, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, F. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Repogle, J.A. Pople, Gaussian Inc., Pittsburgh, PA, 1998.
- [20] P.M. Mayer, C.J. Parkinson, D.M. Smith, L. Radom, *J. Chem. Phys.* 108 (1998) 604.
- [21] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, *J. Phys. Chem. Ref. Data* 17 (Suppl. 1) (1988).
- [22] J. Bastide, J.P. Maier, *Chem. Phys.* 12 (1976) 177.
- [23] D. Poppinger, L. Radom, J.A. Pople, *J. Am. Chem. Soc.* 99 (1977) 7806.
- [24] (a) L.M. Fell, P.C. Burgers, P.J.A. Ruttink, J.K. Terlouw, *Can. J. Chem.* 3 (1998) 1998;  
(b) C.A. Schalley, A. Fiedler, G. Hornung, R. Wesendrup, D. Schröder, H. Schwarz, *Chem. Eur. J.* 3 (1977) 626.
- [25] Q.N. Porter, *Mass Spectrometry of Heterocyclic Compounds*, 2nd Edition, Wiley-Interscience, 1985.
- [26] T. Pasinszki, N.P.C. Westwood, *J. Phys. Chem.* 99 (1995) 6401.
- [27] D. Poppinger, L. Radom, *J. Am. Chem. Soc.* 100 (1978) 3674.
- [28] M. Féher, T. Pasinszki, C.U. Veszprémi, *Inorg. Chem.* 34 (1995) 945.
- [29] J.C. Schwartz, A.P. Wade, C.G. Enke, R.G. Cooks, *Anal. Chem.* 62 (1990) 1809.