



# Influence of the structure of medium-sized aromatic precursors on the reactivity of their dications towards rare gases

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## ABSTRACT

The gas-phase reactivity of dications generated by dissociative electron ionization of several aromatic  $C_mH_nN_o$  precursors with  $4 \leq m \leq 13$ ,  $4 \leq n \leq 21$ , and  $0 \leq o \leq 2$  with rare gases is investigated. Whereas most of these reactions lead to monocations via simple electron transfer, proton transfer, or Coulomb explosion, the formation of organo rare-gas dications is observed in a few cases. Specifically, dications generated from 2,4,6-trimethylpyridine react with krypton and xenon to form organo rare-gas species as major products and under maintenance of the two-fold positive charge. Such a reactivity is not observed in the presence of lighter rare gases. The formation of organo rare-gas dications are also observed for dications generated from 3-vinylpyridine, *N,N*-dimethylaniline, isopropylbenzene, and 4-ethyltoluene as neutral precursors. In some cases, isomeric dications are characterized by very different reactivity toward rare gases, suggesting that the structure of the precursors is crucial and that electron ionization does not lead to a total scrambling of the structures of the doubly charged ions obtained.

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## 1. Introduction

First predicted by Linus Pauling in 1933 [1,2], many rare gas compounds have been synthesized and characterized, from their discovery in 1962 [3–6] until now, using different techniques [2,7]. Theoretical investigations were also carried out to understand the stability of these compounds, to determine their structures [8–13], and to predict their stability prior to an experimental characterization [14–17]. From an experimental point of view, rotationally resolved spectroscopy, for instance, has been used to investigate molecular complexes of one or more rare gas atoms (He, Ne, Ar, Kr or Xe) [18] such as dimethylsilane–Ar [19], difluorodimethylsilane–Ar [20], and a series of argon–fluorocarbon compounds [21]. Several rare-gas hydrides were prepared by photolysis and studied at low temperatures in solid noble gas matrices [22–24]. Different “exotic rare gas compounds”, such as  $CHAr^+$  [25], have been observed or studied theoretically [24,25–30].

Possible reagents capable of activating rare gases must be very electrophilic in order to break down the closed-shell configuration of the rare gases. In this respect, small multiply charged ions are particularly promising candidates for the activation of rare-gas species [31,32]. Mass spectrometric experiments are ideally suited for the investigation of such reactions and these techniques have been successfully applied to generate, to characterize and to study

different organo-rare gas compounds [33,34]. Recently, we have found that  $C_7H_n^{2+}$  dications generated by electron ionization of toluene can react with xenon under termolecular conditions to form novel organo-rare gas species [35]. Due to the continuous interest in rare-gas compounds [36–39], these findings prompted us towards a deeper investigation of these reactions. To this end, we studied the reactions of several organic dications with rare gases using a triple quadrupole mass spectrometer under similar conditions as already used in our laboratory to synthesize and characterize the rare-gas silicon compounds  $NeSiF_2^{2+}$  and  $ArSiF_2^{2+}$  [40,41], the carbon analog  $ArCF_2^{2+}$  [42], and the organo-rare gas dications,  $HCCRg^{2+}$  ( $Rg = Ar, Kr$ ) [33] as well as the argon-carbene monocation  $ArCH_2^+$  [34]. Here, we present results concerning the generation and characterization of new organo-rare gas dications,  $C_mH_nN_oRg^{2+}$  with  $m = 4–13$ ,  $n = 4–21$ ,  $o = 0–2$ , and ( $Rg = Kr, Xe$ ), in reactions of rare gases with several  $C_mH_nN_o^{2+}$  dications (with  $m = 4–13$ ,  $n = 4–21$ , and  $o = 0–2$ ) generated via double ionization of medium-sized, heteroaromatic precursors as well as of medium-sized pure hydrocarbon dications  $C_nH_m^{2+}$ .

## 2. Experimental details

The experimental conditions used were similar to our previous exploratory study of the reactivity of methane with several  $C_mH_nN_o^{2+}$  dications ( $m = 4–13$ ,  $n = 4–21$ , and  $o = 0–2$ ) formed via electron ionization (EI) of different medium-sized aromatic and hetero-aromatic neutral precursors [43–46]. In brief, the reactivity studies were performed with a TSQ Classic mass spectrometer

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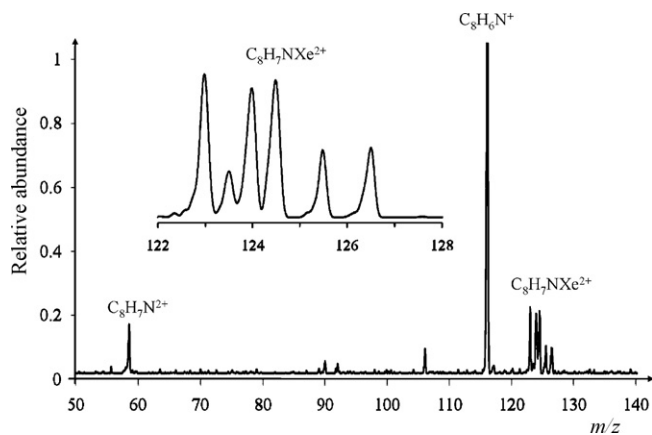
[47,48] equipped with an EI source. The analyzer region of the TSQ Classic bears a QOQ configuration (Q stands for quadrupole and O for octopole), which permits a variety of MS/MS experiments. The octopole serving as a collision cell has a separate housing which limits the penetration of gases admitted to the octopole to the vacuum of the manifold. The kinetic energy of the ions entering the octopole can be varied between 0 and 200 eV, which allows the investigation of ion/molecule reactions at quasi-thermal conditions or collision-induced dissociation (CID) at elevated kinetic energies. The ion/molecule reactions of the  $C_mH_nN_o^{2+}$  dications described below were performed by mass-selecting the ions of interest with the first quadrupole (Q1) at a mass resolution fully sufficient to resolve mono- and dications. Note that within the limits of our instrumentation, we could not further cool the hydrocarbon cations investigated in this work [49]. The mass-selected dications were then reacted with neutral rare gases admitted to the octopole at a typical pressure of  $10^{-4}$  mbar; deliberately the pressure of the neutral gases was also raised above the single-collision regime [50] in order to investigate consecutive reactions as well as termolecular processes [51]; for a recent detailed study of the dynamics of collisional stabilization, see [52]. Unless otherwise specified, the collision energy was adjusted by changing the offset between the first quadrupole and the octopole, while the offset of Q2 was locked to the sum of the offsets of Q1 and O. The zero-point of the kinetic energy scale as well as the width of the kinetic energy distribution were determined by means of retarding-potential analysis; for the dications reported here, the beam width at half maximum was about  $(5 \pm 1)$  eV in the laboratory frame. The bimolecular reactions reported below were recorded at an ion kinetic energy which corresponds to the point of inflection of the curve obtained by retarding-potential analysis. We have shown previously that quasi-thermal reactivity can be monitored under these conditions [53–56]; here the term quasi-thermal appreciates the fact that the ions' average kinetic energy is indeed close to thermal conditions, while the width of the ions' kinetic energy distribution is not. Ionic products emerging from the octopole were then mass-analyzed by scanning Q2, for which unit mass resolution was adjusted. Typically, about hundred scans were accumulated resulting in an average scan time of 5 min per spectrum.

### 3. Results and discussion

We will first describe the reactivity between xenon and  $C_8H_nN^{2+}$  dications ( $n=6-11$ ) generated by electron ionization of 2,4,6-trimethylpyridine, followed by the reactions of the same dications with krypton and lighter rare gases. Then, these reactivities will be compared to those observed in the case of dications generated from other hetero-aromatic precursors, as well as all-carbon aromatic precursors, including different isomers. A general feature of these reactions is that the organo-rare gas ions are only observed at elevated pressures of the rare gases, i.e., beyond the single-collision regime, involving termolecular association processes [57,58]. This is a strong indication for the formation of these products via termolecular collision processes; for the case of  $C_7H_8^{2+}$  this aspect also has been investigated quantitatively [35].

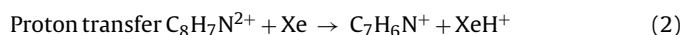
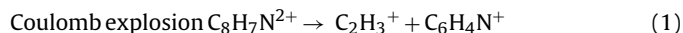
#### 3.1. Reactions of xenon with dications generated from 2,4,6-trimethylpyridine

In addition to much more intense monocations, a series of  $C_8H_nN^{2+}$  dications are generated upon electron ionization of 2,4,6-trimethylpyridine of which six ions are of sufficient abundance for reactivity studies, i.e.,  $C_8H_6N^{2+}$  ( $m/z$  58),  $C_8H_7N^{2+}$  ( $m/z$  58.5),  $C_8H_8N^{2+}$  ( $m/z$  59),  $C_8H_9N^{2+}$  ( $m/z$  59.5),  $C_8H_{10}N^{2+}$  ( $m/z$  60), and  $C_8H_{11}N^{2+}$  ( $m/z$  60.5) [59]. The reactivity of each of these dications

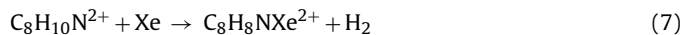
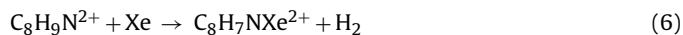


**Fig. 1.** Mass spectrum obtained upon interaction of xenon with the mass-selected  $C_8H_7N^{2+}$  dications generated by dissociative electron ionization of 2,4,6-trimethylpyridine. The inset shows the organo-rare gas dication on an expanded mass scale. The  $XeH^+$  formed as a counterpart according to reaction (2) is converted to  $H_3O^+$  by reaction with water present in the background.

with xenon has been studied. As expected, proton transfer, electron transfer, as well as charge separation reactions leading to the formation of monocationic products prevail in most cases, but in some instances also bond-forming reactions with xenon are observed (see below). As an example for the general reactivity of these energetic dications, Eqs. (1)–(2) show the reactions observed for the  $C_8H_7N^{2+}$  dication ( $m/z$  58.5). Note that the loss of  $H_2$  from the dication, the Coulomb explosions as well as the proton- and the charge-transfer reactions of the  $C_8H_nN^{2+}$  dications generated from 2,4,6-trimethylpyridine have already been studied and reported with other gases [43].



In addition to these expected product ions, the dications react with xenon to form organo-rare gas dications in significant proportions, yielding three different organo-rare gas dications,  $C_8H_6NXe^{2+}$ ,  $C_8H_7NXe^{2+}$ , and  $C_8H_8NXe^{2+}$ , reactions (3)–(7).



As an example, the spectrum obtained for  $C_8H_7N^{2+}$  is shown in Fig. 1. While the major product ion corresponds to proton transfer to afford  $C_8H_6N^{2+}$ , a signal in the range  $m/z$  123–126.5 shows the characteristic isotope pattern of xenon and can be assigned to  $C_8H_7NXe^{2+}$  formed via association of xenon to the precursor dication (reaction (4)). Similar patterns are observed for four other dications from this precursor which are summarized in Table 1 further below.

#### 3.2. Reactions of krypton with dications generated from 2,4,6-trimethylpyridine

Having observed these  $C_8H_nNXe^{2+}$  dications, detection of the analogous products with krypton is an obvious challenge. The  $C_8H_nN^{2+}$  dications with  $n=7-10$  generated via dissociative electron ionization of 2,4,6-trimethylpyridine indeed lead to the formation of organo-rare gas dications, i.e.,  $C_8H_7NKR^{2+}$  (reactions (8))

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