International Journal of Mass Spectrometry 299 (2011) 53–58

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

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

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ARTICLE INFO

*Article history:*
Received 12 August 2010
Received in revised form
15 September 2010
Accepted 16 September 2010
Available online 30 September 2010

*Keywords:*
Dication
Ion/molecule reaction
Krypton
Mass spectrometry
Organo rare-gas dication
Xenon

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.

## 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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doi:10.1016/j.ijms.2010.09.017

[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 ± 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 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].

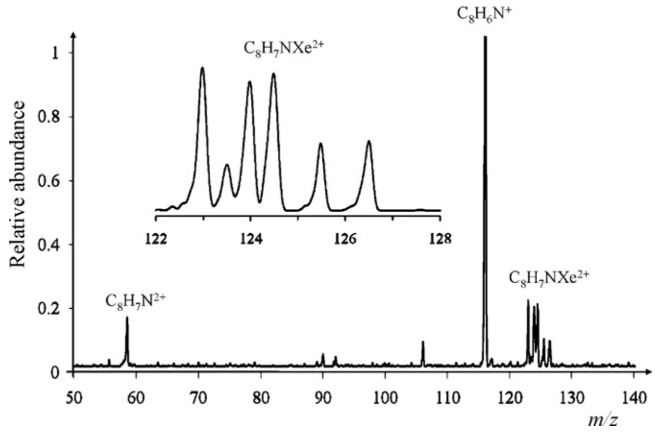

**Fig. 1.** Mass spectrum obtained upon interaction of xenon with the mass-selected $C_8H_7N^{2+}$ dications generated by dissociative electron ionization of 2,4,6-trimethylpyridine. The inset shows the organo-rare gas dication on an expanded mass scale. The $XeH^+$ formed as a counterpart according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

$$\text{Coulomb explosion } C_8H_7N^{2+} \rightarrow C_2H_3^{+} + C_6H_4N^{+} \quad (1)$$

$$\text{Proton transfer } C_8H_7N^{2+} + Xe \rightarrow C_7H_6N^{+} + XeH^{+} \quad (2)$$

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).

$$C_8H_6N^{2+} + Xe \rightarrow C_8H_6NXe^{2+} \quad (3)$$

$$C_8H_7N^{2+} + Xe \rightarrow C_8H_7NXe^{2+} \quad (4)$$

$$C_8H_8N^{2+} + Xe \rightarrow C_8H_8NXe^{2+} \quad (5)$$

$$C_8H_9N^{2+} + Xe \rightarrow C_8H_7NXe^{2+} + H_2 \quad (6)$$

$$C_8H_{10}N^{2+} + Xe \rightarrow C_8H_8NXe^{2+} + H_2 \quad (7)$$

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)

**Table 1**
Summary of the dications generated by dissociative electron ionization of different hetero-aromatic precursors and the organo-xenon dications observed in the presence of Xe.

| Precursor (formula) | Dications studied (*m*/*z*)[a] | Organo-rare gas ions[b] |
|---|---|---|
| Pyrimidine ($C_4H_4N_2$) | $C_4H_4N_2^{2+}$ (40), $C_4H_3N_2^{2+}$ (39.5), $C_4H_2N_2^{2+}$ (39) | |
| Pyridine ($C_5H_5N$) | $C_5H_5N^{2+}$ (39.5), $C_5H_4N^{2+}$ (39) | |
| Benzonitrile ($C_7H_5N$) | $C_7H_5N^{2+}$ (51.5), $C_7H_4N^{2+}$ (51), $C_7H_3N^{2+}$ (50.5), $C_7H_2N^{2+}$ (50) | |
| 3-Vinylpyridine ($C_7H_7N$) | $C_7H_7N^{2+}$ (52.5) | $C_7H_7NXe^{2+}$ (<1%) |
| | $C_7H_6N^{2+}$ (52) | $C_7H_6NXe^{2+}$ (<1%) |
| | $C_7H_5N^{2+}$ (51.5) | |
| *N*-Methylaniline ($C_7H_9N$) | $C_7H_9N^{2+}$ (53.5), $C_7H_8N^{2+}$ (53), $C_7H_7N^{2+}$ (52.5), $C_7H_6N^{2+}$ (52) | |
| 2-Ethylpyridine ($C_7H_9N$) | $C_7H_7N^{2+}$ (52.5) | |
| 2,5-Dimethylpyridine ($C_7H_9N$) | $C_7H_9N^{2+}$ (53.5), $C_7H_8N^{2+}$ (53), $C_7H_7N^{2+}$ (52.5), $C_7H_6N^{2+}$ (52), $C_7H_5N^{2+}$ (51.5), $C_7H_4N^{2+}$ (51) | |
| 2,6-Dimethylpyridine ($C_7H_9N$) | $C_7H_9N^{2+}$ (53.5), $C_7H_8N^{2+}$ (53), $C_7H_7N^{2+}$ (52.5), $C_7H_6N^{2+}$ (52), $C_7H_5N^{2+}$ (51.5), $C_7H_4N^{2+}$ (51) | |
| 2,4,6-Trimethylpyridine ($C_8H_{11}N$) | $C_8H_{11}N^{2+}$ (60.5) | |
| | $C_8H_{10}N^{2+}$ (60) | $C_8H_8NXe^{2+}$ (24%) |
| | $C_8H_9N^{2+}$ (59.5) | $C_8H_7NXe^{2+}$ (41%) |
| | $C_8H_8N^{2+}$ (59) | $C_8H_8NXe^{2+}$ (9%) |
| | $C_8H_7N^{2+}$ (58.5) | $C_8H_7NXe^{2+}$ (27%) |
| | $C_8H_6N^{2+}$ (58) | $C_8H_6N^{2+}$ (6%) |
| *N*,*N*-Dimethylaniline ($C_8H_{11}N$) | $C_8H_{11}N^{2+}$ (60.5), $C_8H_{10}N^{2+}$ (60), $C_8H_8N^{2+}$ (59), $C_8H_6N^{2+}$ (58) | |
| | $C_8H_9N^{2+}$ (59.5) | $C_8H_9NXe^{2+}$ (16%) |
| | $C_8H_7N^{2+}$ (58.5) | $C_8H_7NXe^{2+}$ (3%) |
| Quinoline ($C_9H_7N$) | $C_9H_7N^{2+}$ (64.5), $C_9H_5N^{2+}$ (63.5) | |
| 2-(t-Butyl)-pyridine ($C_9H_{13}N$) | $C_9H_{11}N^{2+}$ (66.5), $C_9H_{10}N^{2+}$ (66), $C_9H_9N^{2+}$ (65.5), $C_9H_8N^{2+}$ (65), $C_9H_7N^{2+}$ (64.5) | |
| 2,6-Di(t-butyl)-pyridine ($C_{13}H_{21}N$) | $C_{13}H_{21}N^{2+}$ (95.5) | |

[a] For the species with integer *m*/*z* values, overlapping monocations interfere in several cases. The pure dications might thus still be more reactive. For screening purposes, this approach is consider to suffice, however.

[b] The numbers in brackets are the percentage of the organo-rare gas dications observed relative to the entire daughter ions formed.

and (10)) and $C_8H_8NKr^{2+}$ (reactions (9) and (11)), which are similar to the those observed with Xe. The organo-rare gas dications observed from the parent ions at *m*/*z* 58.5, 59, 59.5 and 60 represent 10%, 5%, 6%, and 2% of the entire daughter ions formed, respectively. Interestingly, the non-hydrogen-depleted parent dication $C_8H_{11}N^{2+}$ does not lead to the formation of any organo-rare gas compound with either xenon or krypton, which can be ascribed to the lower degree of unsaturation with larger values of *n*.

$$C_8H_7N^{2+} + Kr \rightarrow C_8H_7NKr^{2+} \quad (8)$$

$$C_8H_8N^{2+} + Kr \rightarrow C_8H_8NKr^{2+} \quad (9)$$

$$C_8H_9N^{2+} + Kr \rightarrow C_8H_7NKr^{2+} + H_2 \quad (10)$$

$$C_8H_{10}N^{2+} + Kr \rightarrow C_8H_8NKr^{2+} + H_2 \quad (11)$$

As an example, Fig. 2 shows the mass spectra obtained in the case of the parent ion $C_8H_7N^{2+}$ (*m*/*z* 58.5) in the case of an elevated pressure of the rare gas in the collision cell (0.2 mTorr).

These findings prompted us towards an investigation of the reactions between these dications with lighter rare gases, namely He, Ne, and Ar. Contrary to the results obtained under the presence of Xe or Kr, however, none of these lighter rare gases reacts with the investigated dications under formation of organo-rare gas species. The origin for the lack of reactivity of the lighter rare gases is obvious, because the binding energies of cationic species with rare gases dramatically decrease from xenon to helium [60].

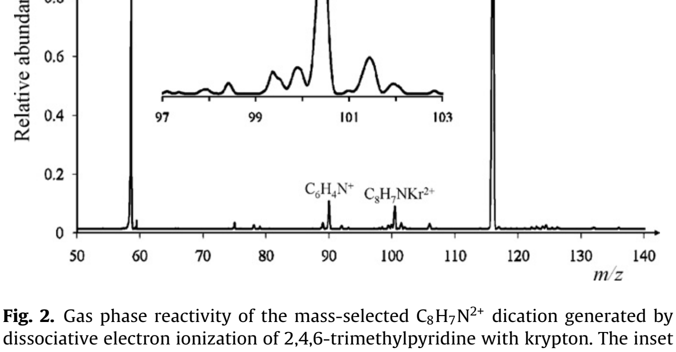

**Fig. 2.** Gas phase reactivity of the mass-selected $C_8H_7N^{2+}$ dication generated by dissociative electron ionization of 2,4,6-trimethylpyridine with krypton. The inset shows the organo-rare gas dication on an expanded mass scale.

### 3.3. *Reactions of xenon with medium sized N-containing dications*

In order to assess whether the reactivity observed in the case of the dications obtained from 2,4,6-trimethylpyridine is a general feature of the medium sized N-containing dications or a specific aspect of this particular precursor, we screened the reactivity between rare gases and dications generated by dissociative electron ionization of a series of nitrogen heterocycles, anilines, and also benzonitrile. Among these precursors, it is worth noting that several precursors are structural isomers (e.g., *N*,*N*-dimethylaniline and 2,4,6-trimethylpyridine) (Chart 1).

Most of the dications investigated do not lead to the formation of organo-rare gas dications under our experimental conditions. Instead, reactions prevail which lead to the formation of monocations, i.e., charge separation of the dications themselves, proton- and electron transfer between the rare gas and the dications. Nevertheless, in addition to such monocations, a small amount of the organo-rare gas dication $C_8H_9NXe^{2+}$ is observed for the dication $C_8H_9N^{2+}$ at *m*/*z* 59.5 generated by dissociative electron ionization of *N*,*N*-dimethylaniline. All other investigated dications generated from this precursor are unreactive towards xenon (Table 1).

The reactivity observed between the dications from 2,4,6-trimethylpyridine and xenon is thus a specific feature of this compound, and not a general characteristic of a wide family of N-containing dications generated via electron ionization. Likewise, the formation of $C_8H_nNKr^{2+}$ appears to be characteristic of the dications formed from 2,4,6-trimethylpyridine as neutral precursor.

### 3.4. *Reactions of rare gases with pure hydrocarbon dications $C_nH_m^{2+}$*

For comparison, the reactivity of several dications generated from benzene, cyclooctatetraene, *m*-xylol, ethylbenzene,

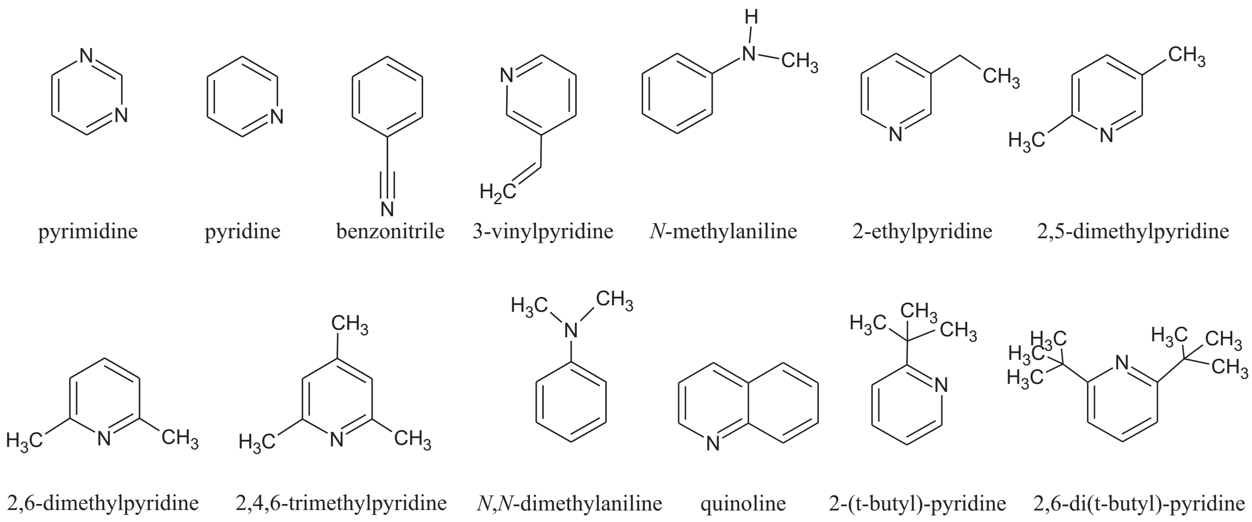

**Chart 1.** Structures of the neutral $C_nH_mN_o$ precursor compounds used in this work.

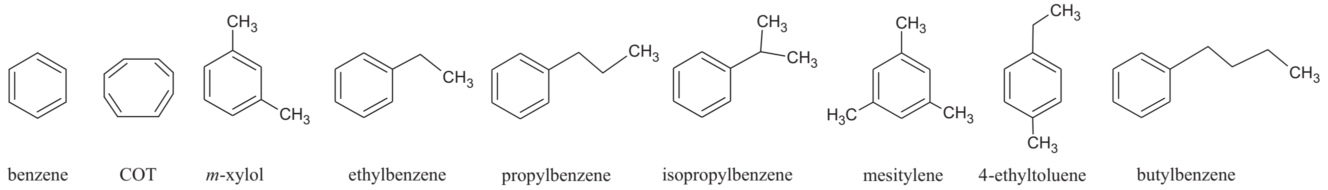

**Chart 2.** Structures of the neutral $C_nH_m$ precursor compounds used in this work (COT = cyclooctatetraene).

propylbenzene, isopropylbenzene, mesitylene, 4-ethyltoluene, and butylbenzene (Chart 2) towards argon, krypton, and xenon were studied. The dications investigated in this study are summarized in Table 2.

Among these dications, two dications from isopropylbenzene react with Xe to form organo-rare gas dications, namely $C_9H_8^{2+}$ and $C_9H_6^{2+}$, leading to the formation of $C_9H_8Xe^{2+}$ (4%) and $C_9H_6Xe^{2+}$ (8%), respectively. Two dications from 4-ethyltoluene, namely $C_9H_9^{2+}$ and $C_9H_6^{2+}$ also slightly react with xenon, but the relative intensities of the resulting organo-rare gas dications are below 1%.

The fact that most of the dications chosen for this study do not form any organo-rare gas dications, and only reactions leading to the formation of monocations via Coulomb explosions, proton- and charge transfer are observed, further supports the above conclusion that the formation of organo rare-gas dications is not a general feature of the dications generated by double ionization of aromatic precursors. Even for those species for which the formation of organo-rare gas dications is observed, a high pressure of the rare gas is needed to support product formation.

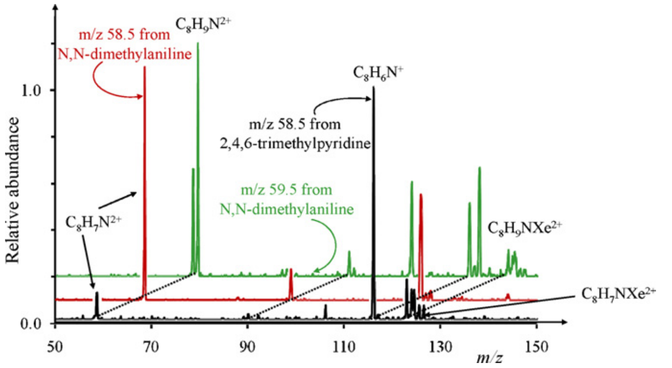

**Fig. 3.** Gas-phase reactivity of xenon with mass-selected $C_8H_7N^{2+}$ (red) and $C_8H_9N^{2+}$ (green), respectively, as an example of two different dications generated by dissociative electron ionization of *N*,*N*-dimethylaniline. For comparison, the mass spectrum obtained under the same conditions for the mass-selected $C_8H_7N^{2+}$ dication generated by dissociative electron ionization of 2,4,6-trimethylpyridine is shown in black.

**Table 2**
Summary of the fragment ions observed after the reactivity between dications generated by dissociative electron ionization of cyclic precursors and Xe.

| Precursor (formula)[a] | Dications studied (*m*/*z*) |
|---|---|
| Benzene ($C_6H_6$)[b] | $C_6H_6^{2+}$ (39), $C_6H_5^{2+}$ (38.5), $C_6H_4^{2+}$ (38), $C_6H_3^{2+}$ (37.5), $C_6H_2^{2+}$ (37) |
| Cyclooctatetraene ($C_8H_8$) | $C_8H_8^{2+}$ (52), $C_8H_7^{2+}$ (51.5), $C_8H_6^{2+}$ (51), $C_8H_5^{2+}$ (50.5), $C_8H_4^{2+}$ (50), $C_8H_3^{2+}$ (49.5), $C_8H_2^{2+}$ (49) |
| *m*-Xylol ($C_8H_{10}$) | $C_8H_{10}^{2+}$ (53), $C_8H_8^{2+}$ (52), $C_8H_7^{2+}$ (51.5), $C_8H_6^{2+}$ (51), $C_8H_5^{2+}$ (50.5), $C_8H_4^{2+}$ (50) |
| Ethylbenzene ($C_8H_{10}$) | $C_8H_{10}^{2+}$ (53), $C_8H_9^{2+}$ (52.5), $C_8H_8^{2+}$ (52), $C_8H_7^{2+}$ (51.5), $C_8H_6^{2+}$ (51), $C_8H_5^{2+}$ (50.5), $C_8H_4^{2+}$ (50) |
| Propylbenzene ($C_9H_{12}$) | $C_9H_{12}^{2+}$ (60), $C_9H_{10}^{2+}$ (59), $C_9H_8^{2+}$ (58), $C_9H_7^{2+}$ (57.5), $C_9H_6^{2+}$ (57), $C_9H_5^{2+}$ (56) |
| Isopropylbenzene ($C_9H_{12}$) | $C_9H_{11}^{2+}$ (59.5), $C_9H_{10}^{2+}$ (59), $C_9H_9^{2+}$ (58.5), $C_9H_8^{2+}$ (58), $C_9H_7^{2+}$ (57.5), $C_9H_6^{2+}$ (57) |
| Mesitylene ($C_9H_{12}$) | $C_9H_{12}^{2+}$ (60), $C_9H_{11}^{2+}$ (59.5), $C_9H_{10}^{2+}$ (59), $C_9H_9^{2+}$ (58.5), $C_9H_8^{2+}$ (58), $C_9H_7^{2+}$ (57.5), $C_9H_6^{2+}$ (57) |
| 4-Ethyltoluene ($C_9H_{12}$) | $C_9H_{12}^{2+}$ (60), $C_9H_{11}^{2+}$ (59.5), $C_9H_{10}^{2+}$ (59), $C_9H_9^{2+}$ (58.5), $C_9H_8^{2+}$ (58), $C_9H_7^{2+}$ (57.5), $C_9H_6^{2+}$ (57) |
| Butylbenzene ($C_{10}H_{14}$) | $C_{10}H_{14}^{2+}$ (67), $C_{10}H_{12}^{2+}$ (66), $C_{10}H_{10}^{2+}$ (65), $C_{10}H_9^{2+}$ (64.5), $C_{10}H_8^{2+}$ (64), $C_{10}H_7^{2+}$ (63.5), $C_{10}H_6^{2+}$ (63) |

[a] For $C_7H_n^{2+}$ dications derived from toluene, see Ref. [35].

[b] The dications at the integer masses *m*/*z* 37, 38, and 39 overlap with the corresponding monocations $C_3H_3^+$, $C_3H_2^+$ and $C_3H^+$, that are known to be particularly intense. Due to the absence of the formation of organo-rare gas compound for most species, we did not try to deconvolute the contributions of mono- and dications.

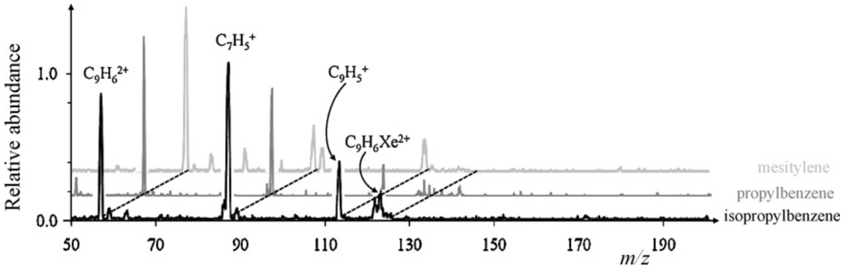

**Fig. 4.** Gas phase reactivity of three different mass-selected isomeric dications $C_9H_6^{2+}$ ($m/z$ 57) generated by dissociative electron ionization of isopropylbenzene (in front) and propylbenzene (middle), and mesitylene (in the back) in the presence of 1 mTorr of xenon in the collision cell.

### *3.5. Influence of the structure of the neutral precursors on the reactivity of dications towards rare gases*

As electron ionization is known as a “hard” ionization method, one question is whether the dications obtained under these conditions keep the structure of their precursors or extensive rearrangements with complete loss of structural memory occur [61,62]. Some insight into this point can be gained from this work, because the reactivity of dications generated from different isomeric neutral precursor are investigated. For example, the dications generated from *N*,*N*-dimethylaniline and 2,4,6-trimethylpyridine react differently with rare gases (Fig. 3). The corresponding neutral precursors notably differ, as in one case the hetero-atom is in the aromatic ring, whereas *N*,*N*-dimethylaniline is a substituted benzene. In order to investigate this aspect also for pure hydrocarbon dications, the reactivity of the $C_9H_6^{2+}$ dications generated via dissociative double ionization of the isomeric $C_9H_{12}$ precursors isopropylbenzene, propylbenzene, and mesitylene is considered (Fig. 4). Whereas the $C_9H_6^{2+}$ dications from propylbenzene and mesitylene only lead to the formation of monocations via charge separation, an organo-rare gas dication is formed with the dication generated from isopropylbenzene. These results imply that despite of the triple dehydrogenation upon dissociative double ionization, the dications generated from these three precursors have different structures. Thus, even if electron ionization can lead to rearrangements or isomerizations of some ions, due to the excess of energy deposited in the ions formed, the present results suggest that the ions are confined in wells and do not probe the entire potential-energy surface. A reviewer correctly argued that due to the lack of ion thermalization in our experiments, the observed differences in reactivity may also be due to a dramatically different internal energy content of the ions formed via double ionization of different neutral precursors. However, for those hydrocarbon dications for which we have studied the bimolecular reactivity using threshold double photoionization [35,44,63], the ions with low internal energies were most reactive in bimolecular collisions, whereas dications with larger internal energy content also easily fragment via dehydrogenation of Coulomb explosions. Therefore, it appears more plausible to relate the differences observed to isomeric structures, although we cannot rule out internal-energy effects.

Fig. 3 also shows that the dications generated from mesitylene do not lead to the formation of organo-rare gas dications with xenon. In contrast, with 2,4,6-trimethylpyridine as a neutral precursor, the species $C_8H_6NXe^{2+}$, $C_8H_7NXe^{2+}$ and $C_8H_8NXe^{2+}$ can be prepared (see above). Thus, it appears that the presence of the hetero-atom in the aromatic ring plays a key role in the reactivity of dication. Nevertheless, hetero-aromatic precursors do not systematically lead to more reactive dications towards rare gases than the corresponding all-carbon aromatic precursors. In fact, $C_7H_n^{2+}$ dications generated from toluene lead to the formation of $C_7H_nXe^{2+}$ dications [35], whereas the corresponding hetero-analogs $C_6H_{n-1}N^{2+}$ generated upon double ionization of 4-methylpyridine do not yield any organo-xenon dications. Accordingly, the reactivity toward rare gases observed for several dications generated from toluene [35], isopropylbenzene, and 4-ethyltoluene as well as 3-vinylpyridine, 2,4,6-trimethylpyridine, and *N*,*N*-dimethylaniline appears to be a specificity of these compounds, rather than representing a general feature of dications generated from aromatic precursors.

## 4. Conclusions

In this work, the reactivity of more than 100 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 $0 \leq o \leq 2$ toward rare gases was investigated. Gas-phase experiments using a triple quadrupole mass spectrometer reveal that most of these dications only lead to the formation of monocations under multiple collisions conditions with rare gases. In addition to these expected channels, eleven new organo-xenon dications $C_mH_nN_oXe^{2+}$ are observed. For dications generated from 2,4,6-trimethylpyridine as a neutral precursor also the organo-krypton dications $C_8H_7NKr^{2+}$ and $C_8H_8NKr^{2+}$ are detected. The expectation that some hydrocarbon dications might be sufficiently strong superelectrophiles to support the formation of stable adducts with rare gases is thus confirmed. The present results also demonstrate that dications generated from isomeric neutral precursors can bear different reactivities toward rare gases, hence excluding a complete loss of structural identity upon dissociative double ionization. Further, the presence of an hetero-atom in the neutral precursor can also dramatically modify the reactivity of the dications generated, in the sense that it can either lead to the formation of organo-rare gas compounds, or inversely prevent such reactions. However, when comprehensively analyzing all data, no obvious correlation between the reactivities observed and the structures of the neutral precursor evolves.

## Acknowledgements

This work was supported by the Czech Academy of Sciences (Z40550506), the European Research Council (AdG HORIZOMS), and the Grant Agency of the Czech Republic (203/09/1223).

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