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Short communication

Mass spectrometric decomposition of *N*-arylbenzonitrilium ions

Rafał Frański[a,*], Maciej Zalas[a], Sebastian Beck[b], Andreas Springer[b], Michael Linscheid[b]

[a] *Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznań, Poland*
[b] *Department of Chemistry, Humboldt Universitaet zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany*

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Abstract

In order to determine the structure of fragment ions formed as a result of the HNCO neutral loss from protonated 1,3,4-oxadiazoles, the following compounds have been studied by electrospray ionisation (ESI) mass spectrometry: 2-(4′-methoxyphenyl)-5-phenyl-1,3,4-oxadiazole (**1**), *N*-(4′-methoxyphenyl)-benzamide (**2**) and 4-methoxy-*N*-phenyl-benzamide (**3**). Collision-induced dissociation mass spectra taken for fragment ions derived from protonated **1**–**3**, namely [**1** + H–HNCO]$^+$, [**2** + H–H_2O]$^+$ (*N*-4′-methoxyphenyl-benzonitrilium ion, **A**) and [**3** + H–H_2O]$^+$ (4-methoxy-*N*-phenyl-benzonitrilium ion, **B**) have shown that upon HNCO loss from protonated **1** formation of ion **B** is favored. As shown by accurate mass measurement, the methyl and CO groups are lost in the next fragmentation step.

Keywords: *N*-Arylbenzonitrilum ions; Collision-induced dissociation; 1,3,4-Oxadiazoles; Fragmentation pathways

1. Introduction

N-Arylbenzonitrilium ions are of practical and theoretical importance in both the condensed and gas phase chemistry. As far as the condensed phase is concerned, these ions react with nucleophilic alkenes giving 3,4-dihydroquinolinium ions [1]; they are important intermediates in *N*-nitrosoamide-mediated Ritter-type reaction [2,3] and interesting reactions of benzonitrilium *N*-phenylimides are also worth noting [4,5]. Recently, a number of solution properties of these ions have been reported by Ruane et al. [6]. As for the gas phase, *N*-arylbenzonitrilium ions are formed by ion–molecule reaction between nitrobenzenes and benzonitrile radical cations (detection of nitroaromatic compounds) [7], and they are products of mass spectrometric decomposition of protonated 2,5-diaryl-1,3,4-oxadiazoles (unusual skeletal rearrangement) [8–11]. In order to determine the structure of these ions, we report the mass spectrometric decomposition of benzonitrilium ion derived from 2-(4′-methoxy)phenyl-5-phenyl-1,3,4-oxadiazole and from *N*-(4′-methoxyphenyl)-benzamide and 4-methoxy-*N*-phenyl-benzamide (compounds **1**, **2** and **3**, respectively).

2. Experimental

Compound **1** was prepared according to the procedure described elsewhere [12]. Amides **2** and **3** were prepared from respective amines and benzoyl chlorides. Their structures were confirmed by NMR and IR spectroscopy.

Electrospray ionization (ESI) mass spectrometric experiments were carried out on a Qstar mass spectrometer (Applied Biosystems, Darmstadt, Germany, hybrid QqTOF instrument; [13]). The compounds were dissolved in methanol at a concentration of about 10^{-5} M and the solutions were directly infused into the ESI source with a flow rate of 10 μl min^{-1}. In order to generate the desired *N*-arylbenzonitrilium ions, the declustering potential was set to 160–200 V and then MS/MS experiments were performed for the ions with different collision energies. The mass spectra shown in Fig. 1 were recorded at the collision energy 30 V. The MS/MS experiments were performed in low resolution mode for the isolation of the precursor ion; therefore, the selected ion beams

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[*] Corresponding author. Tel.: +48 61 829 12 45; fax: +48 61 865 80 08.
E-mail address: franski@main.amu.edu.pl (R. Frański).

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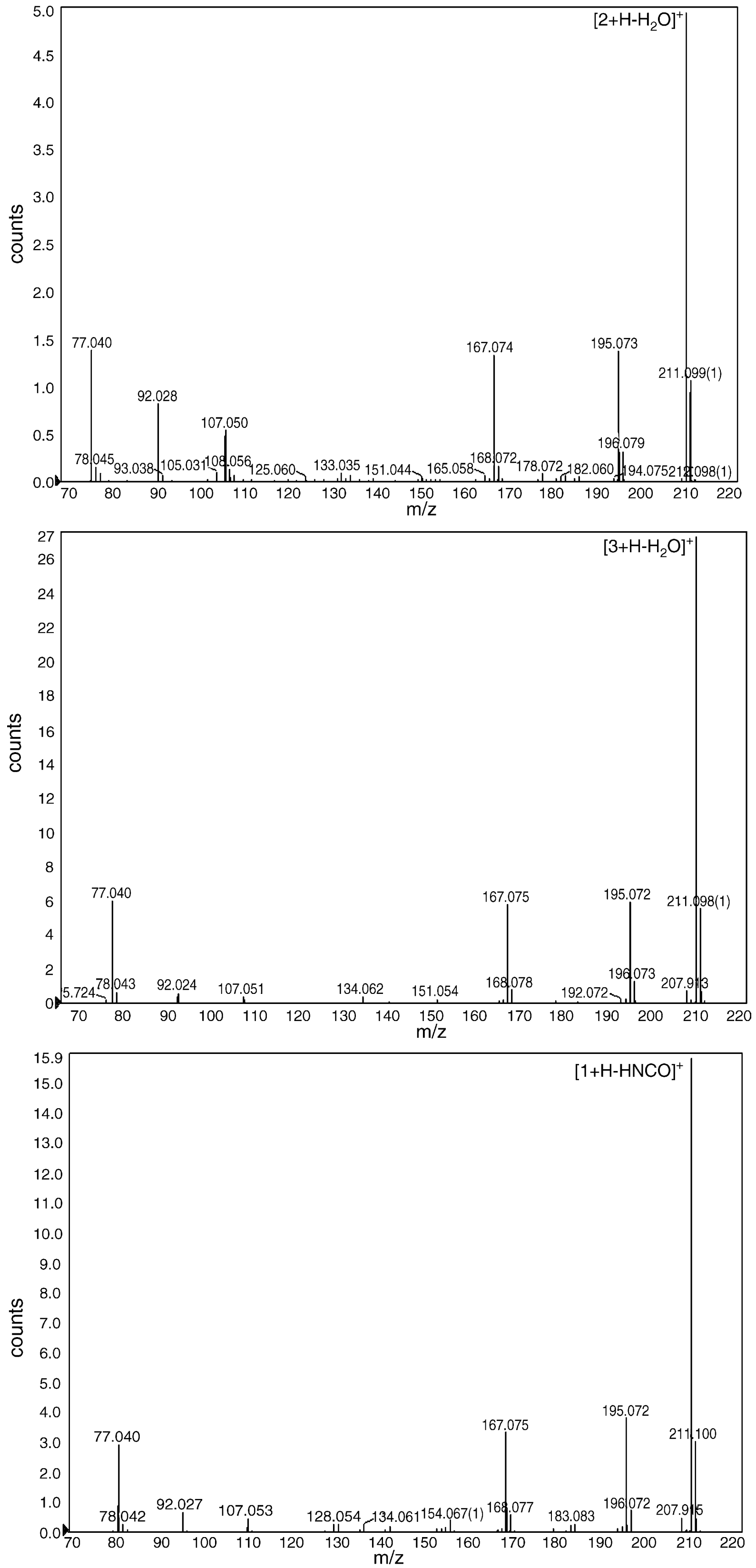
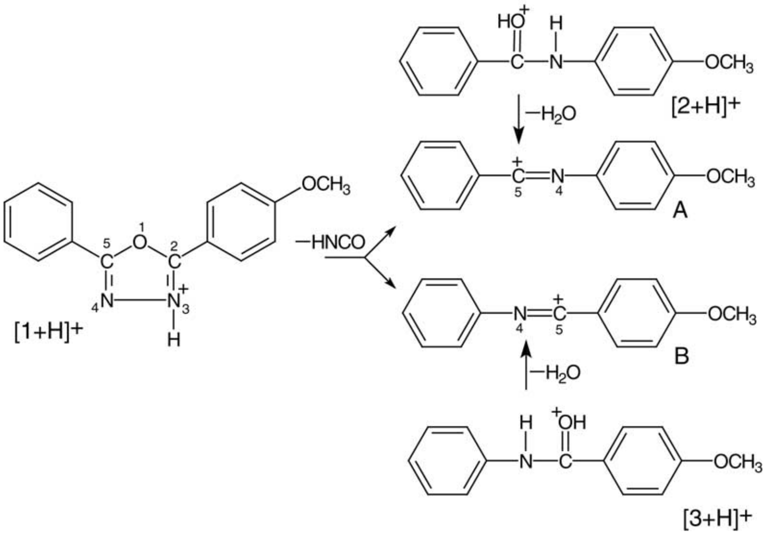


Fig. 1. ESI CID mass spectra of ions $[\mathbf{2}+\mathrm{H}{-}\mathrm{H_2O}]^+$ (ion **A**), $[\mathbf{3}+\mathrm{H}{-}\mathrm{H_2O}]^+$ (ion **B**) and $[\mathbf{1}+\mathrm{H}{-}\mathrm{HNCO}]^+$.



Scheme 1. Loss of the HNCO molecule from protonated **1** and loss of the water molecules from protonated **2** and **3**.

included isotopes. The used collision gas has been nitrogen with a purity of >99.5%. The pressure of the collision gas was set to 4 which resulted in a pressure of about 3.3×10^{-5} Torr within the collision cell and maintained at this value for all fragmentation experiment.

3. Results and discussion

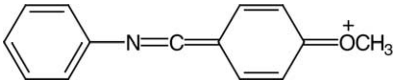
On the basis of the mass spectra recorded for isotope labeled compound, it has been shown previously that the fragment ion formed by HNCO loss from protonated **1** (under ESI condition) contains exclusively C(5) carbon atom of oxadiazole ring [10]. In addition, theoretical calculations performed for various 2,5-diaryl-1,3,4-oxadiazoles have shown that such groups like methoxy or amino (electron-donor groups) at 4′-position favor the protonation of N(3) atom of oxadiazole ring [9,11]. Therefore, formation of *N*-methoxyphenyl-benzonitrilium ion **A** seems to be favored over the formation of its isomeric ion **B** (Scheme 1).

However, for such a complex skeletal rearrangement ion **B** cannot be excluded per se. Thus, MS/MS experiments have been performed for $[\mathbf{2}+H–H_2O]^+$ (ion **A**), $[\mathbf{3}+H–H_2O]^+$ (ion **B**) and for the fragment ion formed by HNCO loss from protonated **1**, which is $[\mathbf{1}+H–HNCO]^+$. The electrospray ionization collision-induced dissociation (ESI CID) mass spectra of these ions are shown in Fig. 1.

By comparison of these MS/MS spectra, it becomes clear that formation of ion **B** from protonated **1** is favored over ion **A** formation. Slightly higher abundances of ions at *m*/*z* 92 and 107 originated from ion $[\mathbf{1}+H–HNCO]^+$ than those for ion **B** show that ion **A** is also formed in low amount. A number of resonance structures (e.g., containing quaternary nitrogen atom) can be drawn for *N*-arylbenzonitrilium ions **A** and **B**. However, the stable quinoid-type structure can be drawn only for ion **B** as shown in Scheme 2. This can explain why formation of ion **B** is favored over ion **A** formation, in spite of the fact that the eliminated HNCO molecule contains N(3) and C(2) atoms (Scheme 1). Formation of ion **B** from protonated **1** can be readily explained by a successive heterolytic cleavage of the N(4)–N(3) bond, 1,2-phenyl shift from C(5) to N(4) atom and 1,2-methoxyphenyl shift from C(2) to C(5) prior the HNCO loss.

Riter et al. have shown (by using isotope labeled compounds) that for *N*-arylbenzonotrilium ions, the N-aryl substituents are more prone to form fragment ions than C-aryl substituents [7]. In other words, the loss of neutral benzonitrile is favored over loss of its neutral structural isomer phenylisonitrile. It explains why in the CID mass spectrum of ion **A** the fragment ions $[C_6H_4OCH_3]^+$ and $[C_6H_4O]^+$ (*m*/*z*, 107 and 92, respectively) are much more abundant than it is for ion **B**. It is clear that ion $[C_6H_4O]^+$ is formed as a result of methyl loss from ion $[C_6H_4OCH_3]^+$ or from ion $[\mathbf{A}–CH_3]^+$ (*m*/*z*, 195) by benzonitrile loss.

Decomposition of a number of *N*-arylbenzonitrilium ions (including ion **B**) has been studied by Riter et al. [7]. For the simplest ion, namely *N*-phenyl-benzonitrilium ion, the authors observed loss of mass 28 which was rationalized, and proved, as H_2CN elimination (radical species). For *N*-methoxyphenyl-benzonitrilium ions, loss of mass 43 proceeded (which is also observed in our work; Fig. 1) which was rationalized by Riter et al. as H_2CN and CH_3 elimination. The authors have performed their research on quadrupole-type instruments which did not allow to measure accurate masses of ions. Our experiments were performed on QqTOF mass spectrometer; thus, the accurate mass of the ions was



Scheme 2. Stable quinoid-type structure of ion **B**.

obtained [13]. The accurate mass shows that the loss of mass 43 corresponds to a CH_3 and CO elimination. The obtained exact mass of these ions is 167.075, the theoretical mass of $C_{12}H_9N$ (composition formed by CH_3 and CO elimination) is 167.0735 and the theoretical mass of $C_{12}H_7O$ (composition formed by H_2CN and CH_3 elimination) is 167.0497. Therefore, the loss of H_2CN and CH_3 elimination has to be excluded. The fragment ion formed by methyl loss (*m*/*z*, 195) is clearly seen in Fig. 1; therefore, fragment ion of *m*/*z* 167 most probably originates from this ion.

Obviously, the obtained exact masses of ions 210 also confirmed their structures. The theoretical mass of $C_{14}H_{12}NO$ is 210.0919 and the obtained masses were 210.0965, 210.0954 and 210.0960 for ion $[\mathbf{1} + H{-}HNCO]^+$, **A** and **B**, respectively.

4. Conclusion

From the data obtained, the following conclusions can be drawn. Firstly, the presence of a methoxy group (and obviously other electron-donor groups as well) on the phenyl ring strongly affects the formation of a benzonitrilium fragment ion from protonated 2-(4′-methoxy)phenyl-5-phenyl-1,3,4-oxadiazole. Upon this rather complex skeletal rearrangement, mainly the 4′-methoxy-*N*-phenylbenzonitrilium ion (**B**) is formed. As mentioned above, this finding was supported by the results published by Riter et al. [7]. Secondly, for methoxy substituted *N*-arylbenzonitrilium ions, the earlier proposed simultaneous loss of H_2CN and CH_3 is not observed (H_2CN loss proceed for unsubstituted ones [7]); instead, the CO molecule and methyl radical are eliminated.

Our findings based on accurate masses have to be considered a complement of previous papers concerning HNCO loss from protonated 1,3,4-oxadiazoles [8–11] and the reactions between nitrobenzenes and benzonitrile radical cations [7].

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