International Journal of Mass Spectrometry 408 (2016) 51–55

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

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

Nitrite and nitrate anions as oxygen donors in the gas phase

Rafał Frański*, Kamila Osińska, Błażej Gierczyk

Adam Mickiewicz University, Faculty of Chemistry, Umultowska 89B, 61-614 Poznań, Poland

ARTICLE INFO

Article history:
Received 14 June 2016
Received in revised form 18 August 2016
Accepted 28 August 2016
Available online 30 August 2016

Keywords:
Nitrite
Nitrate
ESI–MS
Fragmentation
Oxidation

ABSTRACT

Gas phase decomposition of the ions $[M(NO_2)_n]^-$ (M stands for metal), $[ZnI(NO_2)_2]^-$, $[\mathbf{Phen}+ZnNO_2]^+$ and $[\mathbf{Phen}+ZnNO_3]^+$ (**Phen** stands for phenanthroline) have been studied by using electrospray ionization–collision induced dissociation–tandem mass spectrometry (ESI–CID–MS/MS). It was found that nitrite anion can be regarded as good oxygen donor anion in the gas phase, better than nitrate. Oxygen atom can be transferred from nitrite not only to the metal cations but also to the other anions. Both nitrite and nitrate are able to oxidize organic molecule in the gas phase.

1. Introduction

Recently, gas phase clusters of nitrate anion with metal cations have attracted a considerable attention. Respective ionic clusters have been generated in the gas phase by electrospray ionization. One of the gas phase decomposition (mass spectrometric fragmentation pathway) of such clusters, may consist in the oxygen atoms transfers from nitrate anions to the metal cation producing interesting ionic metal oxide species [1–8]. For example from the parent anion $Al(NO_3)_4^-$, the fragment ion $AlO_2(NO_3)_2^-$ is formed [1]. The detailed studies of ionic metal oxide species formed permit better understanding of the metal-oxygen bonding (electronic structure and reactivity).

Electrospray ionization, mainly with ion mobility mass spectrometry, has been also used for quantitative analysis of nitrate anions and also for nitrite anions [9–11]. Obviously, the solution properties, e.g. hydration, of nitrate and nitrite anions have been also studied in details [12].

In this work we decided to check if nitrite anion can also behave as an oxygen donor anion in the gas phase. It is well known that in condensed phase, metal-nitrate interactions may be substantially different from metal-nitrite interactions. For example, nitrate forms stable salts with all metals, whereas nitrite forms stable salts with alkali metals, alkali earth metals and silver, however, nitrite forms with cobalt a characteristic hexanitritocobaltate(III) anion, whereas nitrate does not. Thus, it is also worth comparing the gas phase properties of nitrite and nitrate.

As described further, upon these research we found that nitrite and nitrate anions can behave as oxygen donor not only to metal cation but also to anions. Furthermore, both nitrite and nitrate anions can behave as oxygen donor to organic molecules.

2. Experimental

Except nitrites of alkali metals, only silver nitrite is easy to prepare (these nitrites are commercially available) and from $AgNO_2$ the abundant ion $[Ag(NO_2)_2]^-$ was generated by ESI. By electrospraying solutions containing KNO_2 (KNO_2 was better than $NaNO_2$) and a salt of another metal (usually nitrates) we tried to generate other ions $M(NO_2)_n^-$ (M stand for metal). Such an approach was not always successful since a number of different clusters were formed. However, these metals for which it was successful allowed a satisfactory insight into gas phase decomposition of ions $M(NO_2)_n^-$.

ESI–CID–MS/MS spectra were taken on a Waters/Micromass (Manchester, UK) Q-tof Premier mass spectrometer (software MassLynx V4.1, Manchester, UK). The sample solutions were infused into the ESI source by a syringe pump at a flow rate of 5 ml/min. The electrospray voltage was 2.7 kV and the cone voltage − 30 V. The source temperature was 80 °C and the desolvation temperature was 250 °C. Nitrogen was used as the cone gas and desolvating gas at the flow-rates of 50 and 800 lh^{-1}, respectively. Argon was used as a collision gas at the flow-rate 0.5 ml/min in the T-wave collision cell. The applied collision energy (CE, laboratory frame), the most important parameter for CID-MS/MS experiments, is indicated in each CID-MS/MS spectrum shown. In each CID-MS/MS

---

* Corresponding author.
E-mail address: franski@amu.edu.pl (R. Frański).

http://dx.doi.org/10.1016/j.ijms.2016.08.007
1387-3806/

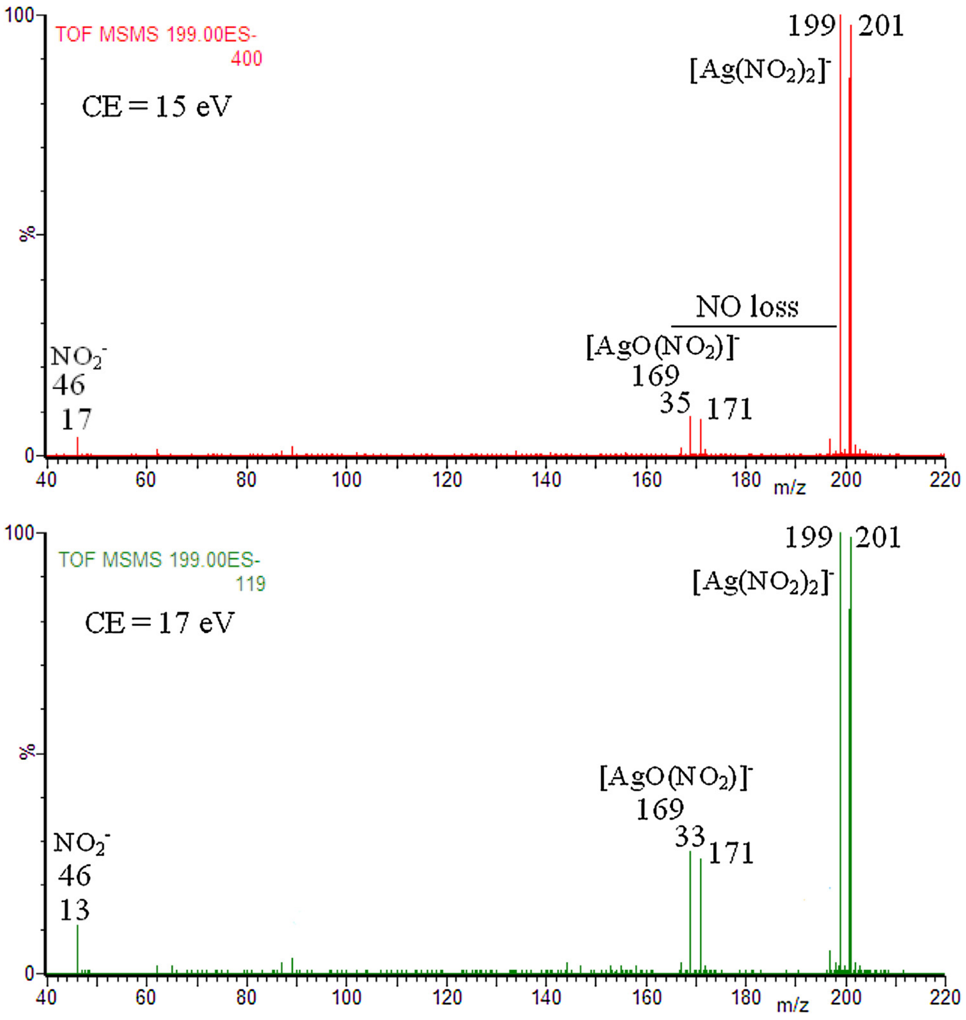

Fig. 1. ESI–CID–MS/MS spectra of ion $[Ag(NO_3)_2]^-$. The fragment ions are labeled by their abundances (arbitrary units) and by *m*/*z* values. The abundances of parent ions are indicated in the left corner (400 and 119).

spectrum the abundance of the most abundant ion (arbitrary units) are also given.

3. Results and discussion

From silver nitrate, the abundant ion $[Ag(NO_3)_2]^-$ was generated and its gas phase decomposition consisted in the formation of abundant fragment ion NO_3^- [6]. From silver nitrite, the abundant fragment ion $[Ag(NO_2)_2]^-$ was generated, however, its gas phase decomposition was not analogous to that of ion $[Ag(NO_3)_2]^-$. Fig. 1 shows the ESI–CID–MS/MS spectra of ion $[Ag(NO_2)_2]^-$ obtained at two collision energies. As clearly seen in Fig. 1, the decomposition of ion $[Ag(NO_2)_2]^-$ involves the formation of two fragment ions, namely ion NO_2^- (decomposition analogous to that of ion $[Ag(NO_3)_2]^-$) and ion $[AgO(NO_2)]^-$ (analogous decomposition was not occurred for ion $[Ag(NO_3)_2]^-$). Obviously ion NO_2^- can be also formed by subsequent decomposition of ion $[AgO(NO_2)]^-$.

At the higher collision energy the abundance of parent ion is more than three times lower than at the lower collision energy. However the abundances of fragment ions increased only slightly at the higher collision energy. The low abundance of fragment ion $[AgO(NO_2)]^-$ can be explained by its subsequent decomposition and by the fact that formation of this ion is not efficient. However, why fragment ion NO_2^- is not abundant at the higher collision energy? A plausible explanation of the low abundance of ion NO_2^- is that formation of this ion is followed be its deionization (electron loss) and formation of neutral NO_2 molecule (quiet stable radical in gas phase).

It has to be stressed that the formation of ion $[AgO(NO_2)]^-$ from ion $Ag(NO_2)_2^-$ (another problem is if ion $[AgO(NO_2)]^-$ can isomerize to ion $[AgNO_3]^-$) indicates that nitrite anion can be a donor of oxygen atom in the gas phase and maybe even a better one than nitrate anion.

Fig. 2 shows the ESI–CID–MS/MS spectra of ions $[Mn(NO_2)_3]^-$, $[Cu(NO_2)_2]^-$ and $[Zn(NO_2)_3]^-$ (although a number of Cu(II) salts were used, ion $[Cu(NO_2)_3]^-$ was not generated). Gas phase decomposition of ions $[Mn(NO_2)_3]^-$ and $[Cu(NO_2)_2]^-$ can be regarded as analogous to the gas phase decomposition of ions $[Mn(NO_3)_3]^-$ and $[Cu(NO_3)_2]^-$ [3,6]. However decomposition of ion $[Zn(NO_2)_3]^-$ is different from that of ion $[Zn(NO_3)_3]^-$ (decomposition of the latter consisted in the formation of two fragment ions namely NO_3^- and $[ZnO(NO_3)_2]^-$) [6].

As shown in Fig. 2 the abundant fragment ion $[ZnO_2]^-$ is formed by loss of NO and NO_2 molecules. Formation of this fragment ion indicates that nitrite is a better donor of oxygen atoms than nitrate.

The question is what is the oxidation state of zinc and oxygen in ion $[ZnO_2]^-$? Ion $[ZnO_2]^-$ can be regarded as similar to ion $[CuO_2]^-$. In our previous paper we have assumed that in ion $[CuO_2]^-$ the oxidation state of copper is +3 (on condition that the oxidation state of oxygen is −2) since the oxidation state +3 for copper is