Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(10):655-658

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Gas phase decomposition of $H_2PO_3^-$ and $H_2PO_2^-$

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ABSTRACT

Gas phase decomposition of hydrogen phosphite $H_2PO_3^-$ and hypophosphite $H_2PO_2^-$ have been studied by using electrospray ionization-collision induced dissociation-tandem mass spectrometry (ESI-CID-MS/MS). Decomposition of these ions involves the loss of H_2 molecules producing fragment ions PO_3^- and PO_2^- respectively (redox processes). The loss of H_2O is a minor decomposition of $H_2PO_3^-$.

Keywords: phosphite; hypophosphite; electrospray; mass spectrometry; oxidation.

INTRODUCTION

There are two phosphorous oxyanions containing phosphorus at oxidation state lower than +5, namely phosphite HPO_3^{2-} (P^{+3}) and hypophosphite $H_2PO_2^-$ (P^{+1}). Both phosphites and hypophosphites exist in the environment [1-7]. Furthermore, it has to be stressed that their oxidation is of crucial interest with respect to the formation of phosphorylated prebiotic molecules on the early Earth [8-10].

Gas phase behavior of orthophosphate and pyrophosphate anions has been studied by many authors [11-18]. To the best of our knowledge phosphite and hypophosphite have not been studied in the gas phase yet. In this communication we discuss the gas phase decomposition (oxidation upon condition of collision induced dissociation - CID) of $H_2PO_3^-$ and $H_2PO_2^-$. The anions were generated by using electrospray ionization mass spectrometry (ESI-MS).

EXPERIMENTAL SECTION

Mass spectra were taken on a Waters/Micromass (Manchester, UK) Q-tof Premier mass spectrometer (software MassLynx V4.1, Manchester, UK). The sample solutions, containing about 10^{-5} mol/dm^3 of Na_2HPO_3 or NaH_2PO_2 in methanol/water 1/1, were infused into the ESI source by a syringe pump at a flow rate of 5 μl/min. The electrospray voltage was 2.7 kV and the cone voltage - 10 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 400 lh^{-1}, respectively. Argon was used as a collision gas at the flow-rate 0.5 ml/min in the T-wave collision cell. This flow rate resulted in the collision cell pressure of about 0.5 Pa. The applied collision energy (laboratory frame), the most important parameter for CID-MS/MS experiments, is indicated in each CID-MS/MS spectrum shown.

When orthophosphate-containing solution is subjected to electrospray ionization mass spectrometric (ESI-MS) analysis, only singly charged anion $H_2PO_4^-$ is generated in the gas phase [19], since doubly and triply charged small anions are unstable in the gas phase [20]. Analogically, phosphite-containing solution yielded singly charged anion $H_2PO_3^-$.

RESULTS AND DISCUSSION

It has been already shown that, in the gas phase, anion $H_2PO_4^-$ loses H_2O molecule producing metaphosphate anion PO_3^- [11]. As shown in Figure 1, anion PO_3^- is also formed from anion $H_2PO_3^-$ by the loss of H_2 molecule. Formally it is a redox process, phosphorus is oxidized ($P^{+3} \rightarrow P^{+5}$) and hydrogen is reduced ($H^{+1} \rightarrow H^0$).

Anion $H_2PO_3^-$ also loses a H_2O molecule producing anion PO_2^- but this is a minor process (anion PO_2^- is not abundant but clearly seen, Figure 1) and it is not a redox process. Anion PO_2^- is the simplest P^{+3}-containing phosphorus oxyanion.

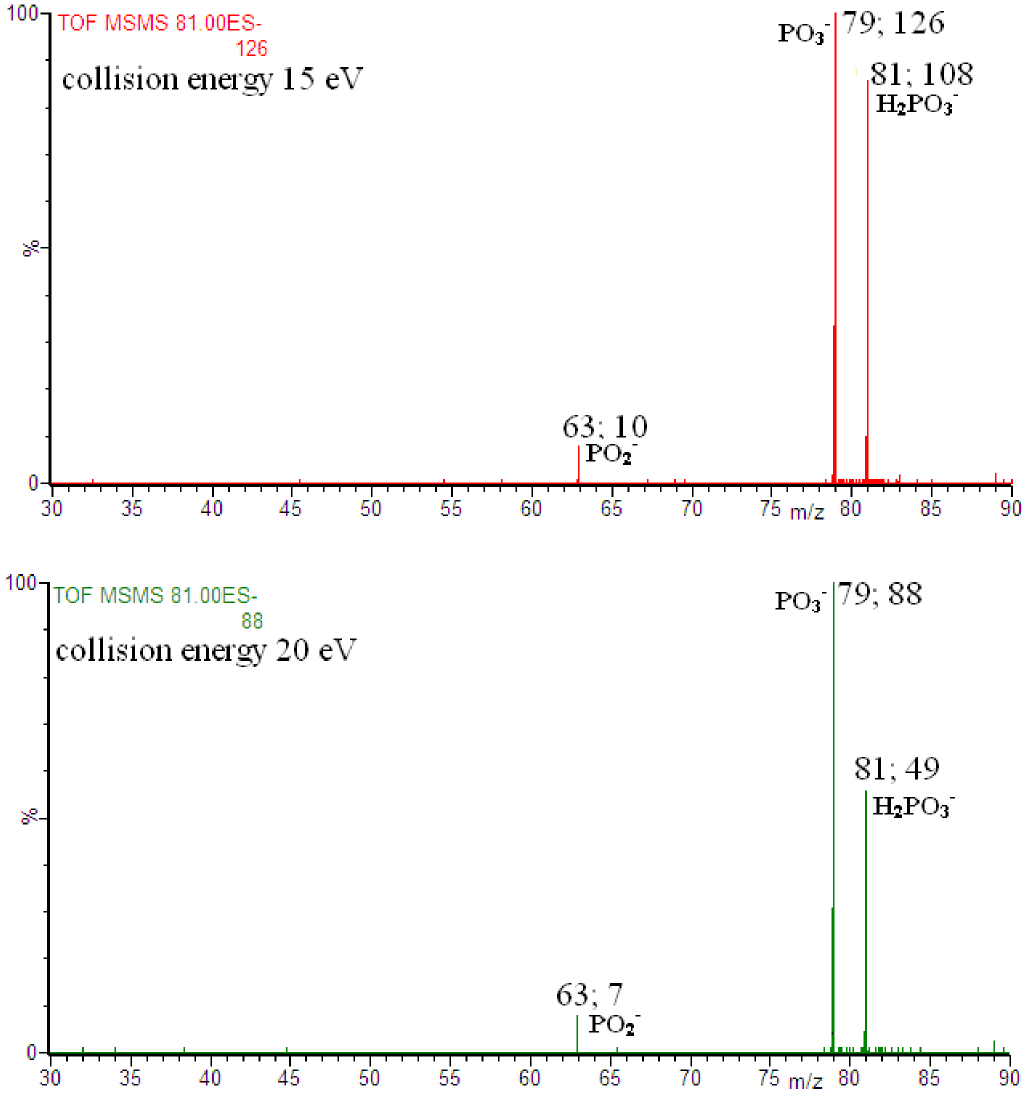

Figure 1. ESI-CID-MS/MS spectra of ion $H_2PO_3^-$
Peaks are labeled by m/z values and abundances (arbitrary units)

Loss of H_2O from anion $H_2PO_3^-$ requires breaking of the O-P bond, whereas loss of H_2 requires breaking of the H-O bond (obviously both require breaking of the H-P bond). The H-O bond is much shorter, as a consequence much stronger, than that of O-P (H-O about 95 pm, O-P about 160 pm, www.wiredchemist.com/chemistry/data/thermodynamic-data). Therefore, the conclusion can be drawn that P^{+1} and P^{+3} are highly prone to be oxidized in the gas phase.

As shown at Figure 1, at collision energy 20 eV, the relative fragment ion abundances (in relation to abundance of parent ion) are higher than at collision energy 15 eV. However the absolute abundances of ion (abundances in arbitrary units are shown in mass spectra recorded) are lower at higher collision energy for both parent and fragment ions. It is reasonable that collision induced electron detachment occurs for fragment ions (free electron and neutral species are formed which obviously cannot be detected by a MS detector). Electron detachment of a number of simple anions by collision with noble gas atoms is a known process, however at high collision energy [21-23]. Electron detachment from anions PO_3^- and PO_2^- has also been studied, however, it was electron impact induced electron detachment [24]. In our study, we found that anions PO_3^- and PO_2^- were highly prone to electron detachment by collisions with noble gas atoms (in our study with argon atoms) at low collision energy.

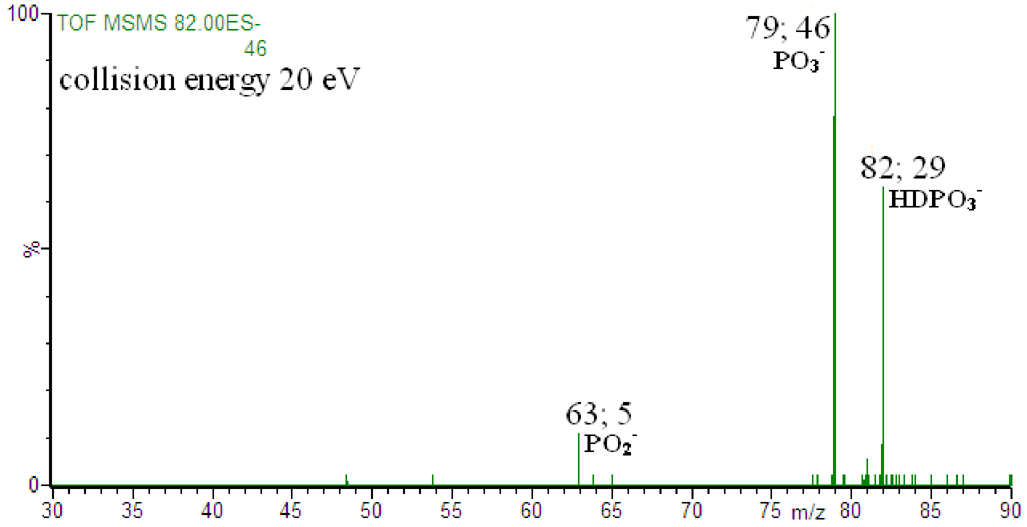

Figure 2. CID MS/MS spectrum of ion $HDPO_3^-$

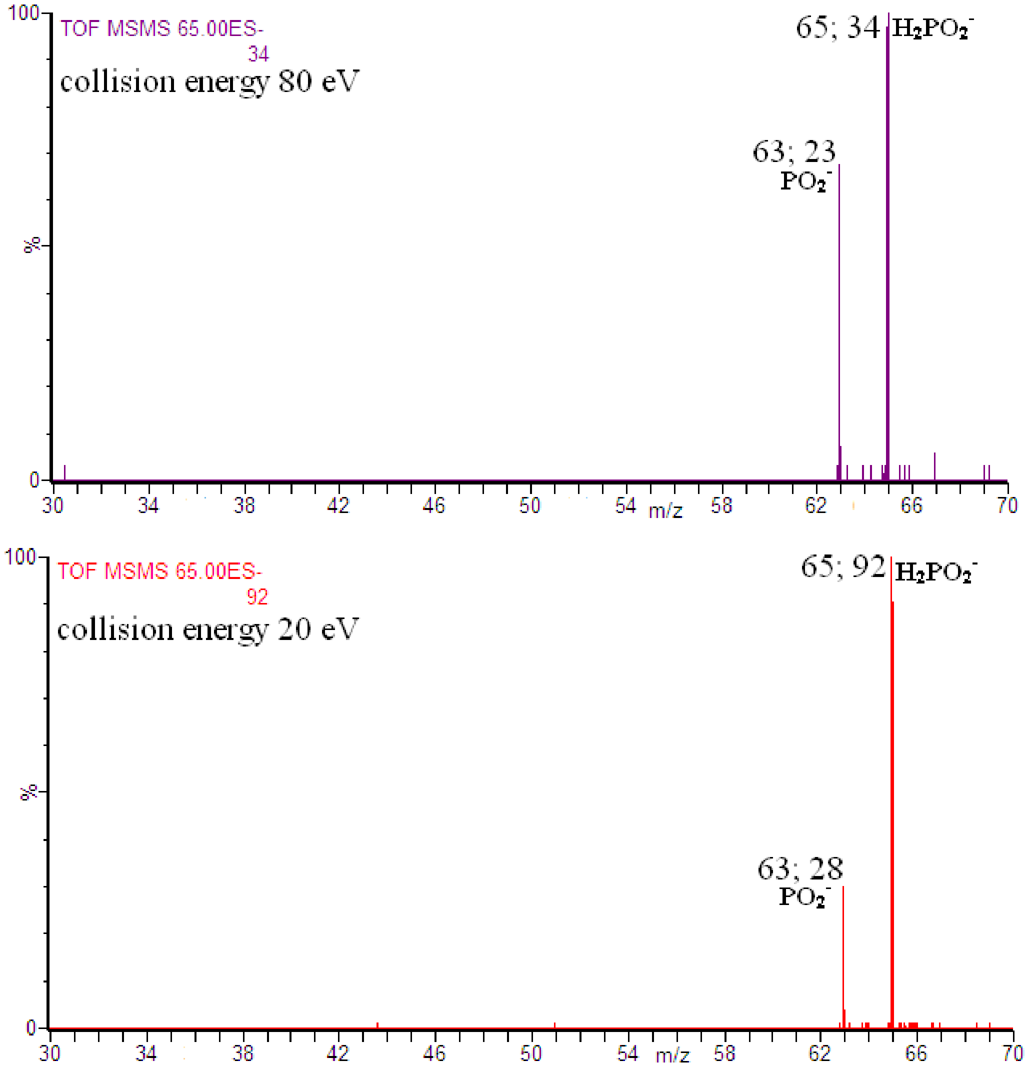

Figure 3. ESI-CID-MS/MS spectra of ion $H_2PO_2^-$

Major decompositions of ion $H_2PO_3^-$ involve the loss of H_2 molecule, while loss of H_2O molecule is a minor decomposition. Therefore, the question is if the isotope effect (substitution of H by D) affects the decomposition. The use of CH_3OD/D_2O as a solvent, instead of CH_3OH/H_2O, resulted in formation of ion $HDPO_3^-$ (even heating for a few hours did not yield ion $D_2PO_3^-$, thus H-P cannot be changed into D-P at this conditions).

Figure 2 shows the CID MS/MS spectrum of ion $HDPO_3^-$ obtained at the collision energy 20 eV.

From a comparison of CID MS/MS spectrum of ion $HDPO_3^-$ (Figure 2) with CID MS/MS spectrum of ion $H_2PO_3^-$ (Figure 1), it is clear that $PO_2^-/HDPO_3^- > PO_2^-/H_2PO_3^-$, whereas $PO_3^-/HDPO_3^- < PO_3^-/H_2PO_3^-$. In other words, gas phase phosphorus oxidation may affected by isotope effect.

Hypophosphite anion $H_2PO_2^-$ is the second anion studied in this work. As shown in Figure 3, its gas phase decomposition involves the loss H_2 molecule to produce anion PO_2^-, and this is the only observed fragmentation pathway. Formally it is also a redox process, $P^{+1} \rightarrow P^{+3}$ and $H^{+1} \rightarrow H^0$.

At collision energy 80 eV, the relative abundance of fragment ion (in relation to abundance of parent ion) is higher than at collision energy 20 eV. However, the absolute abundances of ions are lower at higher collision energy for both parent ion and fragment ion. Thus, analogically as for anion PO_3^-, collision of PO_2^- with argon atoms leads to electron detachment.

CONCLUSION

Summing up the above discussed results, gas phase decompositions of anions $H_2PO_3^-$ and $H_2PO_2^-$ involve the loss of H_2 molecules to produce anions PO_3^- and PO_2^- respectively (redox processes). Formation of anions PO_3^- and PO_2^- is followed by electron detachment. For anion $H_2PO_3^-$, the loss of water molecule occurs as a minor process and for anion $H_2PO_2^-$ it does not occur. Therefore, the conclusion can be drawn that P^{+1} and P^{+3} are highly prone to be oxidized in the gas phase.

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