International Journal of Mass Spectrometry 354–355 (2013) 333–341

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

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

Influence of heteroanion and ammonium cation size on the composition and gas-phase fragmentation of polyoxovanadates

Grant E. Johnson*, Naila M. Al Hasan, Julia Laskin

Physical Sciences Division, Pacific Northwest National Laboratory, P. O. Box 999, MSIN K8-88, Richland, WA 99352, United States

A R T I C L E   I N F O

Article history:
Received 9 May 2013
Received in revised form 18 June 2013
Accepted 18 June 2013
Available online 28 June 2013

Keywords:
Polyoxometalate
Vanadium oxide
Ethylammonium
Butylammonium
Electrospray
Collision induced dissociation

A B S T R A C T

This paper describes the results of a systematic experimental investigation of the influence of different size alkyl ammonium cations and heteroanions on the composition, ionic charge state and gas-phase fragmentation pathways of anionic polyoxovanadates synthesized in solution. Four separate solutions of polyoxometalates (POMs) were prepared using all possible combinations of the tetraethylammonium $[(C_2H_5)_4N^+]$ cation, chloride (Cl^-) heteroanion, tetrabutylammonium $[(C_4H_9)_4N^+]$ cation and acetate ($CH_3CO_2^-$) heteroanion. Employing electrospray ionization combined with high-resolution mass spectrometry (ESI-MS) we demonstrate that POM solutions synthesized using the small $[(C_2H_5)_4N^+]$ cation and Cl^- heteroanion are composed predominately of large doubly and triply charged chlorine containing species with a size distribution centered at 14 vanadium atoms. POM solutions prepared using the Cl^- anion and a larger $[(C_4H_9)_4N^+]$ cation are shown to contain slightly larger species with 15 and 16 vanadium atoms, thereby indicating that the size of the ammonium cation exerts only a weak influence on the size of polyoxovanadates formed in solution. POM solutions prepared using $(C_2H_5)_4NCl$ and $(C_4H_9)_4NCl$ also produced peaks consistent with the attachment of one and two ammonium cations to the larger vanadium oxide species. Solutions prepared using the large $CH_3CO_2^-$ heteroanion, in contrast, contain much smaller singly and doubly charged species with a size distribution centered at six vanadium atoms. In addition, while incorporation of one and two ammonium cations into the smaller vanadium oxide species was observed, no POMs containing the $CH_3CO_2^-$ heteroanion were identified. The gas-phase fragmentation pathways of representative POMs containing one and two ammonium cations were examined using collision induced dissociation (CID) and mass spectrometry. Similar primary fragmentation pathways involving partial loss of the ammonium cation were observed for species containing both one and two ammonium cations largely independent of the size, composition and charge state of the precursor ion. The $[(C_4H_9)_4N^+]$ was found to exhibit stronger interactions with the core of the POMs resulting in higher abundance of fragment ions containing (C_4H_9) units compared to (C_2H_5) units originating from $[(C_2H_5)_4N^+]$. These results provide fundamental insight into the interactions between anionic metal oxides, heteroanions and ammonium cations that are responsible for the size and composition-controlled synthesis of POMs in solution.

Published by Elsevier B.V.

1. Introduction

Polyoxometalates (POMs) are a class of highly charged anionic transition metal oxide clusters that are receiving increasing attention in the research community due to their wide range of chemical and physical properties as well as their ability to form structures that span in length from the molecular to the macroscale [1,2]. The larger polyoxometalates are formed from small metal oxide building blocks (MO_x, x = 4–7) that incorporate relatively inexpensive early transition metals such as V, Mo and W in their highest oxidation states [3]. Simple acid catalyzed condensation of molecular monomeric metal oxide precursors at controlled pH under "one-pot" reaction conditions provides access to a diverse range of POMs in solution. These include heteropolyanions that contain internal heteroanions such as Cl^- and $PO_4{}^{3-}$ and isopolyanions that have a metal oxide framework without an internal heteroanion [4]. POMs have been demonstrated to exhibit a variety of useful properties such as ionic conductivity [5], extensive host-guest chemistry [6] and superacidity [7] which make them promising materials for use in applications like chemical threat detection and molecular sensing [8,9], anticancer pharmaceutical treatment [10,11], batteries [12,13] and catalysis [14,15]. Clearly, each of these applications will require POM materials with different and well-defined size, shape and composition. Therefore, one of the current goals of research in this field is to obtain and apply a fundamental

---

* Corresponding author. Tel.: +1 5093716753; fax: +1 5093716139.
E-mail addresses: Grant.Johnson@pnnl.gov (G.E. Johnson), Julia.Laskin@pnnl.gov (J. Laskin).

1387-3806/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.ijms.2013.06.009

understanding of the solution-phase assembly of small building blocks into larger systems so that POM materials with pre-determined properties may be rationally synthesized across multiple length scales. At the core of these assembling processes in solution are the molecular-level interactions between anionic metal oxides, heteroanions or molecules and ammonium cations.

In recent years high resolution mass spectrometry (MS) has been increasingly employed to determine the composition and structure of POMs synthesized in solution [16–20]. Specifically, MS coupled with soft ionization by electrospray (ESI-MS) enables large anionic clusters to be transferred intact into the gas phase from solution. Due to the fact that POMs are intrinsically negatively charged, MS enables unambiguous determination of their molecular formulae and ionic charge states and provides valuable insight into the relative abundance of different POM species present in solution [16]. Furthermore, MS enables the composition of covalently functionalized POMs [21] and complex clusters containing more than one metal to be assigned in a straightforward manner, which is not always possible with other characterization techniques. The initial steps of POM assembly and nucleation that produce larger species may be investigated by analyzing reacting solutions at different reaction times during synthesis by ESI-MS [22]. In addition to analyzing the content of POMs in solutions during and after synthesis, ESI-MS may be used to introduce POMs into the gas phase for further analysis using mass spectrometry and ion spectroscopy techniques. For example, a recent study by Ma et al. examined the fragmentation of polyoxotungstate anions using collision induced dissociation (CID) coupled with MS [23]. They showed that gas-phase fragmentation of the widely known Keggin $(PW_{12}O_{40})^{3-}$ and Dawson $(P_2W_{18}O_{62})^{6-}$ anions results in the formation of pairs of complementary product ions. In a related publication, Cao et al. employed CID to investigate how the presence of the tetrabutylammonium cation influences the fragmentation of Keggin POMs [24,25]. Photoelectron spectroscopy (PES) of doubly charged POMs in the gas-phase has been used to examine the electronic structure of the clusters and, combined with density functional theory (DFT) calculations, confirm their stability in the gas phase without the presence of positive counterions [26]. Two years later the same group conducted a related study in which they investigated the electronic structure and confirmed the stability of the intact triply charged Keggin anion in the gas phase [27]. More recently, large Keplerate anions were introduced into the gas phase by ESI and analyzed using a combination of ion mobility spectrometry and MS [28]. Therefore, ESI coupled with mass spectrometry, ion spectroscopy and ion mobility are emerging as powerful and widely used characterization tools for highly complex inorganic systems such as POMs.

Polyoxovanadates are one of the more widely studied subgroups of POMs [29–31] due to their propensity to form mixed-valence clusters [32]. They have found applications as cathodes in lithium ion batteries [33] as well as catalysts for promoting various redox reactions [31]. Furthermore, vanadium oxide catalysts are employed in the production of bulk chemicals such as sulfuric acid [34] as well as the selective reduction of nitrogen oxide pollutants that are present in exhaust gases [35]. A variety of MS-based techniques have been employed to examine the composition, size, structure and reactivity of polyoxovanadates. For example, Walanda et al. used ESI-MS to identify isopolyvanadate anions formed under non-equilibrium conditions, thereby providing insight into the nucleation processes occurring in solution [18]. In a similar vein, Truebenbach et al. used a related methodology to examine how acidic versus basic conditions in solution impact the polymerization and growth of larger clusters [17]. In a previous publication, we demonstrated that solution-phase synthesis of tetradecavanadate, $V_{14}O_{36}Cl(L)_5$, combined with ESI-MS and in-source fragmentation may be used to produce a wide array of singly, doubly and triply charged vanadium oxide anions for subsequent study using tandem MS and ion spectroscopy techniques [36]. Closely related singly charged anionic vanadium oxides produced by laser vaporization rather than synthesis in solution also have been investigated using several gas-phase techniques. For instance, Bell et al. employed CID to study the fragmentation of $V_xO_y^-$ revealing that VO_2, VO_3 and V_2O_5 are the main building blocks of these species [37]. In addition, the structures of anionic vanadium oxides have been widely examined using infrared multiple photon dissociation (IRMPD) spectroscopy combined with theoretical calculations [38,39]. For example, Asmis et al. measured the IR action spectra of $(V_2O_5)_n^-$ ($n = 2, 3, 4$) and identified that these species adopt polyhedral cage structures [40]. In a related work Feyel et al. used IRMPD to determine the structures of binary $V_4O_9^-$ and $V_4O_{10}^-$ [41]. The electronic and structural properties of small $V_2O_x^-$ ($x = 3$–7) anions and intermediate size $(V_2O_5)_n^-$ ($n = 2$–4) also have been investigated by Zhai et al. using gas-phase PES and DFT calculations [42,43]. In addition, the relationship between the electron affinity of larger $V_xO_y^-$ ($x = 4$–15; $y = 0$–2) and their size has been examined using PES by Pramann et al. [44]. A great deal of research has been conducted on the reactivity of singly charged cationic vanadium oxides generated by laser vaporization with small hydrocarbon and inorganic gas molecules to gain insight into the molecular-level mechanisms of reactions promoted by bulk vanadium oxide catalysts [45–53]. To better examine the highly size-dependent properties of cationic vanadium oxides, Ard et al. recently used a flow reactor to first ligate and then trap gas-phase vanadium oxide ions and transfer them intact into solvents [54]. The recent availability of extreme ultraviolet (EUV) lasers that enable non-destructive single-photon ionization of metal oxides also has facilitated reactivity studies of neutral vanadium oxides with several different gases [55,56]. Due to the large volume of research in this area, a great deal is currently understood about the size and charge state dependent properties of singly charged bare vanadium oxides. However, multiply charged anionic vanadium oxide clusters (polyoxovanadates) synthesized in solution and containing ammonium cations as well as heteroanions or neutral molecules are largely unexplored using MS-based techniques [57].

Previous studies in the literature have demonstrated that the size and coordination geometry of heteroanions and neutral molecules in POMs may strongly influence the overall symmetry and geometry of the larger cluster [22,58]. In addition, the cationic species present in solution are known to control the structure of POMs [59]. For example, in a recent study Miras et al. demonstrated that the presence of ammonium cations in solution is critical to the formation of the smaller $Mo_{11}V_7$ cluster rather than the larger $Mo_{72}V_{20}$ species that is produced with sodium (Na^+) or potassium (K^+) cations [60]. In this study, we investigate the influence of the size of two alkylammonium cations [$(C_2H_5)_4N^+$ versus $(C_4H_9)_4N^+$] and two heteroanions [Cl^- versus $CH_3CO_2^-$] on the size, charge state and composition of polyoxovanadates synthesized in solution using the same procedure. Employing ESI-MS we demonstrate that the small Cl^- heteroanion favors the formation of large species containing 14 vanadium atoms with both ammonium cations. In contrast, the larger $CH_3CO_2^-$ heteroanion produces a distribution of ions centered at around six vanadium atoms in size. The size of the ammonium cation is shown to exert a weak influence on the size of the polyoxovanadates synthesized in solution with the larger cation favoring slightly larger species. The fragmentation pathways of representative POMs containing one and two ammonium cations were examined using CID. Similar primary fragmentation pathways involving partial loss of an ammonium cation were observed for species containing both one and two ammonium cations. In addition, the larger $(C_4H_9)_4N^+$ ammonium cation was found to exhibit stronger interactions with the POM core resulting in higher