



High-resolution mass spectrometry provides unique insights on the structure and dynamics of polyoxometalates in solution

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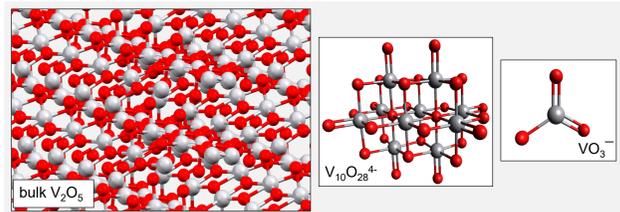
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Overview

- MS reveals novel fragments of Decavanadate (e.g., $V_{10}O_{26}^{2-}$)
- Partial reduction of decavanadate anions evident in the negative-ion ESI MS occurs naturally in solution.
- Decavanadate $^{16}O/^{18}O$ exchange with MS detection provides evidence for the existence of multiple metastable decavanadate structures

Introduction

Polyoxometalates (POMs) are early transition metal/oxygen cluster anions, a unique class of polynuclear inorganic compounds that are frequently viewed as a “missing link” between single-molecule and bulk material scales [1]. Apart from their obvious importance the field of mesoscopies (e.g., helping understand how physical properties of materials are determined by the chemical properties of constituent molecules), POMs continue to enjoy attention in fields as diverse as catalysis, electronics and biology. Decavanadate ($V_{10}O_{26}^{6-}$) is one particularly interesting member of the POM family, which had been shown to interact with a variety of biomolecules *in vivo*, eliciting a range of biological effects that are distinct from those typically associated with simpler oxovanadate species [2].



Although decavanadate and its various protonation states are the predominant vanadium species in moderately concentrated (> 1 mM) and mildly acidic (pH ≤ 6) aqueous solutions, they readily convert to other oxo-forms (e.g., $V_3O_9^{3-}$ at neutral pH, VO_4^{3-}/HVO_4^{2-} at basic pH, or VO_3^-/HVO_3 upon dilution) [3]. Furthermore, the existence of a partially reduced species ($V_{10}O_{26}^{4-}$) has been postulated based on spectroscopic measurements [4]. Lastly, the notion of low-energy metastable configurations of decavanadate (distinct from the crystal structure shown above) has been invoked to explain several phenomena related to its interaction with the solvent [5, 6].

Decavanadate characterization has been carried out using spectroscopic methods (optical and NMR), as well as X-ray crystallography, while mass spectrometry (MS) has played less prominent role. The main goal of this work was to explore the utility of high-resolution MS for characterization of both structure and dynamics of decavanadate species in aqueous solutions with a particular emphasis on potential pitfalls (e.g., artifacts related to redox processes in the electrospray ionization source and gas-phase fragmentation of vanadate ions). We are also interested in exploring both similarities and differences between the decavanadate behavior in solution and in the solvent-free environment, which may provide important insights into the POMs/solvent interactions (and, by extension, phenomena occurring at the reducible metal oxide/water interface).

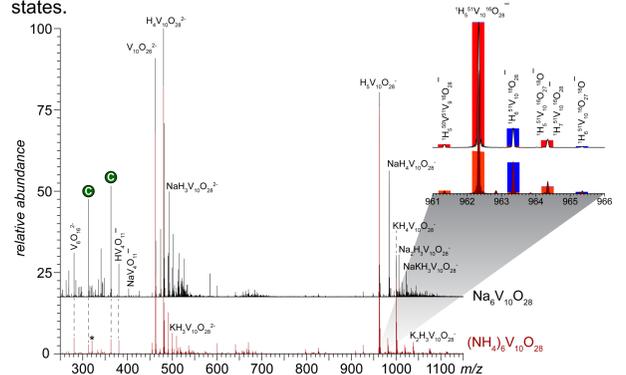
Experimental

Materials. Both sodium and ammonium salts of decavanadate ($Na_6V_{10}O_{28}$ and $(NH_4)_6V_{10}O_{28}$) were produced in the D.C.C. laboratory (at the Colorado State University) following standard protocols.

Methods. A Solarix 7 (Bruker Daltonics, Billerica, MA) hybrid quadrupole-Fourier transform ion cyclotron resonance mass spectrometer equipped with a standard electrospray ionization (ESI) source was used for all MS measurements. Fragment ion spectra were obtained by mass-selecting precursor ions in the front-end quadrupole followed by their collisional activation. LC-MS was performed with an Agilent 1100 Series HPLC and a Hamilton PRP-X300 Column (4.1 mm x 250 mm). Oxygen exchange measurements were carried out by diluting aqueous decavanadate 1:10 in 97% $^1H_2^{18}O$.

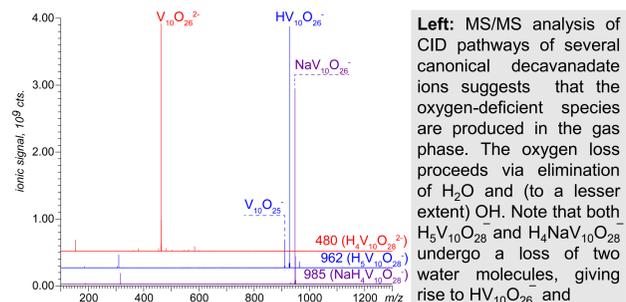
Results and Discussion

Negative-ion ESI MS: decavanadate(V) anions are predominant species, but some anomalies are also evident. Negative-ion ESI mass spectra of 1 mM aqueous solutions of $Na_6V_{10}O_{28}$ (black trace) and $(NH_4)_6V_{10}O_{28}$ (maroon) display prominent decavanadate signal at -1 and -2 charge states.



In addition to these molecular ions, a prominent signal is observed for a $V_{10}O_{26}^{2-}$ ion; a low-abundance signal of $HV_{10}O_{26}^{-}$ is present as well. Also observed are $V_6O_{16}^{2-}$ and $HV_4O_{11}^{-}$ species. Furthermore, a detailed analysis of the isotopic distributions of the decavanadate species (see the insets) reveals anomalously high signal for the $M+1$ isotopolog (with M representing the base peak, $^1H_5^{51}V_{10}^{16}O_{26}^{2-}$): the red bars in the inset represent the theoretical isotopic distribution of the $H_5V_{10}O_{26}^{2-}$ ions. Similar distortions are observed for isotopic distributions of all other molecular ions, regardless of the charge state. Importantly, the anomalously high $M+1$ isotopolog is also present in the isotopic distribution of $V_{10}O_{26}^{2-}$ ion (*vide infra*).

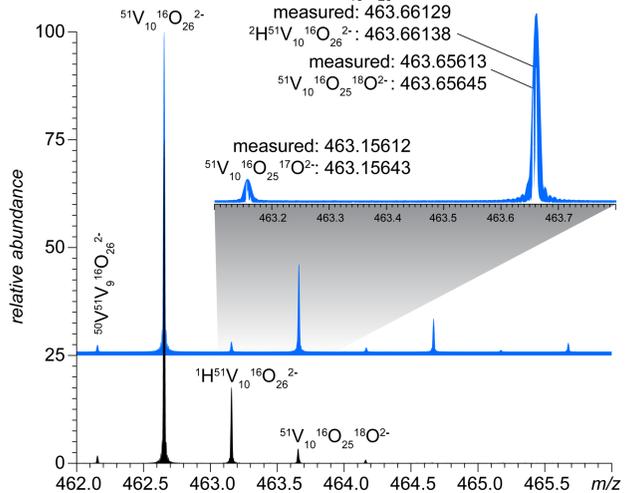
Oxygen extraction from decavanadate occurs in the gas phase and critically depends on the presence of hydrogen atoms.



Left: MS/MS analysis of CID pathways of several canonical decavanadate ions suggests that the oxygen-deficient species are produced in the gas phase. The oxygen loss proceeds via elimination of H_2O and (to a lesser extent) OH . Note that both $H_5V_{10}O_{26}^{2-}$ and $H_4NaV_{10}O_{26}^{2-}$ undergo a loss of two water molecules, giving rise to $HV_{10}O_{26}^{-}$ and $NaV_{10}O_{26}^{2-}$ respectively, while the $V_{10}O_{26}^{2-}$ fragment is only present in the CID mass spectrum of $H_5V_{10}O_{26}^{2-}$. We also note that under identical conditions dissociation of $H_4V_{10}O_{26}^{2-}$ is more efficient compared to $H_5V_{10}O_{26}^{2-}$, explaining high $V_{10}O_{26}^{2-}/HV_{10}O_{26}^{-}$ abundance ratio in MS1.

In contrast to the partial metal reduction within the transient $V_{10}O_{26}^{4-}$ species whose existence has been postulated earlier [4], the charge states of the experimentally observed oxygen-deficient decavanadate species ($V_{10}O_{26}^{2-}$ and $HV_{10}O_{26}^{-}$) indicate that all metal ions are fully oxidized. Furthermore, the ionic abundance ratio for the $V_{10}O_{26}^{2-}/HV_{10}O_{26}^{-}$ pair is very high (ca. 45), while the -2/-1 charge states are nearly equiabundant for “canonical” decavanadate anions. The critical role of hydrogen atoms in oxygen loss from the decavanadate anions in the gas phase clearly reflects formation of oxygen vacancies at oxide surfaces where high-level DFT calculations show that protonation of oxygen atoms weakens interactions with their vanadium neighbors and facilitates oxygen removal [7]. This scenario does not invoke the notion of partial reduction of any of the metal ions and is distinct from the reductive mechanism of oxygen-atom vacancy formation at the surface of polyoxovanadates [8].

Distortions of the isotopic distributions of decavanadate anions reveal partial reduction. The origin of the anomalously high abundance of the $M+1$ isotopolog of the $H_5V_{10}O_{26}^{2-}$ ion in the negative-ion mass spectra of $Na_6V_{10}O_{28}$ and $(NH_4)_6V_{10}O_{28}$ (left) was investigated using high-resolution, high-accuracy MS measurements. The distance between ion peaks $M+1$ and M (the base peak representing $^1H_5^{51}V_{10}^{16}O_{26}^{2-}$) is 1.0071, indicating a difference of one hydrogen atom (mass increase of 1.0078), rather than substitution of a single ^{16}O isotope with ^{17}O (mass increase of 1.0042). The charge balance considerations dictate that one of the metal ions within the $M+1$ species ($^1H_6^{51}V_{10}^{16}O_{26}^{2-}$) is reduced to IV (thus an extra proton is needed in order to keep the overall net charge of this anion at -1). Such satellite species are observed not only for all canonical decavanadate anions (containing the $V_{10}O_{26}$ core), but also for the oxygen-deficient species, such as $V_{10}O_{26}^{2-}$ (*vide supra*).

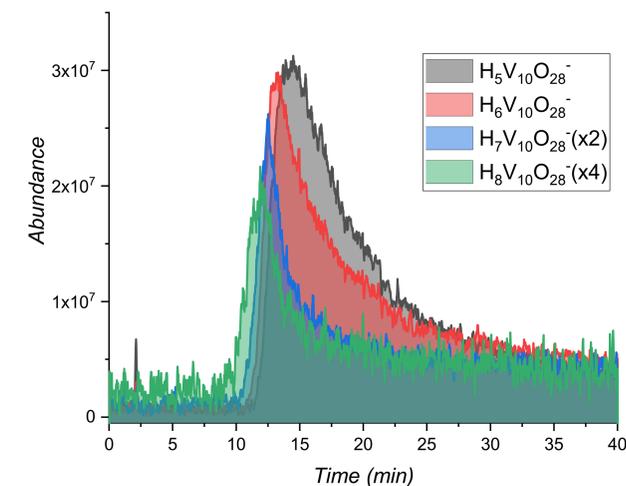


Above: a zoomed view of the isotopic distributions of $V_{10}O_{26}^{2-}$ ions in the decavanadate mass spectra acquired in 1H_2O (black) and 2H_2O (blue). The anomalously high isotopic peak shifts in 2H_2O from $M+1$ to $M+2$, a position consistent with 2H addition to $^{51}V_{10}^{16}O_{26}^{2-}$; the high-resolution MS measurements indicate that the $M+2$ peak contains contributions of both $^2H^51V_{10}^{16}O_{26}^{2-}$ and $^{51}V_{10}^{16}O_{25}^{18}O^{2-}$ ions.

While the negative-ion MS provides unequivocal evidence for partial reduction of decavanadate (the $^1H_6^{51}V_{10}^{16}O_{26}^{2-}$ species is observed even in the presence of 0.5% H_2O_2 in solution), one must be mindful of the possible artifacts caused by ESI MS acting as an electrolytic cell and forcing analyte reduction in the negative ion mode.

IEC-MS provides definitive evidence that partial reduction occurs in solution.

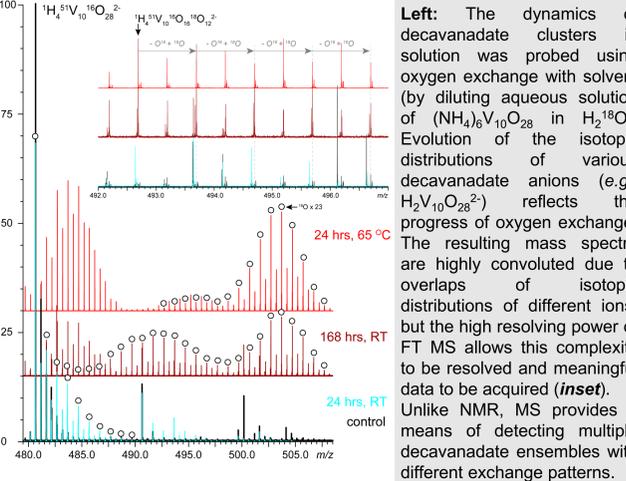
To obtain definitive evidence about the origins of the partially reduced species, Ion Exclusion Chromatography (IEC) was coupled to the MS to perform LC-MS. Initial attempts at IEC analysis of POMs were met with limited success, but the addition of Triethylamine (TEA) to the mobile phase as an ion-pairing agent enabled retention of the sample.



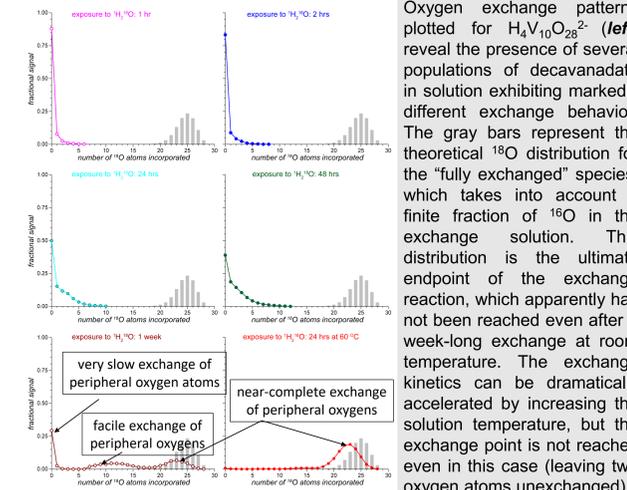
Above: Extracted ion chromatograms (EIC) of the partially reduced Decavanadate species separated on IEC. MS data showed that the distribution of reduced species shifted over the run. The EIC shows that the reduced species elute progressively earlier, and their peaks show less tailing. The demonstrated interaction with the column provides definitive evidence that the reduced species originate in solution.

Despite initial evidence to the contrary, IEC-MS demonstrates that the partially reduced species observed occur naturally in solution. While the mechanism by which they come about is not understood, they likely play a significant role in the solution phase chemistry of decavanadate. Understanding the nature of these reduced species furthers our understanding of the properties of POMs in solution.

$^{16}O/^{18}O$ Exchange reveals complex decavanadate dynamics in solution.



Left: The dynamics of decavanadate clusters in solution was probed using oxygen exchange with solvent (by diluting aqueous solution of $(NH_4)_6V_{10}O_{28}$ in $H_2^{18}O$). Evolution of the isotopic distributions of various decavanadate anions (e.g., $H_2V_{10}O_{26}^{2-}$) reflects the progress of oxygen exchange. The resulting mass spectra are highly convoluted due to overlaps of isotopic distributions of different ions, but the high resolving power of FT MS allows this complexity to be resolved and meaningful data to be acquired (inset). Unlike NMR, MS provides a means of detecting multiple decavanadate ensembles with different exchange patterns.



Oxygen exchange patterns plotted for $H_4V_{10}O_{26}^{2-}$ (left) reveal the presence of several populations of decavanadate in solution exhibiting markedly different exchange behavior. The gray bars represent the theoretical ^{18}O distribution for the “fully exchanged” species, which takes into account a finite fraction of ^{18}O in the exchange solution. This distribution is the ultimate endpoint of the exchange reaction, which apparently has not been reached even after a week-long exchange at room temperature. The exchange kinetics can be dramatically accelerated by increasing the solution temperature, but the exchange point is not reached even in this case (leaving two oxygen atoms unexchanged).

The extremely slow exchange of two (out of twenty-eight) oxygen atoms in decavanadate observed in this work is in excellent agreement with the previously reported ^{17}O NMR measurements for the extremely slow exchange of the two “core” oxygen atoms (purple in the diagram below) of decaniobate [5, 9]. The MS data provide clear evidence that oxygen exchange within decavanadate is not a monotonic process, but rather proceeds through several distinct pathways and involves at least two transiently populated metastable intermediate structures. We propose that the observed exchange patterns reflect the properties of metastable decavanadate structures whose existence was postulated previously [5, 6].



Conclusions

Owing to its ability to resolve minute mass differences, high-resolution ESI MS is a powerful (although currently underappreciated) tool for characterization of structure and dynamics of polyoxometalates (POMs) both in solution and in the gas phase. This characterization is easily supplemented by an HPLC to enable pre-MS speciation of POMs. Wider utilization of this analytical tool will undoubtedly catalyze further progress in the field of POM chemistry by enabling studies that are beyond the reach of the “standard” analytical toolbox typically employed in the studies of POMs.

References

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