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ARTICLE TYPE

The solution chemistry and reactivity of lacunary Keggin silicotungstates monitored in real-time by a combination of mass spectrometry and electrochemistry

Qiaodi Jia, Jie Cao*, Yunpeng Duan and Changwen Hu*

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ABSTRACT: The solution chemistry of a series of mono-, di- and trilacunary Keggin silicotungstates was investigated by electrospray ionization mass spectrometry (ESI-MS) and general electrospray features especially for lacunary POMs were summarized. The reactions of vanadium-incorporation into the lacunary structures were successfully monitored in real-time by a combination of ESI-MS and differential pulse voltammetry (DPV). It was found that all the reactions took place instantaneously and that a subtle speciation change occurred at prolonged reaction times for the pair of reactants, monovacant silicotungstate and sodium metavanadate, suggesting a conversion of mono- to divanadium substituted derivatives. This was shown to result from a solution process, not an ESI-induced reaction, by DPV measurement. The relative stabilities of the V-substituted products was assessed in both solution and gas phases.

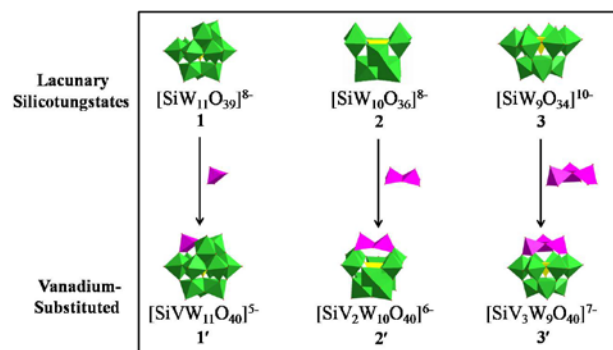
Introduction

Lacunary polyoxometalates (LPOMs), obtained by removing one or more of the MO units from the fully occupied POMs, $[XM^{VI}_{12}O_{40}]^{n-}$ (where X is the heteroatom and M is the addenda atom), giving rise to mono-, di- and trilacunary POMs, $[XM^{VI}_{11}O_{39}]^{(n+4)-}$, $[XM^{VI}_{10}O_{36}]^{(n+4)-}$ and $[XM^{VI}_9O_{34}]^{(n+6)-}$, respectively, represent an important class of compounds due to their unique structural and chemical properties.¹ LPOMs possess reactive nucleophilic polyoxyoxygenated sites that can be readily functionalized, and so they can act as inorganic ligands to incorporate transition metal ions, resulting in products with large structural and compositional versatility and a manifold of properties applicable to catalysis, magnetism, medicine, and material sciences.²

Despite the ever increasing interest in synthesis of new POM architectures based on LPOMs,^{3,4} the investigation of reactive LPOMs in terms of intricate assembly equilibria, solution speciation and stability, still represents a great challenge important for the success of the synthetic strategies and therefore has drawn much attention in recent years.^{5,6} Electrospray ionization mass spectrometry (ESI-MS) has emerged as a powerful tool to characterize a range of stable polyoxoanions^{7,8} and to identify reactive POM building blocks in synthetic media.⁹⁻¹² This approach shows advantages over conventional spectroscopic techniques such as NMR in terms of high sensitivity and wide applicability with no limitation of molecular symmetry and paramagnetism.¹³ Although the complex electrospray behavior of POMs¹⁴⁻¹⁶ has been well documented, a systematic study of mass spectrometric behavior, solution

chemistry and reactivity of LPOMs has yet to appear. This may also provide insight into the intermediates relevant to the formation mechanisms of larger and more complex clusters.

We present here the first systematic investigation of the solution chemistry of a family of lacunary Keggin-type silicotungstates, namely mono-, di- and trivacant species with the formula of $[SiW_{11}O_{39}]^{8-}$ (**1**), $[SiW_{10}O_{36}]^{8-}$ (**2**) and $[SiW_9O_{34}]^{10-}$ (**3**), respectively, and their reactions with sodium metavanadate monitored in real-time by a combination of mass spectrometry and electrochemistry (Scheme 1). This study is an extension of our previous studies of the solution behavior and gas-phase dissociation chemistry of a series of complete POMs with Keggin and Dawson structures.^{17,18}



Scheme 1. Overview of the Keggin clusters studied and the relationship between the lacunary and vanadium-substituted species observed via electrospray mass spectrometry. The $\{WO_6\}$ moieties occupy the green octahedra, the $\{SiO_4\}$ groups are

shown by internal yellow tetrahedra, and the substituted vanadium is represented by purple square-pyramidal geometry.

Results and Discussion

Solution chemistry of lacunary Keggin silicotungstates

The negative-ion ESI mass spectra of alkali metal salts of **1**, **2** and **3** in water (Figs. 1a, 2a, 3a and Table 1 (Supporting Information)) showed a high degree of cationization and dehydration/hydration, indicated by peaks for $[\text{NaH}_3\text{SiW}_{11}\text{O}_{39}]^{4-}$ (m/z 675, 80%), $[\text{KH}_3\text{SiW}_{11}\text{O}_{39}]^{4-}$ (m/z 679, 50%), $[\text{NaH}_4\text{SiW}_{11}\text{O}_{39}]^{3-}$ (m/z 900, 100%) and $[\text{NaKH}_3\text{SiW}_{11}\text{O}_{39}]^{3-}$ (m/z 913, 80%) for **1**, $[\text{K}_2\text{H}_3\text{SiW}_{10}\text{O}_{36}(\text{H}_2\text{O})]^{3-}$ (m/z 847, 100%), $[\text{KH}_4\text{SiW}_{10}\text{O}_{36}]^{2-}$ (m/z 829, 80%) for **2**, $[\text{SiW}_9\text{O}_{30}]^{2-}$ (m/z 1082, 100%), $[\text{NaSiW}_9\text{O}_{31}]^{3-}$ (m/z 734, 80%), $[\text{HSiW}_9\text{O}_{31}]^{3-}$ (m/z 727, 70%), $[\text{NaHSiW}_9\text{O}_{31}]^{2-}$ (m/z 1102, 60%), $[\text{Na}_2\text{SiW}_9\text{O}_{31}]^{2-}$ (m/z 1113, 60%) and $[\text{H}_4\text{KS iW}_9\text{O}_{33}]^{3-}$ (m/z 751, 40%) for **3**, respectively, as a result of (i) ion pairing leading to ion clusters, comprising multiply charged polyoxoanions and different numbers and types of counter cations and (ii) multiple protonation accompanied by either a loss or an addition of water on the cluster framework during ESI, which can effectively lower the charges of the bare lacunary clusters. A notable mass spectrometric feature of LPOMs is the presence of abundant protonated and/or mixed protonated/metalated molecular ions and the absence of bare polyanions that do not contain any $\text{H}^+/\text{K}^+/\text{Na}^+$ in aqueous solution, consistent with the ^{31}P NMR of lacunary analogue $[\text{PW}_{11}\text{O}_{39}]^{7-}$ showing that it existed as $[\text{PW}_{11}\text{O}_{36}(\text{OH})_3]^{4-}$ in solution.^{21,22} The protonation of the terminal oxygen atoms at vacant sites resulting in hydroxo ligands is vital for both the formation of extended architectures and the subsequent dehydration/hydration reactions during ESI, leading to variable oxygen-content adducts, e.g. $[\text{SiW}_9\text{O}_{30}]^{2-} + 4\text{H}^+ \rightarrow [\text{SiW}_9\text{O}_{30}]^{2-} + 4\text{H}_2\text{O}$; $[\text{SiW}_{10}\text{O}_{36}]^{8-} + 2\text{K}^+ + 3\text{H}^+ + x\text{H}_2\text{O} \rightarrow [\text{K}_2\text{H}_3\text{SiW}_{10}\text{O}_{36}(\text{H}_2\text{O})_x]^{3-}$ ($x = 0, 1$); $[\text{SiW}_9\text{O}_{34}]^{10-} + \text{Na}^+ + 6\text{H}^+ \rightarrow [\text{NaSiW}_9\text{O}_{31}]^{3-} + 3\text{H}_2\text{O}$, etc. Moreover, this result may demonstrate as to why LPOMs are particularly active in a humid

time intervals ((b) 0 h, (c) 2 h, (d) 24 h) at room temperature, and (e) ESI-MS spectrum of re-dissolved precipitate **1'** in water. The corresponding solution color was shown beside each spectrum.

atmosphere and why the protonated forms of (L)POMs are essentially the catalytically active species in the oxidation of organic compounds.²³ These unique MS feature can best reflect the structural nature of LPOMs, which are intrinsically less stable than a complete POM in terms of having more negative charges resulting from a formal removal of the positively charged $[(\text{M}^{\text{VI}}\text{O})_n]^{4n+}$ units and higher basicity due to more negative charges and the exposure of more terminal oxo ligands that presumably act as nucleophiles to bind p-, d-, and f-block metal ions or protons from various sources. The complex electrospray behaviors of LPOMs is a diagnostic sign for this particular type of POM in aqueous solution. As a comparison, we have also examined the mass spectrum of the TBA^+ salt of **2** in CH_3CN (Fig. 4a) and found out that protonation/dehydration is inevitable, even in the pure organic media. Well-defined spectra with limited speciation related to the accessible cationated states of the intact cluster demonstrated the advantages of ion-exchange to TBA^+ (or other organic amine cations), a useful strategy for sample pretreatment prior to MS analysis.²⁴ However, this approach may not be applicable to all POM systems, in particular for those of high nucleicity that are vulnerable to such a cation-exchange process.^{25,26}

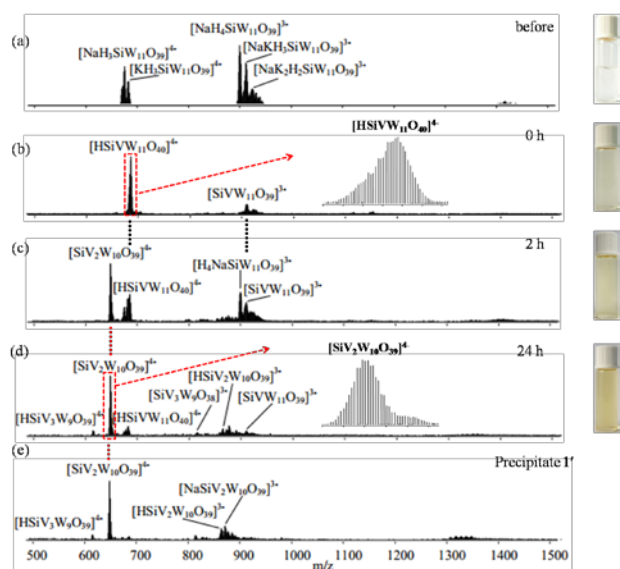


Figure 1. Real-time ESI-MS monitoring of the reaction mixture **1** comprising of **1** (a) and equivalent amounts of NaVO_3 at different

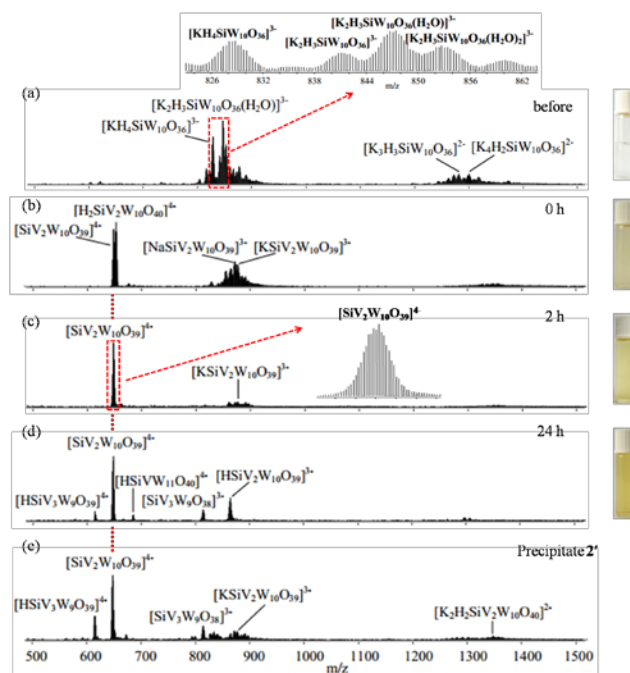


Figure 2. Real-time ESI-MS monitoring of the reaction mixture **2** comprising of **2** (a) and equivalent amounts of NaVO_3 at different time intervals ((b) 0 h, (c) 2 h, (d) 24 h) at room temperature, and (e) ESI-MS spectrum of re-dissolved precipitate **2'** in water. The corresponding solution color was shown beside each spectrum.

Bonchio et al.¹⁵ also reported the intriguing concentration-dependent electrospray behavior of lacunary Keggin-type polyoxotungstates $\alpha\text{-}[\text{XW}_{11}\text{O}_{39}]^p$ ($\text{X} = \text{Si}, \text{P}$) species that readily underwent ESI-induced structural rearrangements into the

saturated W_{12} -containing species $[PW_{12}O_{40}]^{3-}$ (m/z 959, 100%) and the mono-nuclear fragment $[HWO_4]^-$ (m/z 249, 30%) whereas only less than 20% of total ion intensity corresponding to the original W_{11} precursor as $[Li_4HPW_{11}O_{39}]^{2-}$ and $[Li_3HPW_{11}O_{39}]^{3-}$ (m/z 1353 and 900, 5% and 15%) by spraying a dilute solution (0.02 mM) of $Li_7PW_{11}O_{39}$. Noticeably, this particular chemistry only prevailed at low concentrations in their experiment. However, our results showed no resemblance to theirs, even though our concentration regime (ca. 10^{-6} M) is about an order of magnitude lower than theirs. The role of a cation, which is the only source attributed to the disagreement between us, deserves to be further explored in future work. Despite the different behaviors observed by Bonchio group and ourselves, our results agree well with those reported by Ma et al.¹⁴ about the ESI-MS analysis of two lacunary POMs with Keggin and Dawson structures, $Na_7[PW_{11}O_{39}]$ and $K_{10}[P_2W_{17}O_{61}]$, which displayed anions based on $[PW_{11}O_{37}]^{3-}$, $[P_2W_{17}O_{59}]^{6-}$ and $[P_2W_{17}O_{58}]^{4-}$, presumably formed via protonation/dehydration during ESI from their respective precursor ions $[PW_{11}O_{39}]^{7-}$ and $[P_2W_{17}O_{61}]^{10-}$, by spraying of ca. 10^{-4} M aqueous solutions of $Na_7[PW_{11}O_{39}]$ and $K_{10}[P_2W_{17}O_{61}]$, respectively.

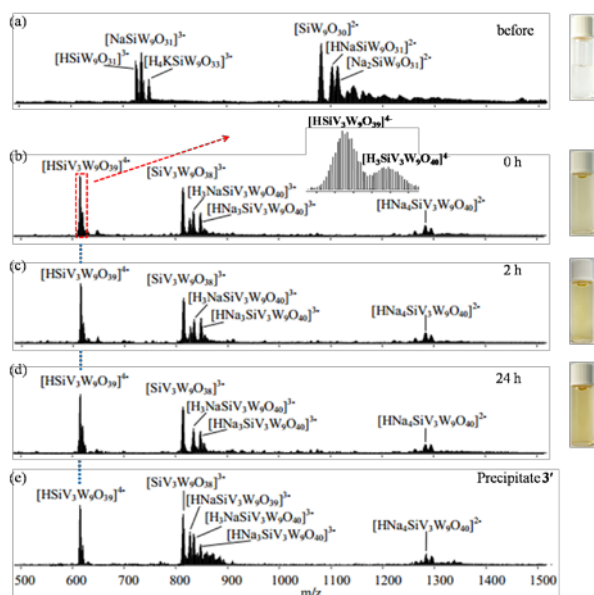


Figure 3. Real-time ESI-MS monitoring of the reaction mixture 3 comprising of 3 (a) and equivalent amounts of $NaVO_3$ at different time intervals ((b) 0 h, (c) 2 h, (d) 24 h) at room temperature, and (e) ESI-MS spectrum of re-dissolved precipitate 3' in water. The corresponding solution color was shown beside each spectrum.

Considering that the structural integrity of a lacunary complex is pH dependent, the solution stability of **1**, **2** and **3** upon standing time was examined while keeping the respective pH values constantly (6.4 for **1**, 6.9 for **2** and 8.9 for **3**) (Fig. S1 (Supporting Information)). It can be seen that **1** is quite stable in solution. However, **2** converts slowly into **1**, while **3** is the least stable species, rapidly changing into **1** (to a greater extent) and **2** (to a lesser extent), the transformations approach completion after a long standing time. This observation indicates the possibility that diverse final structures may result from LPOMs as the starting materials.

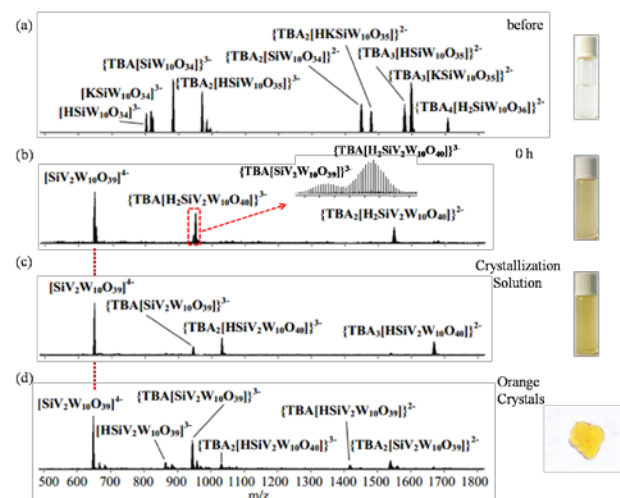
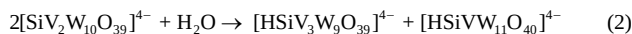
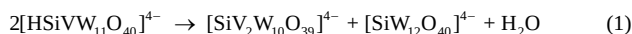


Figure 4. Real-time ESI-MS monitoring of the reaction mixture 4 comprising of 4 (a) and equivalent amounts of $NaVO_3$ at different time intervals ((b) 0 h, (c) crystallization solution) at room temperature, and (d) ESI-MS spectrum of re-dissolved precipitate 4' in acetonitrile. The corresponding solution color was shown beside each spectrum.

Direct detection of the incorporation of VO_3^{3-} units into the lacunary sites of POM framework and chemical transformation of the V-substituted products

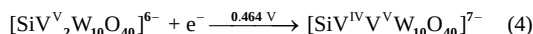
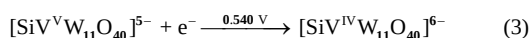
We first monitored the incorporation of vanadium into LPOM's framework, using 1 mM aqueous solutions of alkali metal salts of **1**, **2** and **3** at their respective pHs (6.4 for **1**, 6.9 for **2** and 8.9 for **3**). One to three equivalents of sodium metavanadate were added to solutions **1**, **2** and **3**, respectively, and the reactions were monitored as a function of time by ESI-MS. Note that the pHs for the resultant mixed solutions were changed into 6.9, 7.1, 8.5 and kept in the ranges of 6.9 - 6.8, 7.1 - 6.9 and 8.5 - 8.0 for reaction mixture **1**, **2** and **3**, respectively, during the whole reaction course (0 - 24 hour). It can be seen from Figs. 1b-1d, 2b-2d, 3b-3d and Table 2 (Supporting Information) that the vanadium oxide was rapidly incorporated into the lacunary structures with only a slight change of ca. 0.2-0.5 pH units, reaching near to completion in a matter of seconds. However, the corresponding initially formed V-substituted products, namely $[HSiVW_{11}O_{40}]^{4-}$ (m/z 685, 100%) and $[SiVW_{11}O_{39}]^{3-}$ (m/z 908, 10%) for the reaction mixture **1**, $[H_2SiV_2W_{10}O_{40}]^{4-}$ (m/z 652, 100%), $[SiV_2W_{10}O_{39}]^{3-}$ (m/z 648, 95%), $[NaSiV_2W_{10}O_{39}]^{3-}$ (m/z 872, 40%) and $[KSIV_2W_{10}O_{39}]^{3-}$ (m/z 877, 38%) for the reaction mixture **2**, $[HSiV_3W_9O_{38}]^{4-}$ (m/z 615, 100%), $[SiV_3W_9O_{38}]^{3-}$ (m/z 815, 80%), $[NaH_3SiV_3W_9O_{40}]^{3-}$ (m/z 834, 40%), $[Na_3HSiV_3W_9O_{40}]^{3-}$ (m/z 849, 40%) and $[Na_4HSiV_3W_9O_{40}]^{3-}$ (m/z 1285, 12%) for the reaction mixture **3**, arising from protonation and dehydration from the complete substituted precursors, may undergo subtle speciation changes over time until the most stable species is formed. The reformation of $[SiV_2W_{10}O_{39}]^{3-}$ (m/z 648) is clear from the ESI-MS spectra of the mixed solution **1** (Figs. 1c-1d), which show the initial signals corresponding to $[HSiVW_{11}O_{40}]^{4-}$ (m/z 685) and $[SiVW_{11}O_{39}]^{3-}$ (m/z 908), followed by the appearance of a new signal as $[SiV_2W_{10}O_{39}]^{3-}$ (m/z 648), and finally it becomes the dominant species in the final solution. A hydrolytic disproportionation

reaction is proposed to account for the auto-transformation from one to two V-substitution degrees (eq. 1). Special attention was paid to the presence of $[\text{SiV}_{11}\text{O}_{39}]^{8-}$ in the spectrum, rather than $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, due to degradation of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ at the pH of 6.9. The V₃-substituted species is likely to be present in small amounts after 24 hours (eq. 2).



In contrast, this notable speciation change was not observed for the other two reaction mixtures. The precipitates isolated from the corresponding solutions were shown to have the same composition as their mother liquors by redissolving the samples in water and then subjecting them to ESI-MS analysis (Figs. 1e-3e). Interestingly, the V-incorporation reaction was also accompanied by a progressive change of solution color, from colorless to pale yellow once the reaction starts, and from pale yellow to dark yellow as the degree of V-substitution increases.

To preclude the possibility of ESI-induced speciation changes, differential pulse voltammetry (DPV) was employed as a conventional solution characterization method to follow the same reactions as a function of time (Fig. 5), in keeping pace with MS measurements. As expected, the above processes were nicely reproduced by the electrochemical measurements except that the sensitivity was much lower. Voltammograms of equimolar mixtures of **1** and NaVO_3 (Fig. 5a) showed a gradual shift towards more negative reduction potentials, from 0.540 V to 0.464 V, corresponding to one-electron reductions of **1'** and **2'** (eqs. 3 and 4), respectively, being in excellent agreement with those for the $\{\text{PVW}_{11}\}$ and $\{\text{PV}_2\text{W}_{10}\}$ analogues.²⁷ This may also suggest an easy way to synthesize $\{\text{SiV}_2\text{W}_{10}\}$, simply by aging the equimolar mixtures of **1** and NaVO_3 for a certain time at room temperature. The coincidence of MS with DPV data highlights that ESI-MS provides a faithful image of the reaction mixture and that the conversion of **1'** to **2'** is indeed a consequence of a solution process, not an ESI-induced reaction.



Contrary to the solution behavior of **1'**, the disproportionations of **2'** and **3'** are negligible, the presence of a peak located at 0.464 V and 0.200 V corresponds to the one-electron reductions of $[\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{6-}$ (**2'**) to $[\text{SiV}^{\text{IV}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]^{7-}$ and $[\text{SiV}_3\text{W}_9\text{O}_{40}]^{7-}$ (**3'**) to $[\text{SiV}^{\text{IV}}\text{V}_2\text{W}_9\text{O}_{40}]^{8-}$, respectively (Figs. 5b and 5c). The self-consistent peak potentials measured between the reaction mixtures **1** after 2 hours and the reaction mixtures **2** at any reaction time suggest that $[\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{6-}$ (**2'**) is the main species present in the aged reaction solution **1**.

The distinctly different solution stabilities of the three V-substituted products, that is, the anions with even numbers of vanadium atoms, seem to be more stable than those with odd numbers, inspiring us to pursue further their stability order in the gas phase which will reveal their intrinsic structures. $[\text{HSiVW}_{11}\text{O}_{40}]^{4-}$, $[\text{SiV}_2\text{W}_{10}\text{O}_{39}]^{4-}$ and $[\text{HSiV}_3\text{W}_9\text{O}_{39}]^{4-}$ were chosen as the precursors for the energy-variable CID experiments based on their being the major species in the corresponding reaction mixtures and of having the same charges but with

different degrees of V-substitution (Fig. 6). The relative dissociation energies, defined by the point at which half of the isolated parent ion had dissociated, were determined from the plots of relative abundance of the parent ion versus applied collision energy and were to evaluate their relative order of stability.²⁸ The gas-phase relative stabilities decrease in the order

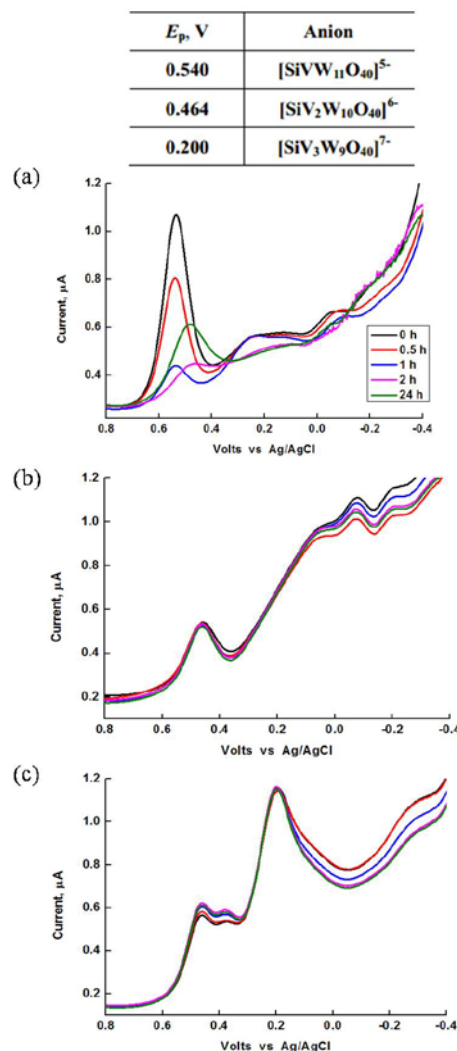


Figure 5. Effect of time on the voltammogram of 0.2 mM reaction solutions 1, 2 and 3 in 1.0 M sodium sulfate at pH = 3.0.

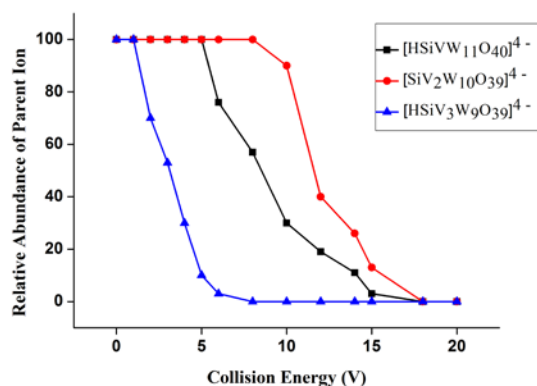


Figure 6. Dissociation curves of (a) $[\text{HSiVW}_{11}\text{O}_{40}]^{4-}$ (black line), (b) $[\text{SiV}_2\text{W}_{10}\text{O}_{39}]^{4-}$ (red line) and (c) $[\text{HSiV}_3\text{W}_9\text{O}_{39}]^{4-}$ (blue line).

$[\text{HSiV}_3\text{W}_9\text{O}_{39}]^{4-} < [\text{HSiVW}_{11}\text{O}_{40}]^{4-} < [\text{SiV}_2\text{W}_{10}\text{O}_{39}]^{4-}$, in keeping with their general stability trend in solution. This result provides a direct correlation between the solution phase and the gas phase.

Finally, the role of solvent in the incorporation reaction was explored by allowing the TBA^+ salt of **2** with the formula $\text{TBA}_4[\gamma\text{-SiW}_{10}\text{O}_{32}(\text{OH})_4]^{4-}$ (**4**) to react with 2 equivalents of sodium metavanadate in 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (reaction mixture **4**). Figure 4b shows that the reaction was also instantaneous like its potassium salt in water, the resulting V_2 -incorporated anions (**2'**) exist in the forms $[\text{SiV}_2\text{W}_{10}\text{O}_{39}]^{4-}$ (m/z 648, 100%), $\{\text{TBA}[\text{H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]\}^{3-}$ (m/z 951, 80%) and $\{\text{TBA}_2[\text{H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]\}^{2-}$ (m/z 1547, 40%), respectively. That **2'** is substantially more stable in the mixed organic solvent than in water, was evidenced by there being no trace of **1'** and **3'** in the solution, illustrating the role of organic solvent in stabilizing the highly charged anion $[\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{6-}$ in solution. After about one week the 1:1 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution of **4** and sodium metavanadate displayed orange crystals whose structure was determined to be $\text{TBA}_4[\gamma\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{29}$ by both powder X-ray diffraction analysis (Fig. S2) and ESI-MS after dissolution in CH_3CN (Fig. 4d), the latter showed mainly two signal envelopes (centered at m/z 648 and 945), assignable to $[\text{SiV}_2\text{W}_{10}\text{O}_{39}]^{4-}$ and $\{\text{TBA}[\text{SiV}_2\text{W}_{10}\text{O}_{39}]\}^{3-}$, respectively. The crystal composition shows the major speciation of its crystallized solution (Fig. 4c), which would not be always meant the same in some cases.³⁰ These results thus link the solid state structure with the solution speciation of re-dissolved crystals in CH_3CN .

Experimental Section

Sample Synthesis

LPOM salts were synthesized by literature procedures as follows: $\text{K}_8[\beta\text{-SiW}_{11}\text{O}_{39}]\cdot 14\text{H}_2\text{O}$ (**1**),¹⁹ $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ (**2**),¹⁹ $\text{TBA}_4[\gamma\text{-H}_4\text{SiW}_{10}\text{O}_{36}]$ (**4**),²⁰ $\text{Na}_9[\beta\text{-HSiW}_9\text{O}_{34}]\cdot 23\text{H}_2\text{O}$ (**3**).¹⁹ All other reagents were obtained from commercial sources and used as received. HPLC grade solvents were generally used.

Experimental Methods

Mass spectra were recorded in the negative mode on an Agilent 6520 Q-TOF LC/MS mass spectrometer. The m/z values refer to the highest peak in the complex isotopic envelope given by W-containing clusters. The dual spray ionization source conditions were as follows: Vcap 3500 V; skimmer 65 V; drying and nebulizer gas N_2 ; nebulizer 300 psi; drying gas flow 10 L/min; drying gas temperature 300 °C; fragmentor 80 V; scan range acquired 50–3000 m/z ; injection volume 0.5 μL . Sample solutions were made to approximately 10^{-6} M in ultra-purified water or acetonitrile and transferred to the electrospray source via an autosampler with a flow rate of 0.2 mL/min. CID experiments were performed using N_2 as the target gas. The desired multiply charged cluster was isolated and subjected to energy-variable CID in which the applied collision energy was raised incrementally. Plots of relative abundance of the parent ion versus applied collision energy were generated with Microcal Origin 5.0 (Microcal Software, Inc., Northampton, MA, USA) to

determine $E_{1/2}$ values. The dissociation curves were measured in triplicate for each cluster. All data were collected and processed using MassHunter (Agilent Technologies (China) Co., Ltd.) workstation software.

Differential pulse voltammetric experiments were performed in a conventional three-electrode system controlled by a CHI 660D electrochemical workstation (Chenhua Instruments, Shanghai, China). The working electrode was a modified glassy carbon electrode (GCE, 3 mm diameter). A saturated Ag/AgCl electrode and a platinum electrode were used as the reference electrode and the counter electrode, respectively. All the measurements were made at ambient temperature (25.0 ± 0.1 °C) in the range of potentials extending from +1.0 V to –0.6 V. The voltammogram for each solution was determined in triplicate.

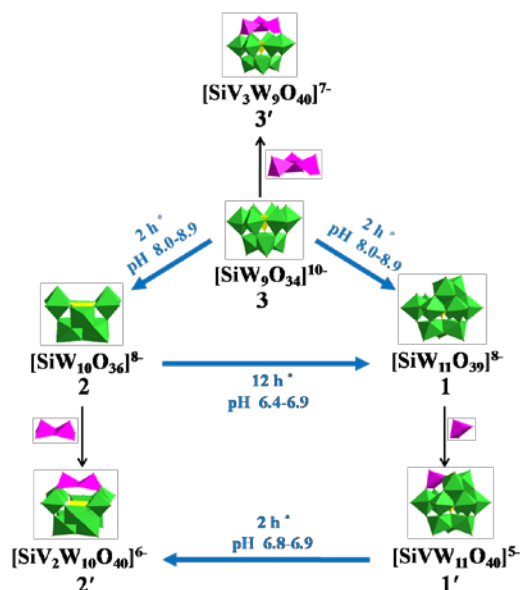
Solution preparation.

1) solutions of LPOMs (**1**, **2**, **3** and **4**) and NaVO_3 were freshly prepared by dissolving 0.01 mmol solute in an adequate solvent (**1**, **2**, **3** in water, **4** in CH_3CN), respectively, timing started at this point for the subsequent stability tests upon standing the solutions at room temperature. An aliquot was removed periodically during the standing course and immediately diluted one-thousand fold for ESI-MS analysis. **2)** Reaction mixtures **1**, **2**, **3** and **4** for ESI-MS were prepared by mixing solutions of LPOM (**1**, **2**, **3** or **4**) and NaVO_3 in stoichiometric ratios (1:1, 1:2 and 1:3 for **1**: NaVO_3 , **2**(**4**): NaVO_3 and **3**: NaVO_3 , respectively), timing started at this point for the subsequent reactivity studies upon standing the mixed solutions at room temperature. An immediate color change of the resulting mixed solutions was observed. An aliquot was removed periodically during the reaction course and immediately diluted by a factor of 10^2 for ESI/MS analysis. Orange precipitates or crystals were grown by slowly evaporation of the solvent of the reaction mixtures at room temperature and their structures were characterized by ESI-MS by redissolving them in an adequate solvent (**1'**, **2'**, **3'** in water, **4'** in CH_3CN). **3).** Reaction mixtures **1**, **2** and **3** for the parallel DPV analyses were prepared by simultaneous addition of solutions of **1** (**2**, or **3**) and NaVO_3 under stoichiometric conditions to 5 mL of 1M Na_2SO_4 solution (pH 3.0) to reach a final concentration of 0.2 mM for the analytes, timing started at this point for the subsequent electrochemical tests upon standing the mixed solutions at room temperature.

Conclusion

In summary, the solution chemistry of a series of mono-, di- and trilacunary Keggin silicotungstates was investigated by ESI-MS and the general electrospray features, particularly for lacunary POMs, were described. The reactions for vanadium-incorporation into the lacunary structures were successfully monitored in real-time by a combination of ESI-MS and DPV. It was found that all the reactions took place instantaneously and that a subtle speciation change occurred at prolonged reaction times for the pair of reactants, monovacant silicotungstate and sodium metavanadate, suggesting a conversion of mono- to divanadium substituted derivatives. This was shown by DPV measurements to be a consequence of a solution process, not an ESI-induced reaction. The relative stability of the V-substituted products in the gas phase provided a direct correlation with that

in the solution phase. The relationship between the lacunary precursors and their V-substituted products are generalized in scheme 2.



Scheme 2. Transformations among 1, 2, 3 and 1', 2', 3' upon standing the corresponding chemically-pure solutions and reaction mixtures containing lacunary silicotungstates and NaVO_3 at constant pH at room temperature (blue arrows). Black arrows link the lacunary precursors with their respective vanadium-substituted derivatives. * values refer to the starting point for the observable changes on the corresponding ESI-MS spectra.

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Notes and references

Key Laboratory of Cluster Science, Ministry of Education of China; Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry, Beijing Institute of Technology, Beijing 100081, People's Republic of China. Fax: +86-10-68912631; Tel: +86-10-68912631; E-mail: jcao@bit.edu.cn; cwlu@bit.edu.cn.

Electronic Supplementary Information (ESI) available: ESI-MS spectra of 1, 2 and 3 upon different standing time; X-ray diffraction pattern of compound 4. See DOI: 10.1039/b000000x/

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Graphical Abstract

The solution chemistry of mono-, di- and trilacunary Keggin silicotungstates was investigated by electrospray mass spectrometry (ESI-MS) and their reactions with sodium metavanadate were monitored in real time by a combination of ESI-MS and differential pulse voltammetry (DPV). A subtle speciation change occurred for the reaction mixture of monovacant silicotungstate and sodium metavanadate at prolonged reaction time, indicating a conversion of mono- to divanadium substituted derivative, which was proved to be a solution process, not an ESI-induced reaction.

