

Acid-Induced, Oxygen-Atom Defect Formation in Reduced Polyoxovanadate-Alkoxide Clusters

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ABSTRACT: Here, we present the first example of acid-induced, oxygen-atom abstraction from the surface of a polyoxometalate cluster. Generation of the oxygen-deficient vanadium oxide, $[V_6O_6(OC_2H_5)_{12}]^{1-}$, was confirmed via independent synthesis. Spectroscopic analysis using infrared and electronic absorption spectroscopies affords resolution of the electronic structure of the oxygen-deficient cluster (oxidation state distribution = $[V^{III}V^{IV}_5]$). This work has direct implications toward the elucidation of possible mechanisms of acid-assisted vacancy formation in bulk transition metal oxides, in particular electron–proton codoping that has recently been described for vanadium oxide (VO_2). Ultimately, these molecular models deepen our understanding of proton-dependent redox chemistry of transition metal oxide surfaces.

Understanding interfacial redox reactions facilitated by transition metal oxides is critically important for the application of these materials in catalysis and energy storage. Over the past 20 years, a range of studies have described the relationship between the surface acid–base chemistry of transition metal oxides and their electronic properties.^{1–4} These contributions summarize the use of proton–electron codoping mechanisms as routes for tuning band edge energies,⁵ mediating phase transitions,^{3,4} and manipulating the surface structure of the material.^{6–9} With particular relevance to the surface dynamics of protons and transition metal oxides, convincing evidence has been provided that these materials participate in proton-coupled electron transfer (PCET).^{10–13} These results include thermodynamic descriptors of these redox processes that shape our thinking about limits of chemical reactivity and energy conversion in these systems.

Despite substantial progress that has been made in this space, an atomic-level understanding of proton–electron codoping interactions at the oxide-terminated surface of transition metal oxides remains elusive. Proton interactions with the surface of a transition metal oxide can range from weak hydrogen bonding contacts, to the formal reduction of M–O bonds to form hydroxide (M–OH) and aqua (M–OH₂) surface ligands.^{3–6,10,13} The bulk structure of transition metal oxides renders distinguishing between these types of metal oxide linkages through surface analysis challenging; while some reports have presented atomic resolution of surface defects through the use of scanning tunneling microscopy (STM), this analytical technique is capable of manipulating the structure of reactive entities at the surface of the material.^{6,14–18} Additionally, the static analysis of samples via STM, following a molecular transformation, renders *in situ* characterization of reaction intermediates nearly impossible.

Toward an atomistic understanding of the interfacial reactivity of transition metal oxides, researchers have turned to homogeneous metal oxide clusters as models for extended

solids. These well-defined assemblies have gained further traction as atomically precise representatives of bulk systems. This is a result of work that has revealed confined electronic communication within transition metal ions that compose bulk metal oxides.^{19–21} Polyoxometalates (POMs), in particular, have been touted as excellent structural models of metal oxides.^{22–26} These clusters are composed of multiple transition metal oxyanions linked together by bridging oxygen atoms.²⁷ With relevance to understanding proton–electron codoping mechanisms in reducible metal oxides, POMs possess rich redox chemistry that is significantly altered in the presence of protons.^{28–30}

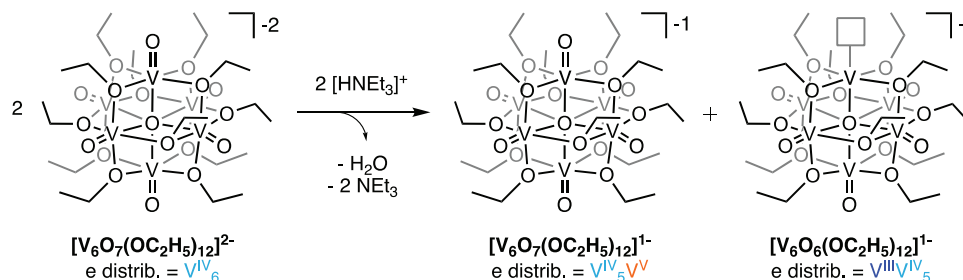
Studies focused on interactions between POMs and protons typically involve acidification of an aqueous solution containing the polyoxoanion; results have predominantly shown cation exchange processes, yielding metal oxide assemblies with one or more bridging hydroxyl ligands.^{31–35} An exception to this is a class of heteropoly “brown” architectures.^{36–39} These six-electron reduced polyoxotungstates are generated via controlled potential electrolysis under acidic conditions, resulting in the formation of three terminal W^{IV} –OH₂ species at a single face of the cluster. It is important to note that without cluster reduction, protons bind to the Keggin ion at the bridging oxide ligands.⁴⁰ These initial reports have inspired several studies demonstrating the use of H-doping in POM scaffolds for hydrogen storage.^{41,42}

Over the past three years, our research team has been studying a class of organofunctionalized vanadium oxide clusters as model systems for reducible metal oxides.^{25,26,43–45}

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Scheme 1. Reactivity of $1\text{-V}_6\text{O}_7^{2-}$ with $[\text{HNEt}_3]\text{BF}_4$ 

The physicochemical properties of polyoxovanadate-alkoxide (POV-alkoxide) clusters, such as their Robin and Day Class II delocalized electronic structure, redox-activity, solubility in organic solvents, and numerous spectroscopic handles (e.g., ^1H NMR, infrared, electronic absorption spectroscopies) make them excellent candidates for *in situ* analysis of the surface reactivity of transition metal oxides.^{46–48} With relevance to understanding the mechanisms of metal oxide mediated reactions, we have reported the formation of oxygen-atom vacancies in these assemblies,^{25,43,44} as well as their oxygen atom transfer reactivity with organic and small molecule substrates.^{25,43–45}

Motivated by recent reports summarizing proton–electron codoping mechanisms for the activation of VO_2 ,^{3,4} as well as a myriad of other studies probing acid-induced surface activation of transition metal oxides,^{5,9,49–52} we became interested in exploring the stoichiometric reactivity of POV-alkoxide clusters with organic acids. Dropwise addition of 1 equiv of triethylammonium tetrafluoroborate ($[\text{HNEt}_3]\text{BF}_4$) to a teal solution of the reduced, dianionic POV-alkoxide cluster, $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{2-}$ ($1\text{-V}_6\text{O}_7^{2-}$; e^- distrib: V^{IV}_6), resulted in a striking color change from teal to brown-green over the course of 5 min (Scheme 1). Analysis of the crude reaction mixture by ^1H NMR spectroscopy revealed a series of paramagnetically shifted and broadened resonances, consistent with the formation of a mixture of products in an approximate 1:1 ratio (Figure 1; ratio of product formation determined by integration of signals corresponding to the distinct cluster species; see Figure S1 for details). Signals located at 26.07 and -2.00 ppm correspond to the protons of the bridging ethoxide

moieties of the monoanionic, POV-ethoxide cluster, $[\text{V}_6\text{O}_7(\text{OC}_2\text{H}_5)_{12}]^{1-}$ ($2\text{-V}_6\text{O}_7^{1-}$).⁵³ The remaining resonances, located at 29.56, 28.53, -1.30 , -2.56 , and -25.66 ppm, suggest formation of an organofunctionalized POV cluster with reduced symmetry as compared to the starting material. Previous results from our laboratory have shown similar patterns of signals corresponding to POV-ethoxide clusters bearing a single, site-differentiated vanadium center.^{26,44} However, these POV-ethoxide clusters (e.g., $[\text{V}_6\text{O}_6(\text{OC}_2\text{H}_5)_{12}]$, $[\text{V}_6\text{O}_6\text{Cl}(\text{OC}_2\text{H}_5)_{12}]^{1-}$) did not possess resonances that matched the unidentified product following acid addition to $1\text{-V}_6\text{O}_7^{2-}$.

To gain further insight into the molecular composition of the products of acid addition to $1\text{-V}_6\text{O}_7^{2-}$, electrospray ionization mass spectrometry (ESI-MS) was employed. Analysis of the resultant spectrum revealed three major signals ($m/z = 958, 961, 974$; ESI-MS(–)ve mode, Figure S2). The first signal, observed at $m/z = 958$, corresponds to complex $2\text{-V}_6\text{O}_7^{1-}$, consistent with ^1H NMR analysis of the crude sample. The remaining signals could be assigned to an oxygen-deficient POV-alkoxide cluster, $[\text{V}_6\text{O}_6(\text{OC}_2\text{H}_5)_{12}]^{1-}$ ($3\text{-V}_6\text{O}_6^{1-}$), plus either a hydronium ion ($m/z = 961$), or an equivalent of methanol ($m/z = 974$).

To confirm formation of complex $3\text{-V}_6\text{O}_6^{1-}$, independent synthesis of the cluster was performed via reduction of the previously reported oxygen-deficient POV-ethoxide cluster, $[\text{V}_6\text{O}_6(\text{OC}_2\text{H}_5)_{12}]^0$ (see Supporting Information for details).⁴⁴ Characterization of the crude product by ESI-MS showed a main signal at $m/z = 974$ (Figure S3). Following workup, analysis of the product by ^1H NMR spectroscopy revealed a set of five paramagnetically shifted resonances, distinct from that of the starting material ($\delta = 29.59, 28.54, -1.28, -2.56$, and -25.60 ppm; Figure 2). These data match those corresponding to the unidentified product of acid addition to $1\text{-V}_6\text{O}_7^{2-}$ (*vide supra*).

The electronic structure of the oxygen-deficient POV-ethoxide cluster was examined by infrared and electronic absorption spectroscopies (Figures S4–S5, Table S1). In the IR spectra, two broad absorption bands centered at 1049 and 951 cm^{-1} were observed and correspond to $\nu(\text{O}_b\text{--C}_2\text{H}_5)$ (O_b = bridging oxo) and $\nu(\text{V=O}_t)$ (O_t = terminal oxo), respectively. These features resemble those reported for the anionic, methoxide-bridged analogue ($[\text{V}_6\text{O}_6(\text{OCH}_3)_{12}]^{1-}$: $1047\text{ cm}^{-1}, 951\text{ cm}^{-1}$), consistent with formation of the reduced ethoxide-bridged species.²⁵ The electronic absorption spectrum presents further evidence for reduction of the hexavanadate core in $3\text{-V}_6\text{O}_6^{1-}$. The starting material, $[\text{V}_6\text{O}_6(\text{OC}_2\text{H}_5)_{12}]^0$, contains two intervalence charge transfer (IVCT) bands at 394 nm ($\epsilon = 2793\text{ M}^{-1}\text{ cm}^{-1}$) and 1000 nm ($\epsilon = 417\text{ M}^{-1}\text{ cm}^{-1}$) associated with an electron transfer from $\text{V}^{\text{IV}} \rightarrow \text{V}^{\text{V}}$ ions within the cluster core.⁴⁴ The lack of these

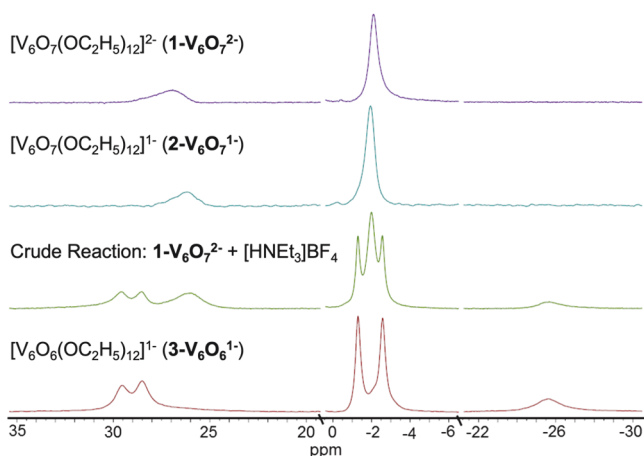
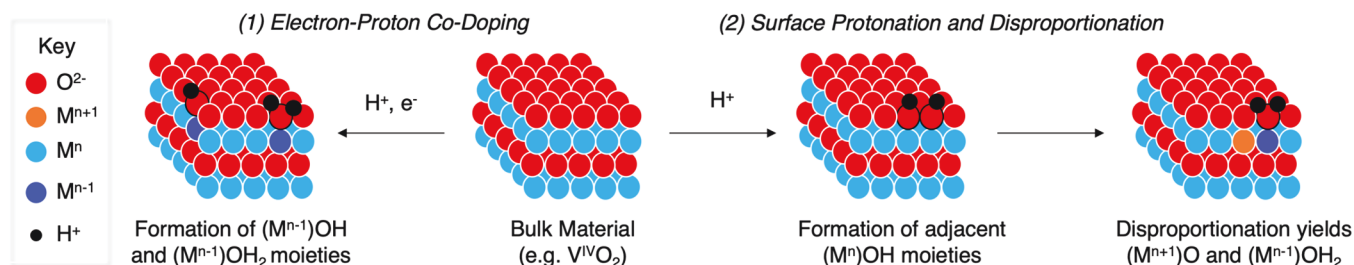


Figure 1. ^1H NMR analysis of acid addition reaction mixture (green), with independently synthesized clusters as references ($1\text{-V}_6\text{O}_7^{2-}$, purple; $2\text{-V}_6\text{O}_7^{1-}$, blue; $3\text{-V}_6\text{O}_6^{1-}$, red) in acetonitrile- d_3 .³⁷

Mechanisms of Acid-induced "M-OH₂" Formation at Reducible Metal Oxide Surfaces

This Work: Acid-induced O-atom Vacancy Formation in POV-alkoxide Clusters

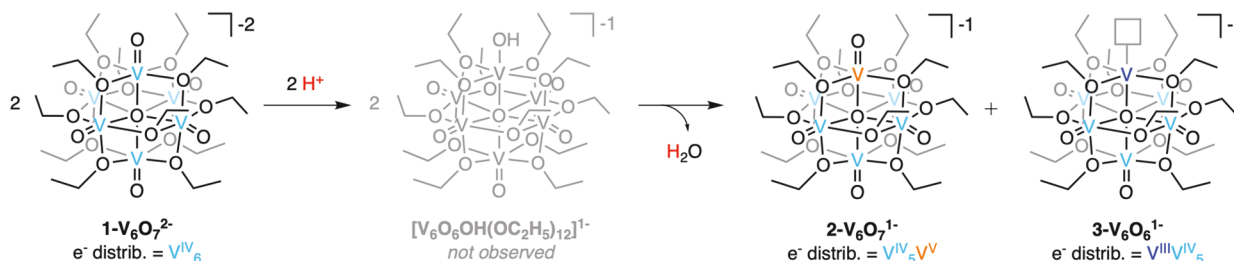


Figure 2. Schematic representation of proton-induced activation on a metal oxide surface (top), and the comparable reactivity observed on a POV-alkoxide cluster (bottom).

IVCT bands observed in the absorption spectra of 3-V₆O₆¹⁻ is consistent with the reduction of the V^V ion in the neutral monovacant cluster to a V^{IV} center. Furthermore, the weak transition observed at 536 nm ($\epsilon = 502 \text{ M}^{-1} \text{ cm}^{-1}$) matches that of previously reported oxygen-deficient polyanions in their most-reduced charge state.^{25,43} Collectively, these characterization techniques suggest an oxidation state distribution of vanadium ions for 3-V₆O₆¹⁻ of (V^{III}V^{IV}₅), matching that reported for the monoanionic POV-methoxide cluster with a single oxygen atom vacancy, [V₆O₆(OCH₃)₁₂]¹⁻.²⁵

The electronic structure of complex 3-V₆O₆¹⁻ is notable in light of recent studies summarizing the reactivity of VO₂ films with acid (Figure 2, Mechanism 1).^{3,4} Upon exposure to acidic media in the presence of an external reductant, formation of an electron–proton codoped material is observed.^{3,4} X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) measurements on the resultant films indicated that V^{IV} ions of the material were partially reduced to V^{III} centers. Additionally, spectroscopic analysis revealed features corresponding to the reduction in bond order of V=O linkages to hydroxide moieties. Similarly, the addition of acid to complex 1-V₆O₇²⁻ results in formation of a surface V^{III} ion and reduction of a vanadyl moiety. However, whereas, in the case of the bulk material, the site-specific structure of reduced vanadium centers is proposed to be V^{III}–OH moieties, characterization of our molecular species suggests the formation of a V^{III}–OH₂ adduct (note: in the case of our POV-ethoxide cluster, the datively bound, surface water ligand is displaced by acetonitrile). The presence of this “vacant” metal cation embedded within the vanadium oxide cluster via acid-induced reduction offers an alternative explanation for the surface site composition following acid–base chemistry on extended solids.

The resultant reduced, oxygen-deficient POV-alkoxide cluster, 3-V₆O₆¹⁻, formed by addition of acid necessitates consideration of the source of reducing equivalents for this oxidation state distribution of vanadium centers (V^{III}V^{IV}₅, *vide*

supra). In the interest of providing a tentative explanation for the formation of 3-V₆O₆¹⁻ in the absence of an external reductant, we pose that protonation of a terminal vanadyl would result in transient formation of a V^{IV}–OH moiety. This hypothesis is supported by a previously reported acid dissociation constant for a molecular vanadium(IV) hydroxyl complex, [(^tBu₂bipy)₂VO(OH)]⁺ (pK_a = 36.7), that would suggest that proton transfer from [HNEt₃]⁺ to a V^{IV}=O moiety of the cluster would be thermodynamically favorable.⁵⁴ Subsequently, the unstable, hydroxide-functionalized POV-ethoxide cluster can undergo rapid disproportionation, resulting in the formation of 2-V₆O₇¹⁻, 3-V₆O₆¹⁻, and H₂O (i.e., V^{IV} → V^V + V^{III}; Figure 2). Indeed, theoretical investigations into the reactivity of vanadium oxides with acid support that the formation of surface V–OH₂ moieties is preferred, given that the subsequent desorption of the H₂O results in the formation of an oxygen-deficient site, which can be stabilized via vacancy-induced lattice relaxation (Figure 2, Mechanism 2).⁵⁵ Likewise, similar mechanisms of acid-induced vacancy formation have been reported for other reducible metal oxides (e.g., TiO₂, ZnO).^{6,8} It is important to note that, at this juncture, this mechanism is speculative and the subject of ongoing investigations in our laboratory.

Here, we present a new route for the formation of an oxygen-deficient Lindqvist cluster via addition of a weak organic acid to the dianionic POV-ethoxide, 1-V₆O₇²⁻. This activity is previously unobserved, being differentiated from other heteropoly “brown” complexes in that the cluster itself contains the electron density required for proton-directed M=O bond activation, where typically this must be added electrochemically during or after cluster synthesis.^{36–39} Overall, our results present an atomic-level model for understanding the physicochemical consequences of acid treatment of redox-active transition metal oxides. The study of atomically precise POV-alkoxides that are soluble in organic solvents enables us to fill fundamental gaps in materials science research, specifically the nature of proton-induced surface

activation via electron–proton codoping mechanisms. Where a multitude of reports have given insight into the physicochemical consequences of codoping bulk transition metal oxides, acquiring sufficient details about the precise activity at a single lattice site remains challenging. By using polynuclear assemblies as a model system for heterogeneous catalysts, we can access the necessary precision to analyze proton interactions with POV-alkoxide clusters.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c03864>.

Materials, experimental procedures, and characterization for all compounds; ^1H NMR and ESI-MS(–)ve spectra of acid addition to $1\text{-V}_6\text{O}_7^{2-}$, ^1H NMR, ESI-MS(–)ve, IR, and electronic absorption spectra of $3\text{-V}_6\text{O}_6^{1-}$ and cyclic voltammogram of $1\text{-V}_6\text{O}_7^{2-}$ (PDF)

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Notes

The authors declare no competing financial interest.

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