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## Site-Specific Studies of CH Bond Activation on Metal Oxide Clusters

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This project attempts to link the acidity or basicity of sites on a metal oxide cluster to their relative reactivity towards CH bonds of simple alkanes. Here we use metal oxide clusters not specifically because they serve as effective catalysts in isolation, but because they are effective model systems to mimic undercoordinated sites on the surface of heterogeneous metal oxide catalysts, supports, and nanoparticles. Computational studies have predicted that, at least for continuous surfaces, the acidity or basicity of sites with bound reactants can be strongly influenced by the presence of additional reactants at nearby sites. Our aim is to provide experimental evidence to test this prediction, using metal oxide clusters that can be produced with atomic precision in large quantities. We also seek to use thermodynamic measurements to evaluate the relative binding affinities of these sites, which offer complementary information to the primary vibrational spectroscopy measurements we have employed. To this end, we have focused on validating our thermochemical measurements by attempting to deduce the binding site of water molecules on organometallic complexes.

### Using Variable-Temperature Ion Traps to Determine Small Molecule Binding Thermodynamics

In collaboration with Prof. Eszter Boros at Stony Brook, we embarked on a series of experiments to evaluate the binding of water to complexes of metal ions with chelating ligands.<sup>1</sup> These complexes have a variety of therapeutic and diagnostic applications in medicine, but also provide us with an opportunity to directly benchmark small molecule binding to Lewis-acidic and Bronsted-basic sites in a well-characterized coordination complex. Examples of such complexes are presented in Figure 1. Here the goal is to determine to which site water is binding by determining the thermodynamics of binding and correlating it to known metal ion hydration numbers. This technique, once validated, could not only be used to survey the thermodynamics of binding of adsorbates to metal oxide clusters, but also to probe the coordination of small molecules to a variety of coordination complexes and bioinorganic supramolecules.

The experimental procedure for these studies is briefly outlined here. Ions are generated in an electrospray ionization source and mass selected by a quadrupole mass filter. They are then stored in a variable-temperature octopole ion trap in the presence of a helium buffer gas with a small partial pressure of water. After residing in the trap for ~500 ms, ions are extracted into a time-of-flight mass spectrometer for mass analysis. If ions adsorb water, new peaks will appear in the mass spectrum corresponding to the uptake of individual water molecules. The ion trap temperature is reduced linearly and mass spectra are recorded in 5-10 K increments. The hydrate peaks in these mass spectra are integrated to give speciation curves as a function of temperature, such as those shown in Figure 1. [Gd(DOTA)]<sup>-</sup> displays an open site for one water molecule coordinated to the metal ion, while [Gd(DO3Apic)]<sup>-</sup> has no open coordination site. As can be seen in Figure 1, the DOTA complex shows single hydration (pink) at substantially higher temperature than does the DO3Apic complex, indicative of a more strongly-bound water to this

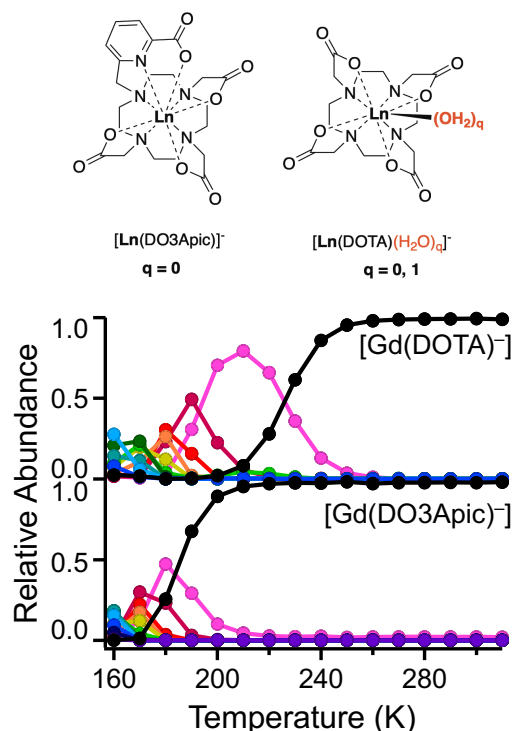


Figure 1: (Top) Two example complexes used in this study, one that can host a single inner-sphere water ligand, and one that can not. (Bottom) Temperature dependent speciation curves for the hydrates. Black denotes unhydrated, pink, singly hydrated, and all other colors, multiply hydrated complexes.

<sup>1</sup> Racow, E. E., Kreinbihl, J. J., Cosby, A. G., Yang, Y., Pandey, A., Boros, E., and Johnson, C. J., "General Approach to Direct Measurement of the Hydration State of Coordination Complexes in the Gas Phase: Variable Temperature Mass Spectrometry," *J. Am. Chem. Soc.*, **141**, 14650-14660 (2019).

complex. We trace this water to the inner-sphere water ligand, while all other water molecules can be attributed to hydration of the ligand itself. Van 't Hoff analysis of these speciation curves shows that this effect is primarily entropic, driven by the ability of the water molecule bound to the metal ion through the oxygen lone pairs to rotate and translate while still bound to the metal. Water is likely bound to the ligand by two hydrogen bonds to neighboring acetate groups, a configuration that results in a more substantial reduction in entropy and thus that occurs at lower temperatures.

This approach is likely to be a general technique to evaluate the single-molecule binding thermodynamics across a range of monometallic and cluster systems, particularly those that are the focus of this project. Upon finishing the development of electrospray methods for metal oxide cluster generation as outlined below, we will be in a position to controllably initiate condensation reactions between metal oxide cluster ions and reactants such as alkanes in a similar way, and probe the products of these reactions by vibrational spectroscopy.

### New Metal Oxide Cluster Preparation Techniques

We have been working to use electrospray ionization to generate metal oxide clusters rather than laser ablation, as we originally planned. This approach integrates much better with our experimental procedure and provides cluster distributions with stoichiometries close to those of bulk metal oxides. Our initial studies have focused on vanadium oxide complexes, which have been extensively studied in solution and the gas phase. We have investigated two approaches to generating clusters, one involving bulk solution phase synthesis, and another in which clusters are generated in situ in the electrospray ionization source. Figure 2 presents early results of one approach, in which we follow a synthesis similar to one that produces larger polyoxovanadates, but stop the reaction at early times and electrospray the raw reaction mixture diluted in methanol. As can be seen in the inset table, this approach produces small clusters stabilized by methoxy ligands, as small as  $V_2O_5(OCH_3)^-$ , as well as smaller clusters lacking methoxy ligands presumably resulting from collisional fragmentation. A second approach involves merely the electrospray of vanadium oxide salts, where cluster formation presumably happens via redox chemistry either in the electrospray tip, or in the nascent droplet before evaporation or ion ejection. Work is ongoing in our laboratory to determine what the mechanisms are underlying this approach, and how they may be harnessed to optimize the generation of cluster stoichiometries of interest.

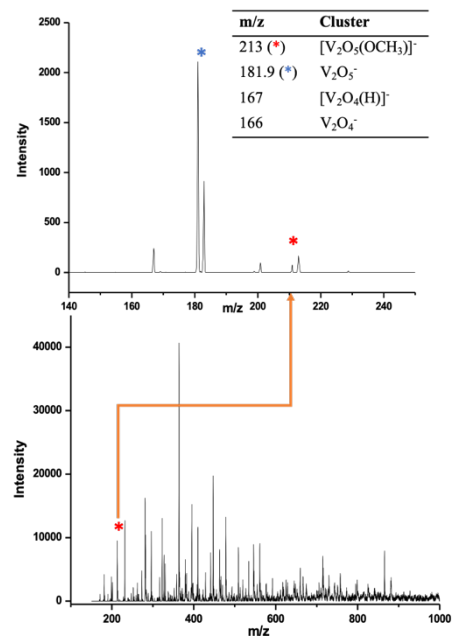


Figure 2: Example mass spectra for electrospray ionization of solution-synthesized vanadium oxide compounds. Above is an expanded view of clusters resulting from collision-induced dissociation. Inset is a table showing assignments of select peaks.

### Impacts on the PI and Supported Students

One student supported by this funding has laid the groundwork for these studies and will graduate in December 2019 with her Ph.D., with a thesis primarily discussing work supported by the ACS PRF. She has presented work funded by this grant at the 2018 ACS Spring National Meeting in New Orleans, where she also had the opportunity to broaden her scientific interests and participate in ACS-organized career development events such as interview training and a discussion of careers for chemists beyond academia. A second student is currently supported by this grant and is continuing the initial work presented here. The development of the variable-temperature ion trap technique discussed above has opened significant new lines of investigation for the PI and has had a major impact on all projects underway in this laboratory. The collaboration with a radiochemist in our department on the lanthanide complexes discussed above has set the stage for fundamental studies of the coordination chemistry of actinide complexes, which show high activity in homogenous reactions but complex mechanisms. Actinide complexes have been shown to have activity towards a host of small molecules of relevance to the petroleum industry, and thus a more thorough understanding of the intermediates and elementary reactions involved in these transformations should guide design of actinide-based catalysts. We expect that the combination of variable-temperature mass spectrometry discussed here and ion-trap based infrared spectroscopy will yield clear insights into these mechanisms.