

## WATER REACTIVITY WITH TUNGSTEN OXIDES: FORMATION OF H<sub>2</sub> FROM W<sub>2</sub>O<sub>y</sub><sup>-</sup> + H<sub>2</sub>O REACTIONS

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In a recent mass spectrometry/photoelectron spectroscopy study on the reactions between W<sub>2</sub>O<sub>y</sub><sup>-</sup> ( $y = 2-6$ ) and water, Jarrold and coworkers (J. Chem. Phys., 130, 12431 2009) observed interesting differences in the reactivity of the different cluster ions. Particularly noteworthy is the observation that the only product with the incorporation of hydrogens is a single peak corresponding to W<sub>2</sub>O<sub>6</sub>H<sub>2</sub><sup>-</sup>. As reactions between metal oxide clusters and small molecules such as water have high potential for catalytic applications, we aim to obtain a mechanistic understanding of this observed reactivity. Using electronic structure calculations, we have identified and characterized multiple modes of reactivity between unsaturated tungsten oxide clusters (W<sub>2</sub>O<sub>y</sub><sup>-</sup> ( $y = 4-6$ )) and water. By calculating the free energy corrected reaction profiles, our results provide an explanation for the formation of W<sub>2</sub>O<sub>6</sub>H<sub>2</sub><sup>-</sup>. We propose a mechanism in which water reacts with a metal oxide cluster and eliminates H<sub>2</sub>. The results from our calculations show that this is nearly a barrierless process for all sub-oxide clusters with the exception of W<sub>2</sub>O<sub>5</sub><sup>-</sup>.