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Gas-phase activation of holmium tetranitrato complexes likely leads to formation of hydroxylated species through the loss of nitric acid, not water splitting

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Background

It has been observed that water can react with activated gas-phase lanthanide tetranitrato complexes ($[Ln(NO_3)_4]^-$) to form a hydroxylated species. These reactions, which are proposed to involve water splitting,[1] are observed for most -- but not all -- of the lanthanides. Thus, study of this system could yield insight into how small changes in electronic structure (through variation of the lanthanide species) influences water-splitting reactions, help guide development of new materials used to convert water to hydrogen using electricity.

The mechanism proposed in the literature[1] is:

(Step 1) $[Ln(NO_3)_4]^- \rightarrow [LnO(NO_3)_3]^- + {}^{\cdot}NO_2$

(Step 2) $[LnO(NO_3)_3]^- + H_2O \rightarrow [LnOH(NO_3)_3]^- + {}^{\cdot}OH$

The purpose of this study is to determine if the reaction mechanism really does involve splitting of water or proceeds through an alternative pathway.

(1) Lucena, A. F. et al. Phys. Chem. Chem. Phys. 2015, 17 (15), 9942–9950, DOI: 10.1039/C5CP00515A.

Methods

We used a combination of mass spectrometry, isotope-labeling, and computational chemistry to elucidate the mechanism of the reaction of water with holmium tetranitrato complexes.

In the mechanism proposed in the literature, all the oxygens in the hydroxylated product ($[LnOH(NO_3)_3]^-$) come from nitrates. We ran the reaction in the mass spectrometer with 18-oxygen-labeled nitrates to test this proposed mechanism.

The results indicated that one of the oxygen must come from water, so the literature mechanism is not correct.

We proposed two new mechanism: one still involving water splitting, and one involving elimination of nitric acid. Our mass spectrometer cannot disinguish between these two mechanisms, so we used computational chemistry to invistigate which was more likely.

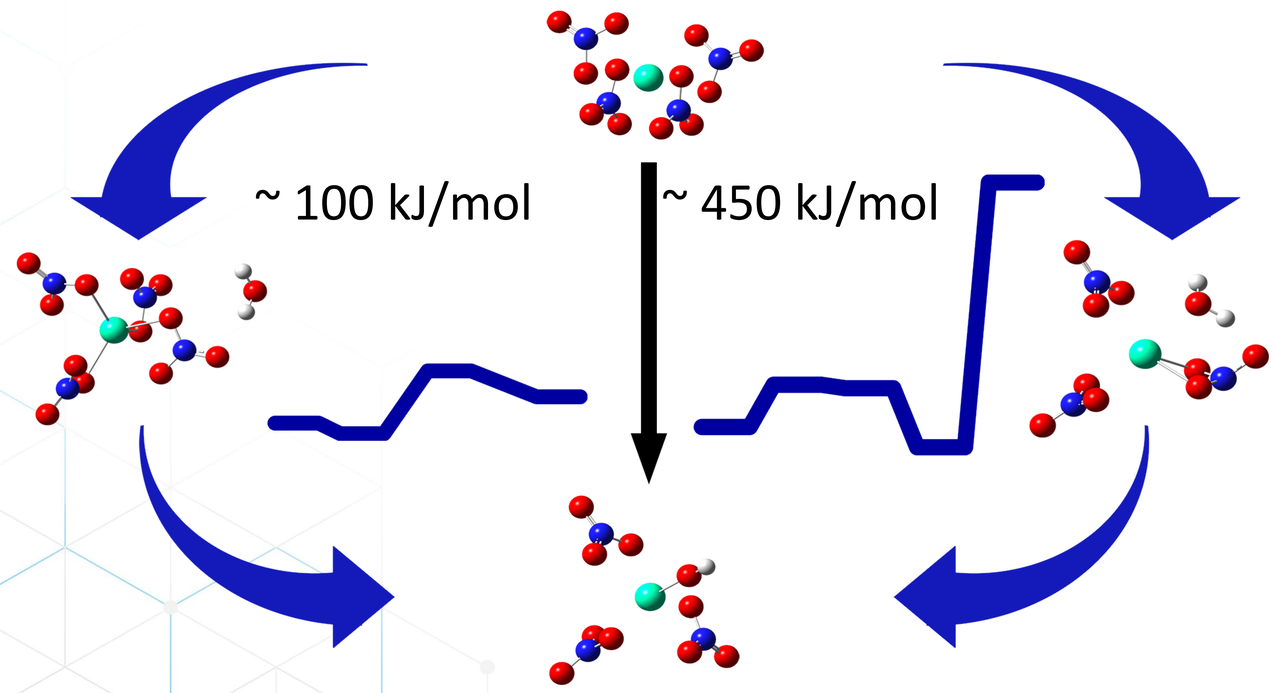
Proposed Mechanism 1: Likely

(Step 1) $[Ln(NO_3)_4]^- + H_2O \rightarrow [LnOH(NO_3)_3]^- + HNO_3$

Proposed Mechanism 2: Unlikely

(Step 1) $[Ln(NO_3)_4]^- \rightarrow [Ln(NO_3)_3]^- + {}^{\cdot}NO_3$

(Step 2) $[Ln(NO_3)_3]^- + H_2O \rightarrow [LnOH(NO_3)_3]^- + {}^{\cdot}H$



JungSoo Kim, Meng Li, Brittany Hodges, and Christopher Zarzana, manuscript submitted

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