

SPECTROSCOPIC CHARACTERIZATION OF REACTIVE INTERMEDIATES IN VARIOUS METAL CATALYSTS

KATHLEEN ANN NICKSON, ETIENNE GARAND, *Department of Chemistry, University of Wisconsin–Madison, Madison, WI, USA.*

In order to improve transition metal catalyst performance, we must first understand the mechanistic features and intermediates in these reactions. Despite great progress in the field, some intermediates can be particularly hard to isolate and investigate. These difficulties can be overcome by forming these intermediates in the gas-phase. Specifically, collision induced dissociation of a precursor creates a vacant ligand position in the precursor which allows for a facile ion-molecule reaction in an ion trap to produce the desired intermediate. These intermediates can then be captured by evaporative quenching of collision complexes and their structures can be probed via cryogenic ion vibrational spectroscopy. In this work, we utilize these gas-phase techniques to focus on two transition metal catalyst systems: a $[\text{Ru}^{II}(\text{bpy})(\text{tpy})(\text{H}_2\text{O})]^{2+}$ water oxidation catalyst as well as two (N-N)PtCl₂ catalysts (N-N= ethylene diamine (en), diamine (NH₃)₂) for C-H activation and functionalization. For the ruthenium water oxidation catalyst, we have formed the elusive oxo intermediate by reacting $[\text{Ru}(\text{bpy})(\text{tpy})]^{2+}$ with O₃ to readily produce $[\text{Ru}(\text{bpy})(\text{tpy})\text{O}]^{2+}$. Interestingly, since the oxo readily forms with ozone but does not with N₂O, this indicates that the spin state of the Ru=O is a triplet. This structure is confirmed by the observation of the Ru=O vibration. For the (N-N)PtCl₂ catalysts, we prepare the sigma-CH intermediates by reacting $[(\text{N-N})\text{PtCl}]^{1+}$ with various alkanes and alkenes such as methane and benzene.