KINETIC AND THERMODYNAMIC STUDIES OF GASEOUS METALLO-ORGANIC CATIONIC COMPLEXES

S. JASON DEE, VANESSA A. CASTLEBERRY, OTSMAR J. VILLARROEL, IVANNA E. LABOREN, SARAH E. FREY and DARRIN J. BELLERT, *Department of Chemistry and Biochemistry, Baylor University, Waco, Texas, 76798*.

The construction of a custom fabricated photodissociation spectrometer permits the determination of thermodynamic properties (activation energies), reaction rates, and mechanistic details of bare metal cation mediated σ-bond activation in the gas phase. Specifically, the products and rates resulting from the unimolecular decomposition of the Ni^+Acetaldehyde adduct are monitored after absorption of a known amount of energy. The two dissociative products which are observed in high yield are Ni^+ and Ni^+CO. The Ni^+CO fragment ion could result from the activation of a C-C σ-bond or from the activation of a C-H σ-bond. The rate constant for the decarbonylation of Ni^+Acetaldehyde was approximately 30 percent greater than that of the rate constant for the decarbonylation of Ni^+Acetone. For the decarbonylation of Ni^+Acetone, there needs to be a methide shift, whereas in the decarbonylation of Ni^+Acetaldehyde one could have C-C insertion followed by an aldhyde H-shift. The rate-limiting step of the decarbonylation process will be discussed.