

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 aldehyde H-shift. The rate-limiting step of the decarbonylation process will be discussed.