ENERGY AND RATE DETERMINATIONS TO ACTIVATE THE C-C σ-BOND OF ACETONE BY GASEOUS NI^+

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A unique application of a custom fabricated photodissociation spectrometer permits the determination of thermodynamic properties (activation energies), reaction rates, and mechanistic details of bare metal cation mediated C-C σ-bond activation in the gas phase. Specifically, the products and rates resulting from the unimolecular decomposition of the Ni^+Acetone (Ni^+Ac) adduct are monitored after absorption of a known amount of energy. The three dissociative products which are observed in high yield are Ni^+, Ni^+CO, and CH3CO$^+$. The latter two fragment ions result from the activation of a C-C σ-bond. It was found that minimally 14 000 cm^{-1} of energy must be deposited into the adduct ion to induce C-C bond breakage. Preliminary results for the Ni^+ activation of the C-C σ-bond of acetone indicate that there are (at least) two low energy reaction coordinates leading to C-C bond breakage. The lower energy pathway emerges from the doublet ground state with an upper limit to the activation energy of 14 000 cm^{-1} and reaction rate $\approx$0.14 molecules/μs. The higher energy path is assumed to be along the quartet reaction coordinate with a minimum activation energy of 18 800 cm^{-1} (relative to the ground state) and a slightly slower reaction rate.