

SINGLE ATOM CATALYTIC CYCLOTRIMERIZATION OF $V(\text{ACETYLENE})_3^+$ STUDIED WITH INFRARED SPECTROSCOPY

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Vanadium cation is studied as a model system for single atom catalysis in the gas phase with infrared photodissociation spectroscopy. Intermediates in the cyclotrimerization of acetylene to form benzene are observed. $V(\text{C}_2\text{H}_2)_n^+$ clusters are produced via laser vaporization of vanadium in a supersonic expansion of argon containing acetylene. Clusters of $V(\text{C}_2\text{H}_2)^+$, $V(\text{C}_2\text{H}_2)_2^+$, and $V(\text{C}_2\text{H}_2)_3^+$ are studied with infrared photodissociation spectroscopy with the aid of argon tagging in the C–H stretching region. These spectra are assigned on the basis of B3LYP computations. $V(\text{C}_2\text{H}_2)^+$ is a three membered metallacycle, where the hydrogens bend away from the vanadium. $V(\text{C}_2\text{H}_2)_2^+$ is a bimetallacycle where both acetylene ligands interact with vanadium symmetrically through their π -bonds in a C_{2v} configuration. The structure of $V(\text{C}_2\text{H}_2)_3^+$ is found to vary with the concentration of acetylene in the supersonic expansion. At low concentrations of acetylene two isomers of $V(\text{C}_2\text{H}_2)_3^+$ are observed, a trimetallacycle, and a bimetallacycle which includes a five membered ring and a three membered ring. As the concentration of acetylene is increased past 5% the trimetallacycle decreases in abundance. Benzene is observed at yet higher concentration of acetylene. An expansion gas consisting of 15% acetylene in argon results in the exclusive formation of $V(\text{Bz})^+$.