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c-C₃H₃⁺ as a Precursor for Aromatic Hydrocarbon Formation

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ABSTRACT to Sigma Xi, 1994

c-C₃H₃⁺ as a Precursor for Aromatic Hydrocarbon Formation

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The C₃H₃⁺ cation has been extensively studied as a precursor ion to the formation of soot in the pyrolysis of fuels and other hydrocarbons. Studies involving soot nucleation in flames point to an ionic mechanism, versus a neutral free radical mechanism, driving the formation of aromatic hydrocarbons. These aromatic hydrocarbons are believed to continue the transformation process from a molecular level to particulate systems to soot aggregates. These studies show that the propargyl C₃H₃⁺ cation is critical to this transformation.

Although the mechanism for the formation of the propargyl cation is not known, it is found to be the dominant ion in fuel-rich hydrocarbon flames. In these types of experiments, two forms of C₃H₃⁺ are observed: i) The reactive linear propargyl cation (l-C₃H₃⁺), and ii) the unreactive cyclopropenyl cation (c-C₃H₃⁺). Because the unreactive cyclopropenyl isomer is the predominate ion formed during pyrolysis (>90%), the reaction barrier for product formation is critical to the ionic mechanism for pyrolysis product formation. Direct observation of the gas-phase reactions of c-C₃H₃⁺ with conjugated dienes has been accomplished using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). This technique permits the determination of both the product distribution and the reaction threshold for these reactions. In addition, deuterium labeling experiments were utilized to postulate a mechanism for the reaction. An ionic model for the gas phase formation of benzene based on a reactive propargyl cation will be presented.

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