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Estimates of the generation of scrap tires produced in the United States are on the order of 2 million tons per year. Recently, pyrolytic recycling of scrap tire (*thermal decomposition in the absence of O₂*) is receiving renewed interest because of its ability to produce hydrocarbon oils. For example, limonene, a C₁₀ aliphatic hydrocarbon is a principle product formed during scrap tire pyrolysis. It has been suggested that the limonene is produced by dimerization of isoprene which is commonly found in tires. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR) was used to analyze the gas-phase reactions of isoprene to investigate the mechanism for aliphatic product formation during tire pyrolysis. It has been determined that isoprene provides a useful model for these reactions and gives a better understanding of the process by which limonene is produced.

c-C₃H₃ AS A PRECURSOR FOR AROMATIC HYDROCARBON FORMATION

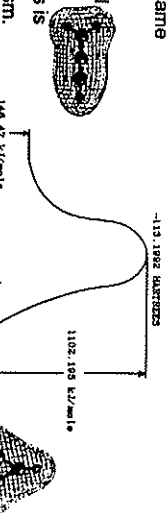
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The propargyl C₃H₃⁺ cation (m/z 39) has been extensively studied as a precursor ion to the formation of soot in the pyrolysis of fuels and other hydrocarbons(1). Studies involving soot nucleation in flames point to an ionic mechanism, versus a neutral 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 (1,2). 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 (1). Studies by Eyerl et al. have involved modeling the soot particle initiation process through reactions of C₃H₃⁺ with acetylene and diacetylene using FT-ICR (3,4,5). Using Fourier transform ion cyclotron resonance (FT-ICR), the gas phase reactions arising during the pyrolysis of hydrocarbons can be modeled.

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⁺)(3,4,5). It is estimated that under flame



conditions that the concentration of the propargyl cation is less than 1% of the total C₃H₃⁺ concentration (2). Therefore, the interconversion between these two isomers is clearly important to the proposed mechanism.

Energy Barrier Considerations. AD

Initial calculation based on Restricted Hartree Fock STO-3G level were performed on the

cyclic and linear forms of C₃H₃⁺ using 18 basis sets. These calculations show heats of

formation of -113.56 Hartrees for the propargyl isomer and -113.62 Hartrees for the cyclic isomer. A additional calculation was performed on a proposed intermediate and resulted in a calculated heat of formation of -113.19 Hartrees (Figure 1). This corresponds to an activation energy of 1102 kJ/mole

(11.43 eV) for rearrangement of the cyclic form to the linear form which is consistent with the literature values. Based on this considerable energy barrier, ions formed from electron impact of a thermal distribution of neutrals should result in a stable population of both isomers.

In order to investigate the reaction barrier existing between the two isomeric forms of C₃H₃⁺, an experiment was performed in which the c-C₃H₃⁺ isomer was isolated and allowed to react with the

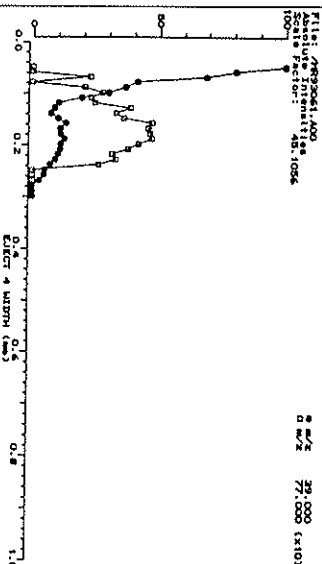


Figure 2. Timeplot showing critical energy required to induce a reaction between c-C₃H₃⁺ and the neutral gas.

the cyclic cation

shows critical energy for the reaction at about .03 ms. The critical energy was determined to be 11 eV, which is consistent with the ab initio calculations discussed above (Figure 2).

The pervasive nature of C₃H₃⁺ suggests that its role in the pyrolysis of fires is consistent with an ionic model. The rapid rate at which it reacts with the small conjugated dienes studied further strengthens the idea of an ionic mechanism driving the formation of products during the pyrolysis process.

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