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Charge exchange reactions of Cycloprophenyl Cation: 43rd ASMS Meeting on Mass Spectrometry and Allied Topics Atlanta, GA. June, 1995.

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Charge Transfer Reactions of the Cyclopropenyl Cation
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INTRODUCTION

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 (1,2,3). 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). These studies show that the propargyl C₃H₃⁺ cation is critical to this transformation.

Studies by Eyley et al. have involved modeling the soot particle initiation process through reactions of C₃H₃⁺ with acetylene and diacetylene using FT-ICR (2,3). 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: 1) The reactive linear propargyl cation (l-C₃H₃⁺) and 2) the unreactive cyclopropenyl cation (c-C₃H₃⁺). Theoretical calculations reported by Wong and Raddom (4) shows a significant activation energy of 97.6 kcal/mole required for rearrangement of the propargyl form to the cyclic form. It is estimated that under flame conditions that the concentration of the propargyl cation is less than 1% of the total C₃H₃⁺ concentration. Therefore, the reactions of the cyclic form is critical to the proposed mechanism.

The scope of the following research centers around developing an understanding of the mechanisms driving the formation of products during the pyrolysis (thermal decomposition in the absence of oxygen) of hydrocarbons, i.e. styrene butadiene rubber (SBR). Among those systems studied using FT-ICR was and 1,3-butadiene which produces C₃H₃⁺ upon electron impact of the neutral target gas. Although this work examines the endohedral charge transfer reactions of cyclopropenyl with small conjugated dienes, the scope of this research centers around developing an understanding of the gas phase reactions of C₃H₃⁺ during the pyrolysis process and the implications of these reactions performed on a large scale.

EXPERIMENTAL

An Ionspec Omega 50 Fourier transform mass spectrometer (FTMS) based on the concept of ion cyclotron resonance was employed for the experiments described in this report. The Omega 50 FTMS instrument uses a Walker Scientific resistive electromagnet which was set with a magnetic field strength of 1.03 T. Samples were introduced through a Varian Series 951 leak valve into a single vacuum chamber. Background pressure was maintained at 8 x 10⁻¹⁰ torr using a Balzers 330 liter/second turbomolecular pump backed by an Alcatel direct drive roughing pump. Pressures were monitored using a Bayard Alpert ionization gauge, with average experimental pressures set between 2.0-3.0 x 10⁻⁹ torr. The temperature was monitored using a calibrated thermocouple attached to the vacuum chamber and the neutral gases were allowed to equilibrate prior to kinetic measurements. Ionization followed a 20 ms electron beam with ion current set between 1.2-1.5 μA and electron energy of 60 eV. Values for the excitation time required for the mass and energy selective partitioning of the molecular ion of butadiene was obtained and compared to the dimensions of the skimmer orifice in the rear trap plate (5). This data was used to calibrate the amplitude of the rf ejection fields used.



Results and Discussion

To study the charge exchange reactions between the cyclopropenyl isomer A stable population of the cyclic isomer of C₃H₃ cation was trapped and thermalized in the FT-ICR mass spectrometer by allowing the more reactive

linear propargyl isomer to react away prior to the isolation of ions of m/z 39. The cyclopropenyl isomer was then allowed to collisionally relax to thermal internal energies by collisions with background neutrals of 1,3-butadiene. These ions were then given increasing amounts of translational energy using resonant rf bursts, and the products were observed. As seen in figure 1, there is no initial intensity of m/z 54 which corresponds to a charge exchange product between the cyclopropenyl cation and the neutral 1,3-butadiene. However, following the resonant acceleration of the ions of m/z 39, the formation of ions of m/z 54 is observed indicating the occurrence of an electron transfer. The empirical threshold was determined to be ca. 6.9 eV. This empirical data was then compared to differences in ionization potential which were calculated at the MP2/6-31G level using Gaussian 92. The results of these calculations are seen in Figure 2. The good correlation between the calculated ionization potentials and the empirical data suggests that in the collision both the neutral 1,3-butadiene and the cyclopropenyl cation are destabilized, resulting in the endothermic charge transfer reaction.

Structure	HF STO-3G	MP2-3-21G	MP2-6-31G*
<chem>C1=CC=C1</chem>	-113.620	-114.327	-115.004
<chem>C1=CC=C1</chem>	-113.760	-114.527	-115.192
<chem>C=CC=C</chem>	-152.808	-153.573	-154.448
<chem>C=CC=C</chem>	-153.017	-154.057	-154.917
<chem>C=CC=C</chem>	-0.140	-0.200	-0.188
<chem>C=CC=C</chem>	-0.209	-0.484	-0.469

Acknowledgements

We would like to express our gratitude for the funding provided by the Small Business Association Grant #SB-BD-92-007-01, the Rease Recycling and Technology Transfer Center, the Department of Chemistry at the University of Northern Iowa, Environmental Programs at the University of Northern Iowa, and the intercollegiate college fund Literature Cited

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5. Beauchamp, J. L.; Armstrong, T. J. *Rev. Sci. Instrum.* 1969, 40, 123-128.

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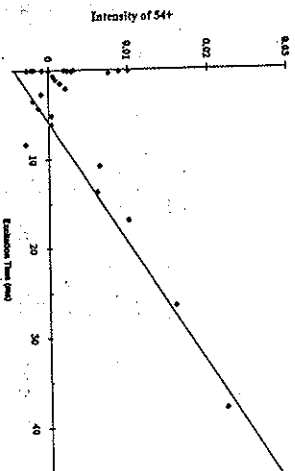
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