Synthesis, Electronic Structure, and Reactivity of the Elusive Phenylethynyl Radical

Ginny Karir[1*], Enrique Mendez-Vega[1], Adrian Portela-Gonzalez[1], Mayank Saraswat[1], Wolfram Sander[1], and Patrick Hemberger[2]

[1]ginny.karir@ruhr-uni-bochum.de, Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany
[2]Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institute, CH-5232 Villigen, Switzerland

In this work, we report the gas-phase generation of the extremely reactive phenylethynyl radical (C_6H_5-CC•) and its reaction with acetylene, using mass spectrometry (MS) and photoion threshold photoelectron spectroscopy (TPES). Flash vacuum pyrolysis (FVP) of the precursors phenylethynyl iodide C_6H_5CC–I and phenylethynyl bromide C_6H_5CC–Br seeded in He were used to generate the highly reactive phenylethynyl radical (C_6H_5-CC•). The elusive radical (m/z 101) and its cation were characterized, along with the H-abstraction product, phenylacetylene C_6H_5CC–H (m/z 102), which was formed in high yields. Pyrolysis at higher temperatures resulted in formation of m/z 100 (C_8H_4) by loss of hydrogen atom from phenylethynyl radical. The potential energy surface of C_8H_4 was explored to identify the thermally formed isomers. The fitting of Frank-Condon simulations of all possible isomers with the experimental TPE spectra confirms the presence of substituted benzynes as well as open chain polyynes. We also investigated the reaction of neat acetylene with the elusive phenylethynyl radical in the gas phase. The reaction results in the formation of an addition product at m/z 126 which can be conferred to a mixture of polyaromatic hydrocarbons (PAHs) with formulae ($C_{10}H_6$).