

PEPICO ANALYSIS OF C₆H₆ ISOMERS PRODUCED THROUGH THE RECOMBINATION OF PROPARGYL (C₃H₃) RADICALS

H.R. HRODMARSSON, *Laboratoire Interuniversitaire des Systèmes Atmosphériques, CNRS UMR 7583, Université Paris-Est Créteil et Université Paris Cité, IPSL, 61 av. Général de Gaulle, 94010 Créteil, France*; **G.A. GARCIA, L. NAHON, L. BOUREHIL**, *Synchrotron SOLEIL, LOrme des Merisiers, St Aubin, BP 48, Gif sur Yvette, France*; **B. GANS, S. BOYE-PERONNE**, *Institut des Sciences Moléculaires dOrsay, CNRS, Université Paris-Saclay, 91405 Orsay, France*; **J.-C. GUILLEMIN**, *Institut des Sciences Chimiques de Rennes, CNRS UMR 6226, Université Rennes 1, 263 Avenue Général Leclerc, 35700 Rennes, France*; **J.-C. LOISON**, *Institut des Sciences Moléculaires, UMR 5255 CNRS—Université de Bordeaux, F—33405 Talence Cedex, France*

The growth of polycyclic aromatic hydrocarbons (PAHs) is initiated by the formation of the first closed-ring species and is the quintessential step in incipient particle formation in aliphatic fuels. Among the most prominent formation pathways is the recombination of two propargyl (C₃H₃) radicals. Experimental validation of the recombination of propargyl radicals and a quantification of the benzene exit channel is challenging due to the complexity of the propargyl self-reaction and the number of possible intermediates and final products. A universal real-time method of detection is necessary to account for multiple C₆H₆ species simultaneously and in real-time. Mass spectrometry coupled to tunable vacuum ultraviolet (VUV) radiation from synchrotron sources has been used successfully in the past for species determination in complex media. Recently, photoionization efficiency curves were used to tentatively infer the formation of benzene molecules from the propargyl self-reaction along with a more clear detection of three of the other structural isomers. A shortcoming of using photoionization efficiency curves for isomer separation is that these curves, particularly for the species in question, look exceedingly similar which makes disentangling a total ion yield comprising multiple isomers problematic when the isomers have ionization offsets close to each other. A more sensitive method of isomer detection in mass spectrometric studies is using the threshold photoelectron spectroscopic method (TPES) which offers a more unique fingerprint to identify molecules in complex media as a TPES is more unique to the molecule than its total ionization efficiency curve. Isomer differentiation is achieved by simultaneously recording the vibronic structures of all isomers present in a single mass signature. In this work, we have employed a microwave discharge flowtube reactor to produce C₃H₃ radicals in a continuous and stable manner. The flowtube is coupled to a synchrotron VUV radiation source at the French national facility SOLEIL, and the mass selected photoelectron spectra were recorded to identify and disentangle all isomeric C₆H₆ reaction products via *i*²PEPICO techniques. Besides the primary product of interest, benzene,

we also detect most of the reaction intermediates formed from head to head, tail to tail collision of the propargyl radicals.