Pyrolysis Mechanism of Cyclopentadienone Revealed by Synchrotron Radiation

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The study of the pyrolysis of complex fuels is carried out in a heated, CW micro-reactor. Reactions are studied in a resistively-heated SiC microtubular (0.66 mm i.d. x 2.5 cm) flash pyrolysis flow reactor from 1000 −1800 K. The standard reactor operating conditions of 280 sccm He flow have been studied by computational fluid dynamics. [International J. Phys. Chem. 2014, (submitted)]. The gas flow has been found to be laminar and the residence time in the reactor is of the order 25 —150 μsec.

The reaction mechanism for the pyrolysis of cyclopentadienone, $C_5H_4=O$, has been studied. Cyclopentadienone is an intermediate in the high temperature oxidation of aromatic fuels and in the thermal cracking of biomass. The molecular structure of $C_5H_4=O$ is known by microwave spectroscopy (J. Phys. Chem. Letts. 2014, 5, 2201-2207); polarized IR spectroscopy has established the vibrational force field (J. Phys. Chem A 2014, 118, 708-718). We have studied the pyrolysis of $C_5H_4=O$ over a 1000 K —1600 K

range. We find two channels: Reaction (1) $C_5H_4=O$ (+ M) → CO + 2 HC≡CH and Reaction (2) $C_5H_4=O$ (+ M) → CO + HC≡C-CH=CH2. The decomposition of $C_5H_4=O$ is

shown to be unimolecular and the products, HC≡CH from (1) and HC≡C-CH=CH2 from (2), were detected in situ by means of tunable synchrotron photoionization mass spectroscopy at LBNL's ALS. The temperature-dependent branching ratio of

[HC≡CH]/[HC≡C-CH=CH2] was established and the ratio of k1/k2 was measured. Separate iPEPICO measurements at the PSI's SLS were used to measure IE($C_5H_4=O$) = 9.408 ± 0.011 eV.

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