

A comprehensive experimental and kinetic modeling study of aromatics combustion

Yuyang Li^{1,*}, Wenhao Yuan², Long Zhao², and Fei Qi¹

1. Key Laboratory for Power Machinery and Engineering of MOE, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

2. National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China

Aromatic fuels are major components of petroleum based transportation fuels and are widely used as major components in surrogate fuels of gasoline, diesel oil and kerosene. Combustion of aromatic fuels are also an ideal system to investigate soot formation mechanism due to the direct formation of abundant polycyclic aromatic hydrocarbons (PAHs) which are key soot precursors. Consequently, understanding the combustion chemistry of aromatic hydrocarbons is crucial for the development of kinetic models of surrogate fuels, and increases our knowledge of the gas molecular growth process in soot formation mechanism. Previous experimental studies have been focused on the oxidation properties of alkylbenzenes and the measurement of the global combustion parameters such as ignition delay times and laminar flame speeds. Only a little comprehensive kinetic modeling work has been proposed for aromatic fuels. A major difficulty is the complex chemical structures of aromatics combustion due to the existence of multiple functional groups in aromatic molecules such as benzene rings and various alkyl sidechains. Experimental breakthroughs in the diagnostics of aromatics combustion are desired for the development of comprehensive kinetic models of aromatic fuels.

In this work, we report the progress in using the synchrotron radiation ultraviolet photoionization mass spectrometry (SVUV-PIMS) [1-2] to investigate the chemical structures of aromatics combustion. Different types of aromatic fuels have been studied, such as mono-alkylbenzenes (toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene), bi-alkylbenzenes (*o*-xylene, *m*-xylene and *p*-xylene) and polycyclic aromatics (tetralin). The wide tunability and high energy resolution of synchrotron VUV light facilitate the isomer-specific detection of different types of intermediates in aromatics combustion, such as radicals, reactive molecules and PAHs (Fig. 1).

Based on the experimental progress, detailed kinetic models of aromatic fuels have been developed. Taking the toluene model [4-6] as an example, the model mainly includes the base C₀-C₄ sub-mechanism and the sub-mechanisms of toluene, benzene, 1,3-cyclopentadiene and PAHs. Among them, the sub-mechanism of benzene, 1,3-cyclopentadiene and the C₀-C₄ sub-mechanism were optimized by validating a variety of experimental data available. The sub-mechanism of PAHs was developed using the experimental and theoretical progresses about PAHs kinetics, as well as the analogous method to reactions with known rate constants. The model was validated against comprehensive experimental datasets of toluene combustion,

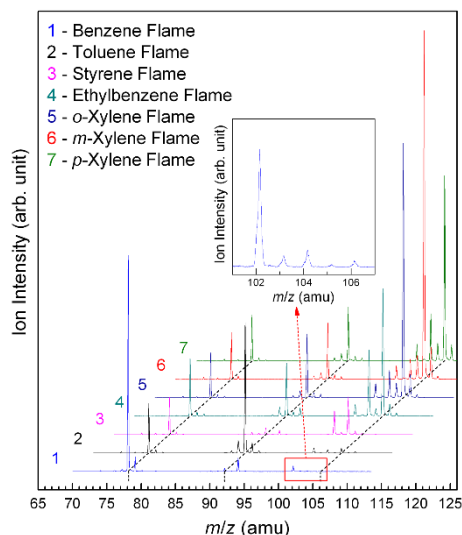


Fig. 1. Mass spectra in seven aromatics flames with molecular weights from 70 to 126 [3].

including the new speciation data of laminar premixed toluene flames and flow reactor toluene pyrolysis using SVUV-PIMS, jet-stirred reactor (JSR) oxidation data, shock tube pyrolysis and oxidation data, flow reactor oxidation data, and global combustion parameters such as ignition delay times and laminar flame speeds. Some model analysis methods were also used to reveal the key reaction pathways in toluene combustion and PAHs formation.

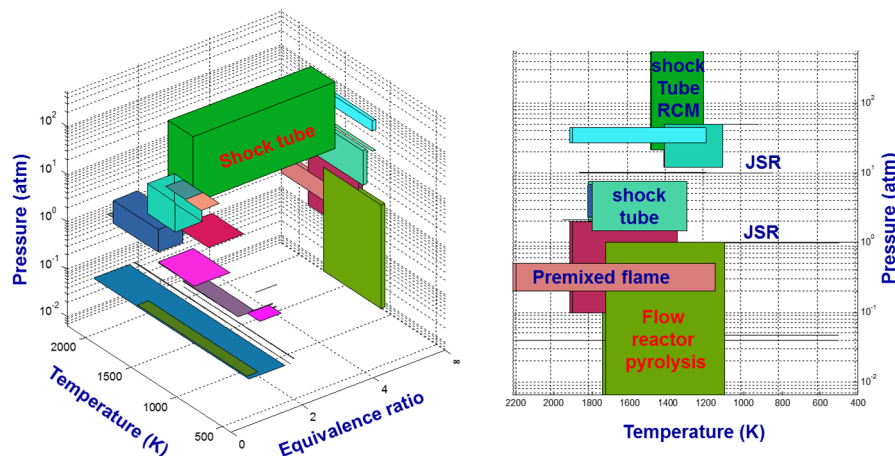


Fig. 2. The validated experimental datasets of the toluene model.

Our work concluded that benzyl-like radicals (e.g. benzyl radical, 1-phenylethyl radical, xylyl radicals, 1-tetralyl radical) play a key role in the decomposition of most aromatic fuels, especially in the pyrolysis and rich premixed flames. Specific benzyl decomposition products, such as fulvenallene and its radical, cyclopentadienyl radical and propargyl radical, were unambiguously detected using SVUV-PIMS, providing solid validation to the benzyl chemistry. At strong oxidation circumstances, many oxidation reactions can occur to produce oxygenated aromatics and hydroperoxides. As the sidechain length increases, the low temperature reactivity of alkylbenzene is also enhanced. In the PAHs formation process, benzyl radical, phenyl radical and cyclopentadienyl radical are demonstrated to be the most important PAH precursors which contribute to the formation of first bicyclic PAH species like indene and naphthalene. In particular, benzyl radical was found to have strong relevance to the formation of PAHs in alkylbenzene flames. Fuel-specific PAH formation pathways were found in the combustion of many aromatic fuels such as *n*-propylbenzene, *o*-xylene and tetralin.

References

- [1] Y. Y. Li, F. Qi, Recent Applications of Synchrotron VUV Photoionization Mass Spectrometry: Insight into Combustion Chemistry, *Accounts of Chemical Research* 43 (2010) 68-78.
- [2] F. Qi, Combustion chemistry probed by synchrotron VUV photoionization mass spectrometry, *Proceedings of the Combustion Institute* 34 (2013) 33-63.
- [3] Y. Y. Li, L. D. Zhang, T. Yuan, K. W. Zhang, J. Z. Yang, B. Yang, F. Qi, C. K. Law, Investigation on fuel-rich premixed flames of monocyclic aromatic hydrocarbons: Part I. Intermediate identification and mass spectrometric analysis, *Combustion and Flame* 157 (2010) 143-154.
- [4] Y. Y. Li, J. H. Cai, L. D. Zhang, T. Yuan, K. W. Zhang, F. Qi, Investigation on Chemical Structures of Premixed Toluene Flames at Low Pressure, *Proceedings of the Combustion Institute* 33 (2011) 593-600.
- [5] W. H. Yuan, Y. Y. Li, P. Dagaut, J. Z. Yang, F. Qi, Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. I. Flow reactor pyrolysis and jet stirred reactor oxidation, *Combustion and Flame* 162 (2015) 3-21.
- [6] W. H. Yuan, Y. Y. Li, P. Dagaut, J. Z. Yang, F. Qi, Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. II. A comprehensive kinetic modeling study, *Combustion and Flame* 162 (2015) 22-40.