Experimental and kinetic modeling study of premixed *o*-xylene flames

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Abstract

Three premixed *o*-xylene/O_2/Ar flames with various equivalence ratios (0.75, 1.00 and 1.79) have been carried out at low pressure (4.0 kPa). Synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) was used for the identification of flame species and the measurement of their mole fractions. A detailed kinetic model consisting of 236 species and 1331 reactions was developed and validated against the measured mole fraction profiles of flame species. According to the rate of production analysis, *o*-xylene mainly decomposes via radical attack reactions, including the H-abstraction and ipso-addition reactions. *o*-Xylyl radical is yielded from the H-abstraction of *o*-xylene, and is a key intermediate leading to the formation of smaller species. In the formation of polycyclic aromatic hydrocarbons (PAHs), the structure of adjacent methyl groups facilitates the formation of bicyclic aromatic species such as indane and 1,4-dihydronaphthalene, and leads to several fuel-specific pathways for the formation of indene and naphthalene in *o*-xylene combustion. Consequently, relatively high concentration levels of small PAHs are produced in *o*-xylene combustion while phenyl and benzyl radicals cannot be sufficiently produced, which explains the comparable sooting tendency of *o*-xylene to those of toluene and ethylbenzene.
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1. Introduction

Aromatic hydrocarbons are important components in petroleum-derived transportation fuels and their surrogates. Their combustion will lead to heavy emissions of polycyclic aromatic hydrocarbons (PAHs) and soot. The two pollutants are known as great threats to environmental security and human health [1–3]. Among numerous aromatics, xylene is the smallest one with multi-substituted alkyl groups which is a common structure in aromatics. The volume fractions of xylene isomers in gasoline can reach up to 10% [4]. With relatively high octane numbers (113 for *o*-xylene, 117.5 for *m*-xylene and 116.4 for *p*-xylene) [5], xylene isomers can significantly improve the anti-knock properties of gasoline. They are also

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widely used as representative multi-substituted aromatic components in surrogates of gasoline, diesel, and jet fuels with the maximum proportion up to 20% [6,7].

Despite the importance of xylene isomers in practical fuels and their surrogates, our knowledge on their combustion chemistry is far from enough. Compared with the situations of benzene and mono-substituted aromatics, previous experimental and theoretical studies on the combustion of xylenes are very limited. For *o*-xylene, only a few experimental studies were performed on its combustion [4,5,8–14], among which the measurements of species profiles are especially insufficient. Up to now, only Gaïl et al. [11] used gas chromatography (GC) to measure the stable species profiles in the atmospheric jet-stirred reactor (JSR) oxidation of *o*-xylene over the temperature range of 900–1400 K at the equivalence ratios (ϕ) of 0.5–1.5. Based on previous experimental results, two kinetic models of *o*-xylene have been developed [4,11]. However, recent investigations [5,14] demonstrated that the insufficient validation of previous *o*-xylene models severely limits their performance on predicting new sets of experimental data. New experimental investigations on measuring chemical structures of *o*-xylene combustion are necessary for the development and validation of more accurate *o*-xylene models.

In this work, three premixed *o*-xylene/O$_2$/Ar flames with equivalence ratios of 0.75, 1.00 and 1.79 were carried out at low pressure to represent the lean, stoichiometric and rich conditions. Synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) were employed to detect flame species and measure their concentrations. A new kinetic model of *o*-xylene was developed and validated against the experimental data, and was used to analyze the decomposition processes of *o*-xylene under different reaction circumstances and the growth process of aromatics under the rich condition.

2. Experimental method

The experiments were performed at the National Synchrotron Radiation Laboratory in Hefei, China. Detailed description of the two beamlines and flame apparatus used in this work can be found elsewhere [15–17]. The flame

conditions are listed in Table 1. The premixed *o*-xylene/O$_2$/Ar flames were studied using SVUV-PIMS at 30 Torr and three equivalence ratios including 0.75, 1.00 and 1.79. To compare the flame chemistry, the pressure, inlet percentage of Ar and cold gas velocity of the inlet mixtures were kept identical in all flames. The flame temperatures were measured by using a 0.1-mm-diameter Pt-6%Rh/Pt-30%Rh thermocouple coated with Y$_2$O$_3$–BeO anti-catalytic ceramic [18], and were then corrected for the radiative heat loss [19] and cooling effects of sampling nozzle [20]. The uncertainties of the maximum flame temperatures were estimated to be within ±100 K. The methodologies of intermediate identification and mole fraction evaluation have been described in detail previously [12,16,21]. The uncertainties of evaluated mole fractions are estimated to be within ±10% for major flame species, ±25% for intermediates with known photoionization cross sections (PICSs), and a factor of 2 for those with estimated PICSs. The PICSs of flame species are available in the online database [22].

3. Kinetic model

In this work, a new kinetic model of *o*-xylene (o-C$_8$H$_{10}$) consisting of 236 species and 1331 reactions was developed from our previous models of toluene and ethylbenzene [23,24]. There are two major parts in this model, representing the decomposition of *o*-xylene and growth of aromatics, respectively. Different classes of reactions, such as the unimolecular decomposition reactions of *o*-xylene and its radicals, the H-abstraction reactions and ipso-addition reaction of *o*-xylene, and the oxidation reactions of *o*-xylene and its radicals, composed the decomposition submechanism of *o*-xylene. Two typical formation pathways of large aromatics like PAHs, i.e. the odd- and even-carbon addition pathways, were taken from our previous models [23,24]. Special growth pathways of aromatics from *o*-xylene were also included, and will be introduced in detail in the following discussion. The reaction mechanism, thermodynamic data and transport data are provided in the Supplementary Materials. The simulation was carried out using the Premixed Laminar Burner-Stabilized Flame model in the CHEMKIN-Pro software [25].

Table 1
Flame conditions.

ϕ	C/O	P/kPa	X_{Fuel}	X_{O_2}	X_{Ar}	V/cm s^{-1}
0.75	0.29	4.0	3.33	46.67	50	35.00
1.00	0.38	4.0	4.35	45.65	50	35.00
1.79	0.68	4.0	7.27	42.73	50	35.00

Note: X_i is the inlet mole fraction of species i; V is the flow velocity of inlet mixture at 300 K.