A comprehensive experimental and kinetic modeling study of ethylbenzene combustion

Wenhao Yuan [a,b], Yuyang Li [c,*], Gaëlle Pengloan [b], Casmir Togbé [b], Philippe Dagaut [b,*], Fei Qi [c]

[a] State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China
[b] C.N.R.S.-I.N.S.I.S., Institut de Combustion, Aérothermique, Réactivité et Environnement, 1C, Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France
[c] Key Laboratory for Power Machinery and Engineering of MOE, Shanghai Jiao Tong University, Shanghai 200240, PR China

ABSTRACT

The flow reactor pyrolysis and jet-stirred reactor (JSR) oxidation of ethylbenzene are investigated in this work. The flow reactor pyrolysis is studied at pressures of 0.04, 0.2, and 1.0 atm and temperatures from 850 to 1500 K using synchrotron vacuum ultraviolet photoionization mass spectrometry. The jet-stirred reactor oxidation is studied at 1 atm with three equivalence ratios ($\phi = 0.5$, 1.0, and 1.5) and at 10 atm with the equivalence ratio of 1.0, using gas chromatography and Fourier transform infrared spectroscopy for mole fractions measurements. A detailed kinetic model of ethylbenzene pyrolysis and oxidation is developed by extending our recently reported oxidation models for toluene and styrene, and is validated on the new experimental data reported here. The benzyl radical and styrene are demonstrated to be the most important intermediates in both the pyrolysis and oxidation of ethylbenzene. For the JSR oxidation of ethylbenzene, the low temperature chemistry is found to play a significant role at 10 atm. The present model is also validated on the experimental data from the literature, including the species concentration profiles and global combustion parameters such as ignition delay times and laminar flame speeds. The good performance of the model for reproducing these data reveals its ability to predict ethylbenzene combustion over a wide range of conditions.

© 2016 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

Ethylbenzene is an important component of commercial gasoline and its surrogate fuels [1–3]. It is also proposed as an aromatic component of surrogate fuels for kerosene [4]. Compared to benzene and toluene, ethylbenzene has higher reactivity, corresponding to shorter ignition delay times [5]. As the simplest alkylbenzene with the crucial benzylic C–C bond structure, ethylbenzene is a prototypical fuel for larger alkylbenzene fuels, such as *n*-propylbenzene, *n*-butylbenzene, or *n*-decylbenzene which are used to represent aromatic components in kerosene and diesel oil. Its combustion can easily produce high concentration levels of precursors of polycyclic aromatic hydrocarbons (PAHs) such as the benzyl radical and phenylacetylene [6], leading to an ideal case for investigating the formation of PAHs and soot.

The previous experimental studies of ethylbenzene combustion are limited compared to those of benzene and toluene combustion. Robaugh and Stein [7] studied the thermal decomposition of

ethylbenzene using the very-low-pressure pyrolysis (VLPP) method. Venkat et al. [8] studied the oxidation of ethylbenzene in an atmospheric flow reactor at 1168 K with the equivalence ratio (ϕ) of 0.49 and at 1164 K with ϕ of 0.79, respectively. Litzinger et al. [9] investigated the oxidation of ethylbenzene in an atmospheric flow reactor at ca. 1160 K with ϕ of 0.56–1.3. Pamidimukkala and Kern [10], Mizerka and Kiefer [11], and Muller-Markgraf and Troe [12] measured the rate constant of the unimolecular decomposition of ethylbenzene. Ergut et al. [13–16] studied the laminar premixed flame of ethylbenzene at 1 atm and measured the mole fractions of PAHs and other pollutants (soot, CO and unburned light hydrocarbons) using gas chromatography (GC). Li et al. [6,17] investigated the laminar premixed flames of ethylbenzene at 0.04 atm with the equivalence ratios from 0.75 to 1.90 using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Husson et al. [18] studied the oxidation of ethylbenzene in a jet-stirred reactor (JSR) at 800 Torr, 750–1100 K, a mean residence time (τ) of 2 s, and $\phi = 0.25$, 1, and 2. The global combustion parameters of ethylbenzene were also measured in the last decade, including ignition delay times [19–21] and laminar flame speeds [5,22]. To extend our knowledge on ethylbenzene combustion, further experimental studies of ethylbenzene combustion with

comprehensive speciation and at a variety of experimental conditions are needed.

Based on the experimental results, several kinetic models of ethylbenzene were proposed. Dagaut [23] proposed a detailed kinetic model of monocyclic aromatic hydrocarbons and validated it on the ignition delay times of ethylbenzene. Li et al. [17] proposed a kinetic model of ethylbenzene and validated it on the speciation data of premixed ethylbenzene flames. Husson et al. [18] proposed a kinetic model of ethylbenzene and validated it on the low-temperature JSR oxidation data. Mehl et al. [22] simulated the laminar flame speeds of ethylbenzene using a detailed kinetic model based on the toluene model of Metcalfe et al. [24]. All of these kinetic models validate one or two sets of experimental data, which cover relatively narrow conditions. It is noticed that a kinetic model of ethylbenzene with comprehensive validation is still lack and few concerns have been paid on the formation of PAHs.

This work reports a new experimental investigation on the flow reactor pyrolysis of ethylbenzene at 0.04, 0.2, and 1 atm using SVUV-PIMS and the JSR oxidation of ethylbenzene at 1 and 10 atm using GC. A new kinetic model of ethylbenzene is developed and validated on experimental data at a wide range of conditions, including the flow reactor pyrolysis and jet-stirred reactor oxidation data in this work and the experimental data from the literature.

2. Experimental methods

2.1. Flow reactor pyrolysis

The flow reactor pyrolysis experiment is performed at National Synchrotron Radiation Laboratory in Hefei, China. Detailed descriptions of the beamlines and pyrolysis apparatus have been presented in our previous work [25–29]. In brief, the pyrolysis apparatus consists of a pyrolysis chamber with an electrically heated flow reactor, a differentially pumped chamber with a molecular beam sampling system and a photoionization chamber with a home-made reflectron time-of-flight mass spectrometer (RTOF-MS). Ethylbenzene with a purity of $\geq$99.5% is purchased from Aladdin Industrial Inc., Shanghai, China. It is gasified in a vaporizer with the temperature maintaining at 453 K which is about 40 K higher than its boiling point. After the vaporization, the gas mixture of ethylbenzene (1 vol%) and argon (99 vol%) with a total flow rate of 1000 standard cubic centimeters per minute (sccm) is fed into the flow tube in the reactor. The flow tube is made of α-alumina to reduce wall catalytic effects [30–32] and has a 150 mm heating length. A small inner diameter (7.0 mm) is used to ensure strong radial diffusion effects, reduce radial concentration gradients and achieve adequately homogeneous reaction circumstances according to the experiences in previous laminar flow reactor experiments [33–35]. The temperature distributions along the centerline of the flow tube are measured by an S-type thermocouple. Detailed description of the temperature measurement method has been provided in previous studies [27,28]. Methodologies for intermediates identification and mole fractions evaluation were also reported in detail previously [28]. The uncertainties of evaluated mole fractions are estimated to be within$\pm$ 25% for pyrolysis products with known photoionization cross sections (PICSs),

and a factor of 2 for those with estimated PICSs. The PICSs of pyrolysis species are available in the online database [36].

2.2. Jet-stirred reactor oxidation

The JSR oxidation experiment is performed at C.N.R.S in Orléans, France. Table 1 lists the detailed experimental conditions. The jet-stirred reactors used in this work and the experimental procedure are similar to those used before [37–39]. It consists of a small fused silica sphere of 40 mm inner diameter (ID). Four 1 mm ID nozzles are mounted in the sphere to feed the gases and achieve stirring. A regulated heating wire of ca. 1.5 kW maintained the temperature of the reactor at the desired working temperature. Good thermal homogeneity along the whole vertical axis of the reactor (gradients of ca. 1 K/cm) is observed for each experiment by thermocouple (0.16 mm chromel-alumel or Pt/Pt–Rh 10%) measurements (typical change$\leq$ 5 K) [38,39]. A high-pressure liquid chromatography pump (Hewlett Packard 1100) is used to deliver sonically degassed ethylbenzene (99.8% purity, Sigma Aldrich) to an atomizer–vaporizer assembly maintained at 453 K. A high degree of dilution (0.2% volume of fuel) is used in order to reduce temperature gradients in the reactor caused by the oxidation heat release. High-purity oxygen (99.995%) is used in the experiment. The reactants are diluted by nitrogen ($<$ 50 ppm O_2, $<$1000 ppm Ar, $<$5 ppm H_2) and mixed at the entrance of the injectors. All the gases are preheated before injection to minimize temperature gradients inside the reactor.

The reacting mixtures are sampled by means of a fused silica low-pressure sonic probe. The samples are analyzed online by Fourier transform infrared spectroscopy to quantify H_2O, CO, CO_2, CH_2O and by GC combined with mass spectrometer and flame ionization detector (FID) to measure the other species. The offline analyses are performed for the samples stored in 1 L Pyrex bulbs. Gas chromatographs equipped with capillary columns (DB-5 ms, Al_2O_3-KCl, Poraplot U and Carboplot-P7), a thermal conductivity detector, and an FID are used to analysis the offline samples.

3. Kinetic model

The detailed kinetic model of ethylbenzene ($A1C_2H_5$, nomenclature in the present model) consisting of 229 species and 1563 reactions is developed by extending our recently published toluene [40,41] and styrene [42] models. The detailed description of the sub-mechanisms of styrene ($A1C_2H_3$), toluene ($A1CH_3$), benzene (A1), 1,3-cyclopentadiene (C_5H_6), and PAHs has been presented in those previous work [40–42], and will not be repeated here. The development of the sub-mechanism of ethylbenzene is introduced below. Some key reactions in the sub-mechanism of ethylbenzene are listed in Table S1 in the *Supplementary material*.

According to the pioneering work of Litzinger et al. [9], there are three important types of reactions that contribute to the decomposition of ethylbenzene, namely, the homolysis of the side ethyl chain (R1) forming benzyl ($A1CH_2$) and methyl (CH_3) radicals, ipso-substitution by H and OH ((R2), (R3)) and H-atom abstraction reactions ((R4)–(R6)). In this work, the rate constant of (R1) is derived from the previous experimental results of Pamidimukkala and Kern [10], Mizerka and Kiefer [11], and Muller-Markgraf and

Table 1
Experimental conditions of the JSR oxidation of ethylbenzene.

ϕ	T (K)	Ethylbenzene (%mol)	O_2 (%mol)	N_2 (%mol)	P (atm)	τ (s)
0.50	999–1216	0.13	2.60	97.27	1	0.12
1.00	999–1378	0.13	1.30	98.57	1	0.12
1.50	1097–1398	0.13	0.87	99.00	1	0.15
1.00	800–1280	0.10	1.05	98.85	10	0.70