



Contents lists available at ScienceDirect

## Combustion and Flame

journal homepage: [www.elsevier.com/locate/combustflame](http://www.elsevier.com/locate/combustflame)

## Experimental and kinetic modeling study of styrene combustion

Wenhao Yuan<sup>a,b</sup>, Yuyang Li<sup>a,\*</sup>, Philippe Dagaut<sup>b,\*</sup>, Jiuzhong Yang<sup>c</sup>, Fei Qi<sup>a,c</sup><sup>a</sup>State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China<sup>b</sup>C.N.R.S.-I.N.S.I.S., Institut de Combustion, Aérodynamique, Réactivité et Environnement, 1C, Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France<sup>c</sup>National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China

## ARTICLE INFO

## Article history:

Received 13 November 2014

Received in revised form 6 December 2014

Accepted 8 December 2014

Available online xxx

## Keywords:

Styrene

Laminar premixed flame

Jet stirred reactor

Kinetic model

PAHs formation

## ABSTRACT

The aim of this work is to report new experimental data on styrene combustion and develop a kinetic model for styrene combustion. Three laminar premixed flames of styrene with equivalence ratios of 0.75, 1.00 and 1.70 were studied at low pressure (0.0395 atm) using synchrotron vacuum ultraviolet photoionization mass spectrometry. The JSR oxidation of styrene/benzene mixtures with three equivalence ratios of 0.50, 1.00, and 1.50 was studied at atmospheric pressure using gas chromatography. The mole fraction profiles of flame species and oxidation species were measured. A kinetic model of styrene combustion with 290 species and 1786 reactions was developed from our recently reported toluene model, and was validated on the new experimental data from this work and previous ignition delay time data. The O-atom attack reactions, H-atom abstraction reactions and other H-atom attack reactions were found to dominate the consumption of styrene. In particular, the O-atom attack reactions on the double bond of styrene play an important role in the JSR oxidation and the lean and stoichiometric flames, while the pyrolytic reactions have increasing contributions as the equivalence ratio increases. The phenyl radical plays a crucial role in the decomposition of styrene since it affords most of the reaction fluxes from styrene. In the aromatics growth process, phenylacetylene, the 1-phenylvinyl radical, the phenyl radical, and styrene serve as major precursors of polycyclic aromatic hydrocarbons (PAHs), leading to the high sooting tendency of styrene compared to toluene and ethylbenzene.

© 2014 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

## 1. Introduction

Styrene is one of the most important petrochemicals with a global production of 26.4 million tons in 2012 [1], and is mainly used as the precursor of polystyrene (PS) and many copolymers such as acrylonitrile–butadiene–styrene copolymers (ABS), styrene–acrylonitrile copolymers (SAN), styrene–butadiene rubber (SBR) and styrenic block copolymers (SBC). These polymers are the most widely used plastics and synthetic rubbers, and their wastes are generally processed by thermal degradation and incineration methods. Combustion chemical kinetics of styrene is of high value for understanding the chemistry in the thermal degradation and incineration processing of these polymers due to the decoupling of the depolymerization/decomposition processes that are associated with pyrolysis of these polymers, prior to their oxidation [2]. For example, styrene is abundantly produced in the thermal decomposition of PS, even at rather low temperatures [3]. Combustion of styrene also deserves to be studied since waste styrene can

also be processed by incineration [2]. On the other hand, styrene is a significant product with high concentration levels in combustion and pyrolysis of most aromatic fuels [4–11] and biomass combustion [12]. Styrene can also be formed from the reactions of the cyclopentadienyl radical with the propargyl radical [13] and 1,3-cyclopentadiene [7,13]. So its importance should also be assessed in the rich combustion environment where the cyclopentadienyl radical is a major product. Furthermore, the styrene chemistry also plays an important role in the formation of polycyclic aromatic hydrocarbons (PAHs). For example, in the combustion of larger alkylbenzenes [8], the decomposition of styrene is the major source of phenylacetylene which can produce naphthalene through hydrogen-abstraction–carbon-addition (HACA) pathways [14,15].

There have been very few experimental studies on the combustion of styrene. Litzinger et al. [16] investigated the oxidation of styrene in an atmospheric-pressure flow reactor at temperatures around 1060 K and equivalence ratio ( $\phi$ ) of 0.56. Pengloan et al. [17,18] investigated the ignition delay times of styrene in a shock tube at the pressures of  $\sim 1.43$  atm and temperatures of 1300–2000 K. Their data were used to validate a comprehensive

\* Corresponding authors.

E-mail addresses: [yuygli@ustc.edu.cn](mailto:yuygli@ustc.edu.cn) (Y. Li), [dagaut@cns-orleans.fr](mailto:dagaut@cns-orleans.fr) (P. Dagaut).

combustion kinetic model by Dagaut [19]. Westblad et al. [2] investigated the emissions of PAHs, particulates, CO and CO<sub>2</sub> from the batch combustion of styrene in a two-stage muffle furnace. Grela et al. [20] investigated the unimolecular decomposition of styrene into benzene and acetylene between 1180 and 1350 K in a low-pressure flow reactor using on-line mass spectrometry. They proposed that benzene and vinylidene are the primary unimolecular decomposition products of styrene. To the best of our knowledge, no systematic theoretical or modeling work has been performed on the combustion of styrene, though simple reaction schemes of styrene widely exist in kinetic models of aromatics combustion and PAHs formation mechanisms.

A target of this work is to report new experimental studies on the laminar premixed flames of styrene at 0.0395 atm ( $\phi = 0.75, 1.00$  and  $1.70$ ) and jet stirred reactor (JSR) oxidation of styrene/benzene mixtures at 1 atm ( $\phi = 0.50, 1.00$  and  $1.50$ ). Synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) [21] was used to detect the flame species and measure their mole fractions as the function of distance from the burner surface. Gas chromatography (GC) combined with flame ionization detector (FID), thermal conductivity detector (TCD) and mass spectrometry (MS) was used to detect the species in the JSR oxidation and measure their mole fractions as the function of heating temperature. The other target of this work is to report the first effort on the development of a comprehensive kinetic model for styrene combustion. The model was validated on the new laminar premixed flame and JSR oxidation data and literature ignition delay time data. Rate of production (ROP) analyses and sensitivity analyses were also performed to provide insights into the chemistry of styrene decomposition, oxidation, and aromatics growth.

## 2. Experimental section

### 2.1. Laminar premixed flame

The laminar premixed flame experiment was performed at the National Synchrotron Radiation Laboratory in Hefei, China. Detailed descriptions of the synchrotron beamlines and flame apparatus have been published elsewhere [22,23]. Briefly, the flame apparatus contains three parts, i.e. a low-pressure flame chamber with a McKenna burner, a differentially pumped chamber with a flame-sampling system, and a photoionization chamber with a home-made reflectron time-of-flight mass spectrometer (RTOFMS). The flame species were sampled by a quartz nozzle with a  $\sim 500\text{-}\mu\text{m}$ -diameter orifice on the tip, and then formed a molecular beam in the flame-sampling system. The molecular beam passed through a nickel skimmer and entered into the photoionization chamber where it was crossed by the tunable synchrotron VUV light. The ionized species were detected by the RTOFMS.

Styrene for the flame experiment was purchased from Sinopharm Chemical Reagent Limited Co., Shanghai, China, with a purity of  $\geq 99\%$ . The flow rate of styrene was controlled by a syringe pump (ISCO 1000D, USA) at room temperature, and the gas flow rates of O<sub>2</sub> and Ar were controlled separately by mass flow controllers (MKS, USA). The styrene was gasified in a vaporizer with the temperature maintaining at 435 K. The flame conditions are listed in Table 1. For a better comparison of flame chemistry, the pressure, inlet percentage of Ar and cold gas velocity of inlet mixtures were kept identical in all flames. All measurements were performed along the centerline of the burner. The flame temperature profiles were measured using a 0.10-mm-diameter Pt–6%Rh/Pt–30%Rh thermocouple coated with Y<sub>2</sub>O<sub>3</sub>–BeO anti-catalytic ceramic to inhibit the catalytic effects [24]. The temperatures were corrected for radiative heat loss [25] and cooling effects of the sampling nozzle [26]. The uncertainties of the maximum flame

**Table 1**  
Experimental conditions of the three styrene flames.

$\phi$	$P$ (atm)	Styrene (% mol)	O <sub>2</sub> (% mol)	Ar (% mol)	$v$ (cm/s)
0.75	0.0395	3.49	46.51	50.00	35.00
1.00	0.0395	4.55	45.45	50.00	35.00
1.70	0.0395	7.27	42.73	50.00	35.00

Note:  $v$  is the flow velocity of inlet mixture at 300 K.

temperatures were estimated to be within  $\pm 100$  K. Methodologies of intermediate identification and mole fraction evaluation were reported in detail previously [22,27]. The uncertainties of evaluated mole fractions are within  $\pm 10\%$  for major species,  $\pm 25\%$  for intermediates with accurately known photoionization cross sections (PICS), and a factor of 2 for those with estimated PICS [22]. The PICS data used in this work are available from the online database [28].

### 2.2. Jet stirred reactor oxidation

The JSR oxidation experiment was performed at C.N.R.S in Orléans, France. Table 2 lists the detailed experimental conditions. The jet stirred reactor used in this work and the experimental procedure are similar to what was used earlier [29]. It consists of a small fused silica sphere of 40 mm inner diameter (30.5 cm<sup>3</sup>). Four nozzles of 1 mm inner diameter were 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) was observed for each experiment by thermocouple (0.16 mm chromel–alumel) measurements (typical change  $\leq 5$  K). A high-pressure liquid chromatography pump (Hewlett Packard 1100) was used to deliver sonically degassed styrene (99.8% purity, Sigma Aldrich) and benzene (99.8% purity, Sigma Aldrich) mixture to an atomizer–vaporizer assembly maintained at 453 K. A high degree of dilution (0.2% volume of fuel) was used in order to reduce temperature gradients in the reactor caused by the oxidation heat release. High-purity oxygen (99.995% pure) was used in the experiment. The reactants were diluted by nitrogen ( $< 50$  ppm O<sub>2</sub>,  $< 1000$  ppm Ar,  $< 5$  ppm H<sub>2</sub>) and mixed at the entrance of the injectors. All the gases were pre-heated before injection to minimize temperature gradients inside the reactor. The reacting mixtures were sampled by means of a fused silica low-pressure sonic probe. The samples were analyzed online by GC–MS–FID and off-line after collection and storage in 1 L Pyrex bulbs. Off-line analyses were done using gas chromatographs equipped with capillary columns (DB-5ms, Al<sub>2</sub>O<sub>3</sub>–KCl, Poraplot U and CarboPlot-P7), a TCD, and an FID.

## 3. Kinetic model

A detailed kinetic model of styrene combustion including 290 species and 1786 reactions was developed from our recently developed toluene model [7,30]. Table 3 lists some key reactions discussed in the following sections. Table S1 in Supplementary Material lists the molecular weights, formulas, names, nomenclatures in the present model and structures for the C<sub>2</sub> and larger species mentioned below. The detailed descriptions and validation of

**Table 2**  
Experimental conditions of the JSR oxidation of styrene/benzene mixtures.

$\phi$	$T$ (K)	Styrene (% mol)	Benzene (% mol)	N <sub>2</sub> (% mol)	$P$ (atm)	$\tau$ (s)
0.50	1000–1300	0.05	0.15	96.55	10	0.07
1.00	1020–1324	0.05	0.15	98.18	10	0.07
1.50	1053–1357	0.05	0.15	98.72	10	0.07

Download English Version:

<https://daneshyari.com/en/article/10264292>

Download Persian Version:

<https://daneshyari.com/article/10264292>

[Daneshyari.com](https://daneshyari.com)