Combustion and Flame 000 (2018) 1–10

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

An experimental and modeling study on the low temperature oxidation of surrogate for JP-8 part I: Neat 1,3,5-trimethylbenzene

Bing-Yin Wang[a,b], Dan Yu[a], Guan-Fu Pan[a,b], Yue-Xi Liu[a,b], Jun-Jie Weng[a], Zhen-Yu Tian[a,b,*]

[a] *Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 13 July 2017
Revised 26 September 2017
Accepted 23 December 2017
Available online xxx

Keywords:
1,3,5-Trimethylbenzene
Surrogate
Kerosene
Low-temperature oxidation
JSR
Reaction flux analysis

ABSTRACT

This work describes the experimental and modeling study of low temperature oxidation of 1,3,5-trimethylbenzene (T135MB) in a jet-stirred reactor over the temperature range of 700–1100 K at atmospheric pressure under fuel-lean and stoichiometric conditions. 9 C_0–C_5 hydrocarbons, 6 oxygenated products and 6 aromatic compounds were identified and quantified using GC and GC-MS. A detailed kinetic based on T135MB model of Diévart et al. was proposed to simulate the low-temperature experimental results in the present work. Rate constants of T135MB decomposition and metatheses reactions were calculated with CBS-QB3 method implemented in Gaussian 09. The performance of proposed mechanism in reproducing the experimental data is reasonably good. Reaction flux analysis shows that dominant consumption channels for T135MB oxidation are H-abstraction reactions to form 3,5-dimethylbenzyl radicals, while reactions with O/OH radicals to generate 1,3,5-trimethylphenoxyl/1,3,5-trimethylphenyl and ipso-addition to form m-xylene play minor roles. Sensitivity analysis reveals that H-abstraction from side methyl groups of T135MB by OH radical is the most inhibiting reaction oxidation at $\Phi = 1.0$, while it is a promoting reaction at $\Phi = 0.4$. Moreover, current model were validated against experimental results on T135MB oxidation in flow reactor from Diévart et al. as well as global combustion property ignition delay times from Rao et al. and Diévart et al. with reasonable predictions.

1. Introduction

Combustion of jet fuels in engines is the main power source of civilian and military aircraft. Since jet fuels consist of multiple classes of complex components [1,2] and it is unrealistic to establish a detailed kinetic model to emulate the combustion characteristics of real fuel [1,3], it has been widely accepted to use surrogate fuel to simplify the chemical kinetic for real jet fuel [4,5]. Surrogate fuel are comprised of several components but be capable of reproducing the gas phase combustion characteristics of studied real fuel. Aromatic compounds are major components in many sorts of jet fuels, and understanding their combustion characteristics is very important in optimizing engine performance and exploring the influence of fuel variability on pollutant formation and engine efficiency. The preference of 1,3,5-trimethylbenzene (T135MB) as representative aromatic specie in practical surrogate fuel is due to the symmetry of molecule structure allowing a simplification of model construction. It is also utilized to increase the average molecular weight of surrogate fuel and provide further insight into the combustion characteristic and soot formation study of surrogate fuel [6]. Thus, it is meaningful to establish a detailed T135MB kinetic mechanism and couple it with computational fluid dynamics.

In recent years, T135MB, one crucial component in surrogate fuel, has captured attention in the measurement of macroscopic combustion parameters [6–11]. Experimental data and chemical kinetic mechanism of T135MB have been studied mostly at relatively high temperature (>1000 K). Previous T135MB work was mainly investigated with shock tube [12], laminar [13,14] and counterflow diffusion flames [15]. High temperature flow reactor oxidation [6,7,16], diffusion flame extinction limits [11,17,18], ignition delay times and laminar burning velocities [8,9,19,20] were carried out to study the combustion characteristic of T135MB. To facilitate the comparison between different methods, experimental conditions for previous T135MB-related studies were included in Table 1. These experimental results, including both global combustion properties and chemical details are then used to examine newly developed kinetic mechanism in current work.

Roubaud et al. [7] measured the auto-ignition feature of T135MB at stoichiometric condition with a rapid compression machine, over temperature range of 600–900 K and pressure of 5–25 bar. Rao et al. [10] studied the ignition delay times of T135MB

---

[*] Corresponding author.
E-mail address: tianzhenyu@iet.cn (Z.-Y. Tian).

https://doi.org/10.1016/j.combustflame.2017.12.030

Please cite this article as: B.-Y. Wang et al., An experimental and modeling study on the low temperature oxidation of surrogate for JP-8 part I: Neat 1,3,5-trimethylbenzene, Combustion and Flame (2018), https://doi.org/10.1016/j.combustflame.2017.12.030

Table 1
Experimental condition for T135MB studies in the present work and the literature.

Experiments	Temperature	Pressure	Φ	Ref.
Flow reactor	638–948 K	12.5 atm	1.0	[6]
Shock tube reactor	1017–1645 K	20, 50 atm	0.51–1.86	[21]
Jet-stirred reactor	700–1100 K	1 atm	0.4–1.0	Present work
Flame extinction limits	300, 500 K	1 atm	0.6–1.3	[11]
	400 K	1 atm	0.8–1.6	[8]
Laminar flame speeds	353 K	1 atm	0.7–1.5	[9]
	400 K	1 atm	0.71–1.39	[6]
	400, 700 K	1 atm	0.7–1.4	[8]
Ignition delay times	600–900 K	5–25 bar	1.0	[7]
	1080–1560 K	1.0–5.0 atm	0.5–2.0	[10]
	1111–1468 K	10, 20 atm	0.5–2.0	[6]

Table 2
Summaries of relevant T135MB kinetic model.

Model	Species	Reactions	Source of T135MB sub-model	Ref.
Present model	910	5330	calculation	Present work
Diévart et al.	450	4569	toluene	[6]
Gudiyella et al.	202	882	m-xylene	[21]

with shock tube over $\Phi = 0.5–2.0$, 1080–1560 K and 1.0–20.0 atm. Won et al. [11] found that extinction limits of T135MB/air diffusion flames were determined by the capability of fuel to establish a radical pool governed by molecular structure. Hui et al. [8] and Ji et al. [9] measured the premixed extinction limits of T135MB/O_2/N_2 mixtures ($\Phi = 0.8–1.6$ at 400 K and 700 K) and the laminar burning velocities of premixed T135MB/air flames (counter-flow configuration, under atmospheric pressure and 353 K), respectively. Compared to the macroscopic combustion study, speciation investigation in the oxidation of T135MB are relatively limited. The speciation profiles for T135MB oxidation at 1017–1646 K, equivalence ratios from 0.51 to 1.86 and pressure of 20 and 50 atm in a reflected shock tube were reported by Gudiyella and Brezinsky [21]. Recently Diévart et al. [6] presented the reflected shock ignition delay times, laminar burning velocities and oxidative reactivity profiles in a high-pressure flow reactor at 12.5 atm, showing that neat T135MB has no negative temperature coefficient (NTC) effect. An estimated kinetic model proposed to predict the species profiles can simulate some specific experimental results for high temperature chemistry of T135MB. However, it has not been extensively validated. There is even scarce work on the low-temperature oxidation of T135MB in micro-kinetic perspective regarding the speciation analysis and observation of more stable intermediates species. Low-temperature kinetic is very crucial to reveal the ignition process and validate the universality of proposed models. Thus, it is desired to study the low temperature oxidation of T135MB. Relevant T135MB kinetic models were summarized in Table 2.

In this work, low temperature oxidation of T135MB within jet-stirred reactor (JSR) system was investigated over temperature range of 700–1100 K and equivalence ratios of 0.4 and 1.0. The species measurements were conducted by gas chromatographic techniques. Goal of present study is to develop a more extensively universal kinetic mechanism for combustion of T135MB. Theoretical calculations have been performed to acquire more appropriate rate constants for key elementary steps and low-temperature kinetic characteristics of T135MB oxidation was performed using the current updated model. These results will provide more insights into better understanding the low temperature oxidation of T135MB and formation of stable intermediates.

2. Experimental

The detailed information of current low-temperature oxidation system was described in earlier publications [22,23], therefore only a brief introduction is given here. A spherical fused silica JSR with 50 mm inner diameter was designed for low-temperature oxidation of T135MB from 700 to 1100 K at atmospheric pressure. The whole system consists of high pressure infusion pump (FL2200, China), evaporation chamber (self-assembled, diameter of 5 cm, able to be heated above 600 K), JSR, GC (Agilent 7890B, USA) and GC-MS (Agilent 7890B-5977A, USA), as shown in Fig. S1 in the Supplemental Material (SM). Residence time τ is calculated by equation $\tau = V/Q$. V and Q stand for volume of used JSR and volume flow rate of mixture in JSR. Experimental conditions are listed in Table 3. Liquid T135MB with feeding rate of 0.061 ml/min (1% in gas phase) was heated to 473 K above boiling point (438 K) and carried into JSR by Ar (purity of 99.999%). Flow rate of oxygen (purity of 99.999%), controlled by MKS mass-flow controller, is 30% and 12% of total 1.000 standard liter per minute diluted in Ar, corresponding to $\Phi = 0.4$ and 1.0, respectively. All transfer lines were preheated to 473 K to eliminate temperature gradients and experimental uncertainties, particularly for aromatic intermediates with high boiling point. Target temperature was achieved by a regulated heating controller (HT60, Horst Germany) and measured by a K-type thermocouple located inside the center space of sphere. The outlets were analyzed by online GC using thermal conductivity detector (TCD) and flame ionization detector (FID), which is equipped with capillary columns (Al_2O_3-KCl and HP-INNOWax). Good experimental reproducibility and repeatability were guaranteed by multiple measurements at each experimental condition. Uncertainty of temperature measurement was estimated to be within ±5K. Estimated experimental uncertainties of mole fractions were within ±5% for major species and ±10% for intermediates.

3. Modeling

A detailed kinetic model of T135MB oxidation was developed based on mechanism proposed by Diévart et al. [6]. The detailed kinetic model includes a C_0–C_2 core subset, a mechanism to simulate the oxidation of C_3–C_5 and aromatic species, especially T135MB sub-mechanism. Rate constants of some reactions in T135MB sub-mechanism proposed by Diévart et al. [6] were estimated by analogy to that of toluene. Sensitivity analysis under current experimental conditions revealed that unimolecular decomposition and H-abstraction reaction are two types of key pathways in fuel destruction. It should be noted that rate constants of T135MB decomposition and H-abstraction were simply considered three times as those reactions of toluene in the literature [6]. However, there is only one benzyl type methyl in the structure of toluene,

Please cite this article as: B.-Y. Wang et al., An experimental and modeling study on the low temperature oxidation of surrogate for JP-8 part I: Neat 1,3,5-trimethylbenzene, Combustion and Flame (2018), https://doi.org/10.1016/j.combustflame.2017.12.030