Postprint of Experimental and Theoretical Study on Low-Temperature Oxidation of Pseudocumene

Authors: Weng Junjie, Yu Dan, Liu Yuexi, Wang Bingyin, Xing Lili, Zhang Lidong, Tian Zhenyu (1,2)

Date: 2018-01-05T00:00:00+00:00

Abstract

The low-temperature oxidation of hemimellitene was investigated using a jet-stirred reactor at an equivalence ratio of 1.0 and a temperature range of 700–1100 K. Based on experimental and theoretical calculation results, a kinetic mechanism comprising 544 species and 3248 reactions was developed, with updated rate constants for hemimellitene decomposition, ipso-addition, and hydrogen abstraction reactions, and dehydrogenation reactions at the 1- and 2-position methyl groups of hemimellitene were introduced in the new mechanism. This mechanism shows good agreement with experimental results. Reaction path analysis indicates that dehydrogenation at positions 1, 2, and 4 are the primary consumption pathways of hemimellitene. Sensitivity analysis reveals that dehydrogenation reactions and the HO2 + dimethylbenzyl reaction exhibit inhibiting and promoting effects, respectively.

Full Text

Preamble

Experimental and Theoretical Study of 1,2,4-Trimethylbenzene Low-Temperature Oxidation

Jun-Jie Weng[1], Dan Yu[1], Yue-Xi Liu[1],[2], Bing-Yin Wang[1],[2], Li-Li Xing[3], Li-Dong Zhang[3], Zhen-Yu Tian[1],[2],*

[1] Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China
[2] University of Chinese Academy of Sciences, Beijing 100049, China
[3] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, China

Abstract

The present work aims to perform the experimental and kinetic study of 1,2,4-trimethylbenzene (TMB124) low-temperature oxidation under stoichiometric conditions in a jet-stirred reactor (JSR). The experiment was carried out in the temperature range of 700–1100 K at atmospheric pressure. According to the measurements and theoretical calculations, a detailed chemical kinetic model involving 544 species and 3248 reactions was developed. Rate constants of TMB124 decomposition, reaction with HO , ipso-additions, and metatheses with abstraction of methyl H-atom were updated. New pathways of H-abstraction from the 1- and 2-methyl groups were considered. The established model reproduces the measured mole fraction profiles of the major species and intermediates well. Rate-of-production analysis indicates that TMB124 is dominantly consumed by metatheses giving rise to three dimethyl benzyl radicals. Sensitivity analysis shows that the H-abstraction reactions of TMB124 exhibit strong inhibiting effects, while the reactions of HO radical and the three dimethyl benzyl radicals have promoting effects.

Keywords: 1,2,4-Trimethylbenzene; Low-temperature oxidation; JSR; Rate-of-production analysis; Sensitivity analysis

Introduction

Real aviation fuels are composed of numerous aliphatic and aromatic hydrocarbons, including straight-chain alkanes, branched alkanes, cycloalkanes, and aromatics [1]. Due to the extremely complex composition, it is difficult to develop detailed kinetic models to describe the combustion processes of these complex fuels. Currently, surrogate fuels containing multiple representative compounds are widely used to simulate and study the physicochemical properties of real aviation fuels [2, 3]. The combustion processes of typical aromatic fuels such as benzene [4], toluene [5, 6], xylene [7-9], and ethylbenzene [10] have been extensively studied. However, the molecular weights of these fuels still differ from the average molecular weight of real aviation fuels (approximately 140–150 g/mol) [11], and thus cannot fully reflect the combustion characteristics of real aviation fuels. Moreover, the chemical structures of these fuels are relatively simple and cannot simulate the complex aromatic compounds present in real aviation fuels. Recently, 1,2,4-trimethylbenzene has been selected as an aromatic component for surrogate kerosene due to its higher molecular weight and more complex chemical structure [2]. Therefore, studying the combustion characteristics of 1,2,4-trimethylbenzene is of great significance.

Currently, experimental and theoretical studies on the oxidation characteristics of 1,2,4-trimethylbenzene are limited. Roubaud et al. investigated the autoignition characteristics of 1,2,4-trimethylbenzene using a rapid compression machine and found that it could be ignited at relatively low temperatures and pressures, exhibiting complex characteristics similar to alkanes and alkenes, and classified 1,2,4-trimethylbenzene into the "o-xylene group" [12]. Bikas developed a low-temperature oxidation mechanism for 1,2,4-trimethylbenzene [13], which was built upon a toluene mechanism and assumed that the early oxidation process of 1,2,4-trimethylbenzene mainly involved hydrogen abstraction reactions at the 4-position methyl group. Bikas' mechanism was used to validate experimental data such as ignition delay times [12] and critical conditions for auto-ignition in counterflow flames [13]. Subsequently, Honnet et al. proposed an Aachen surrogate fuel for Jet-A aviation kerosene, consisting of 20% 1,2,4-trimethylbenzene and 80% n-decane (by weight), and studied the extinction limits, auto-ignition, and soot volume fractions of laminar non-premixed flames of this surrogate fuel [2]. Based on this work, Honnet et al. proposed a semi-empirical mechanism for 1,2,4-trimethylbenzene, which updated Bikas' mechanism [13]. Hui et al. studied the laminar flame speeds and extinction strain rates of 1,2,4-trimethylbenzene using a counterflow reactor and found that Honnet' s mechanism significantly underestimated the extinction strain rates and laminar flame propagation speeds [14, 15]. Won et al. studied the extinction characteristics of 1,2,4-trimethylbenzene diffusion flames using a counterflow reactor and found that Honnet' s mechanism severely underestimated the extinction limits [16]. Therefore, the mechanism for 1,2,4-trimethylbenzene urgently needs to be updated to provide more reliable predictions of experimental data, especially considering that the reported mechanisms only accounted for the dimethyl benzyl radical at the 4-position while neglecting those formed at the 1- and 2-positions. Furthermore, studies on the product structures and concentration distributions during low-temperature oxidation of 1,2,4-trimethylbenzene are scarce, which hinders in-depth analysis of the kinetic characteristics of surrogate fuels like 1,2,4-trimethylbenzene.

In this work, the low-temperature oxidation process of 1,2,4-trimethylbenzene was studied using a self-designed jet-stirred reactor experimental platform at temperatures of 700–1100 K, atmospheric pressure, and an equivalence ratio of 1.0. Based on our experimental work and theoretical calculations, combined with previous literature results [2], a new detailed chemical kinetic mechanism for 1,2,4-trimethylbenzene was proposed. This work expands the database for 1,2,4-trimethylbenzene under low-temperature oxidation conditions and deepens the understanding of surrogate fuel combustion processes and soot precursor formation.

Experimental and Kinetic Simulation Methods

Experimental Setup

[Figure 1: see original paper] shows a schematic diagram of the experimental system for low-temperature oxidation of 1,2,4-trimethylbenzene. The parameters of the jet-stirred reactor (JSR) used in this work have been described in detail in the literature [17]; only a brief introduction is provided here. The reactor is made of fused quartz, with a central spherical chamber of 50 mm diameter containing four nozzles with inner diameters of 0.3 mm.

1,2,4-Trimethylbenzene was purchased from TCI with purity higher than 98% and used without further purification. The fuel was vaporized in a vaporization tank maintained at 473 K, slightly above its boiling point (443 K). The liquid flow rate of 1,2,4-trimethylbenzene was 0.061 ml/min (corresponding to a volume fraction of 1.0% in the gas mixture), precisely controlled by a high-pressure liquid pump (FL2200, Fuli Instruments Co., Ltd.). The flow rates of oxygen (99.999% purity) and argon (99.999% purity) were precisely controlled by mass flow controllers (MKS, USA), accounting for 12.0% and 87.0% of the total gas volume, respectively. The total reactant flow rate was 1.0 SLM, with an equivalence ratio of 1.0 and a carbon-to-oxygen ratio (C/O) of 0.38. Temperature was monitored by several temperature controllers (Horst, Germany) and measured by K-type thermocouples. All reactants were preheated to 473 K before entering the reactor. The gaseous reactants continuously flowed into the reactor, and samples were taken through a six-port valve when steady state was reached. Gaseous products were analyzed by gas chromatography-mass spectrometry (GC-MS, Agilent 7890B-5977A) and gas chromatography (GC, Agilent 7890B). Three chromatographic columns (Molecular Sieve-5A, Al O -KCl, and HP-INNOWax) were used to detect inorganic species, light hydrocarbons, and aromatic compounds, respectively, with thermal conductivity detector (TCD) and flame ionization detector (FID). The instrument was calibrated with standard gases before each measurement. The temperature uncertainty was ±5 K, the error for major product mole fractions was ±5%, and the error for intermediate species was ±10%.

Kinetic Modeling

The PSR code in Chemkin-II software was employed for kinetic simulations [18]. The kinetic mechanism developed in this work was built upon Honnet' s 1,2,4-trimethylbenzene mechanism [2] and Diévart' s 1,3,5-trimethylbenzene mechanism [19], with sub-mechanisms for o-xylene [7], m-xylene [9], and p-xylene [8] added. Quantum chemical calculations (CBS-QB3 method) [20] were also used to compute rate constants for several key reactions, such as 1,2,4-trimethylbenzene decomposition, reaction with HO radical, ipso-addition, and hydrogen abstraction from methyl groups. It should be noted that new pathways for hydrogen abstraction from the 1- and 2-position methyl groups and reactions of their derived intermediates were added to the model, which were not considered in previous work. The developed model includes 544 species and 3248 reactions. Table 1 lists some modified and newly added chemical reactions related to 1,2,4-trimethylbenzene and its derived intermediates. Thermodynamic data for most intermediate species were obtained using THERGAS [20] and Gaussian [21] software. For intermediate products whose thermodynamic data could not be calculated by THERGAS, *ab initio* methods were employed, specifically the CBS-QB3 method [20] using Gaussian 09 software. Finally, rate-of-production (ROP) analysis and sensitivity analysis were performed using the model to investigate the main consumption pathways and sensitive reactions of 1,2,4-trimethylbenzene. Rate constants for some reactions were calculated using electronic structure theory combined with transition state theory. Geometry optimization and vibrational frequency analysis were performed using the CBS-QB3 method [20]. Intrinsic reaction coordinate calculations were also used to verify the connection between the specified transition state and the reactants or products. All quantum chemical calculations in this work were performed using Gaussian 09 software. Kinetic parameters were obtained from transition state theory combined with the ChemRate program. In addition to the mechanism developed in this work, Honnet' s 1,2,4-trimethylbenzene mechanism was also used to simulate the experimental results for comparison.

Results and Discussion

Major Species Mole Fractions

A total of 22 species were detected by gas chromatography, among which ethylbenzene (C H C H), m-xylene (1,3-C H), p-xylene (1,4-C H), and acrolein (C H CHO) were not detected in previous experimental studies and were not considered in Honnet' s 1,2,4-trimethylbenzene mechanism [2].

The current mechanism overestimates the peak concentrations of H and CO while underestimating the peak concentration of CO . ROP analysis reveals that 77% of H is produced from reactions of 1,2,4-trimethylbenzene with H atoms and OH radicals, 90% of CO originates from HCO reactions with O and decomposition of active products, and approximately 65% of CO is formed from CO reactions with OH and HO radicals. Therefore, we speculate that the deviations between experimental and simulated values arise from uncertainties in the rate constants of some elementary reactions. Additionally, experimental errors may also contribute to these deviations.

Typical species including reactants, aromatics, and major products were selected, with experimental and simulation results shown in Figures 2-3. Figure 2 presents the experimental and simulated mole fraction profiles of 1,2,4-trimethylbenzene, H , CO, and CO . The results show that 1,2,4-trimethylbenzene begins to decompose above 750 K, while H , CO, and CO start to form above 975 K, 900 K, and 950 K, respectively. Compared with Honnet' s 1,2,4-trimethylbenzene mechanism, the mechanism developed in this work better reproduces the experimental results. However, the current mechanism still shows some deviation from the experimental data, which may be attributed to uncertainties in the rate constants of certain reactions. The present work represents a preliminary attempt to simulate the low-temperature oxidation process of 1,2,4-trimethylbenzene, and more oxidation experimental data will be needed in the future to validate the current mechanism.

Figure 3 shows the experimental and simulated mole fraction profiles of C -C aromatic products from low-temperature oxidation of 1,2,4-trimethylbenzene. Benzene (C H), toluene (C H CH), and ethylbenzene reach their maximum mole fractions at 975 K, while o-xylene, m-xylene, and p-xylene peak at 925 K. Overall, the current mechanism simulates the aromatic products more accurately than Honnet' s mechanism. Notably, the mole fractions of the three xylene isomers (o-, m-, and p-xylene) are of the same order of magnitude, indicating that 1,2,4-trimethylbenzene may simultaneously decompose through three pathways to form the three xylene isomers. Although the predicted temperatures for the maximum mole fractions of the three xylenes are about 25 K lower than the experimental values, the mechanism satisfactorily reproduces the peak concentrations.

Rate-of-Production Analysis

[Figure 4: see original paper] shows the ROP analysis for low-temperature oxidation of 1,2,4-trimethylbenzene at 925 K and 51% conversion. The main reaction pathways for 1,2,4-trimethylbenzene low-temperature oxidation are metathesis reactions with H, OH, and HO radicals to generate three dimethyl benzyl radicals (d12mb4CH , d24mb1CH , and d14mb2CH), as shown in the three red boxes in Figure 4. It should be noted that Bikas and Honnet' s mechanisms [13] only considered the formation of dimethyl benzyl radical d12mb4CH , neglecting the two dimethyl benzyl radicals d24mb1CH and d14mb2CH formed by C–H bond breaking at the 1- and 2-positions. The reactions forming d24mb1CH Oj and d14mb2CH Oj radicals account for 9% and 11% of the total 1,2,4-trimethylbenzene consumption, respectively. Small amounts of xylenes can be formed through ipso-substitution reactions on 1,2,4-trimethylbenzene.

In addition to regenerating 1,2,4-trimethylbenzene, the d12mb4CH radical mainly converts to o-xylene and d12mb4CHO. A small amount of d12mb4CH can form d12mb4CH OH through addition reactions with OH radicals. According to Bikas' assumption [13], the decomposition pathway of 1,2,4-trimethylbenzene is similar to that of toluene, implying that d12mb4CH and benzyl radicals should have similar decomposition pathways and reaction proportions. However, according to the toluene mechanism developed by Metcalfe et al. [28], the reaction pathways forming C H CH O radical, ethylbenzene, and bibenzyl (C H) account for 52%, 23%, and 16% of benzyl radical consumption, respectively. This differs significantly from the reaction pathways of d12mb4CH radical in our mechanism, with the discrepancy arising from differences in chemical structure between d12mb4CH and benzyl radicals and the associated rate constants.

The d12mb4CHO radical can react with H atoms, OH radicals, and O atoms to form the d12mb4COj radical, which accounts for 71% of d12mb4CHO consumption. The d12mb4COj radical eliminates CO to form the CH34jC H CH -12 radical, which subsequently reacts with O to form the d12mb4Oj radical. Thirty-six percent of d12mb4Oj radicals eliminate CO and H atoms to form toluene. The remaining d12mb4Oj radicals react with H atoms to form d12mb4OH. Through reactions with OH radicals, O atoms, and O , approximately 23% of d12mb4CHO can form o-xylyl radicals, which eventually produce benzocyclobutene and o-xylylene. Furthermore, almost all d12mb4CH OH can regenerate 1,2,4-trimethylbenzene through reaction with H atoms.

This study reveals that the methylene position significantly affects the decomposition pathways of 1,2,4-trimethylbenzene. At the 1-position, the d24mb1CH radical can form d24mb1CHO, m-xylene, 1,2,4-trimethylbenzene, and d24mb1CH OH through a series of reactions. Through similar reactions, the d14mb2CH radical can form d14mb2CHO, p-xylene, 1,2,4-trimethylbenzene, and d14mb2CH OH. Roubaud et al. [12] showed that 1,2,4-trimethylbenzene has auto-ignition characteristics similar to o-xylene, suggesting that d24mb1CH and d14mb2CH radicals have similar reaction characteristics to o-xylyl radicals. However, as discussed previously, most o-xylyl radicals in our mechanism produce benzocyclobutene and o-xylylene, based on the o-xylene mechanism proposed by Battin-Leclerc et al. [8] used in our 1,2,4-trimethylbenzene mechanism. These differences arise from structural differences between d24mb1CH and d14mb2CH radicals and o-xylyl radicals, as well as differences in the associated reaction rate constants.

Seventy-six percent of d24mb1CHO can react with H atoms, O atoms, OH radicals, HO radicals, and CH radicals to form the d24mb1COj radical. Another reaction channel for d24mb1CHO involves reactions with OH radicals, HO radicals, O atoms, and O to form m-xylyl radicals, accounting for 21% of d24mb1CHO consumption. A small amount of d24mb1CHO (about 1%) can also react with H atoms to form m-xylene. The d24mb1COj radical eliminates CO to form the CH34jC H CH -13 radical, which then reacts with O to form the d24mb1Oj radical. Sixty-four percent of d24mb1Oj radicals eliminate CO and H atoms to form toluene. Through reactions with H atoms and HO radicals, 34% of d24mb1Oj radicals can form d24mb1OH. However, unlike the decomposition pathway of d12mb4OH, 96% of d24mb1OH regenerates d24mb1Oj radicals. In contrast to d12mb4CH OH, d24mb1CH OH mainly forms d24mb1CH Oj radicals through reactions with H atoms, O atoms, and OH radicals. The difference in decomposition pathways arises from different activation energies for similar reactions. A small amount of d24mb1CH OH can convert to 1,2,4-trimethylbenzene, m-xylene, and d24mb1CHO.

Similar to d24mb1CHO, d14mb2CHO can convert to d14mb2COj radicals, p-xylyl radicals, and p-xylene. The d14mb2COj radical eliminates CO to form the CH32jC H CH -14 radical, which subsequently reacts with O to form the d14mb2Oj radical. Sixty-four percent of d14mb2Oj radicals eliminate CO and H atoms to form toluene, while 34% react with H atoms and HO radicals to form d14mb2OH. Similar to d24mb1OH, 96% of d14mb2OH regenerates d14mb2Oj radicals through reactions with OH radicals, CH radicals, and O atoms. Similar to d24mb1CH OH, d14mb2CH OH decomposes to form d14mb2CH Oj radicals, 1,2,4-trimethylbenzene, p-xylene, and d14mb2CHO.

In addition to the pathways forming the three dimethyl benzyl radicals, small amounts of 1,2,4-trimethylbenzene can react with OH radicals to form d24mb1CH Oj (9%) and d14mb2CH Oj (11%) radicals. The reaction forming d24mb1CH OH consumes 81% of d24mb1CH Oj radicals, while the reaction forming d14mb2CH OH consumes 28% of d14mb2CH Oj radicals. Through loss of CH O, d24mb1CH Oj and d14mb2CH Oj radicals can form CH34jC H CH - 13 and CH32jC H CH -14 radicals, respectively. Through similar reactions, d24mb1CHO and d14mb2CHO can be formed from d24mb1CH Oj and d14mb2CH Oj radicals, respectively. Although the rate constants for similar reactions are identical, the proportions of these reactions in the decomposition pathways of d24mb1CH Oj and d14mb2CH Oj radicals differ.

Sensitivity Analysis

[Figure 5: see original paper] shows the sensitivity analysis results for low-temperature oxidation of 1,2,4-trimethylbenzene at 925 K and 51% conversion. The results indicate that H-attack reactions on 1,2,4-trimethylbenzene have a strong inhibiting effect on its consumption. Additionally, unimolecular decomposition reactions involving C–H bond breaking at the 1- and 2-position methyl groups also inhibit 1,2,4-trimethylbenzene consumption. In contrast, reactions of HO radicals with the three dimethyl benzyl radicals significantly promote 1,2,4-trimethylbenzene consumption. Beyond these consumption pathways, the 1- and 2-position methyl groups of 1,2,4-trimethylbenzene can also react with OH radicals to form d24mb1CH Oj and d14mb2CH Oj radicals, representing important consumption pathways. Unimolecular decomposition reactions involving C–H bond breaking at the 4-position methyl group promote 1,2,4-trimethylbenzene consumption, opposite to the effect of C–H bond breaking at the 1- and 2-positions. Thus, the methyl group position in 1,2,4-trimethylbenzene has different effects on its consumption process, demonstrating that 1,2,4-trimethylbenzene chemistry is more complex than that of toluene [5, 6], xylene [7-9], and 1,3,5-trimethylbenzene [19].

Conclusions

This paper presents experimental and kinetic modeling studies of low-temperature oxidation of 1,2,4-trimethylbenzene. Experiments were conducted in a self-designed jet-stirred reactor at temperatures of 700–1100 K, an equivalence ratio of 1.0, and atmospheric pressure. Twenty-two species were detected by gas chromatography. A new kinetic mechanism for 1,2,4-trimethylbenzene was developed, and the simulation results agree well with experimental data. ROP analysis shows that the formation of three dimethyl benzyl radicals at the 1-, 2-, and 4-positions represents the main consumption pathways for 1,2,4-trimethylbenzene. Sensitivity analysis indicates that H-attack reactions have strong inhibiting effects on 1,2,4-trimethylbenzene consumption, while reactions of HO radicals with the three dimethyl benzyl radicals significantly promote its consumption.

References

[1] Edwards T, Maurice L Q. Surrogate mixtures to represent complex aviation and rocket fuels [J]. Journal of Propulsion and Power, 2001, 17(2): 461-466

[2] Honnet S, Seshadri K, Niemann U, et al. A surrogate fuel for kerosene [J]. Proceedings of the Combustion Institute, 2009, 32(1): 485-492

[3] Won S H, Sun W T, Ju Y G. Kinetic effects of toluene blending on the extinction limit of n-decane diffusion flames [J]. Combustion and Flame, 2010, 157(3): 411-420

[4] Saggese C, Frassoldati A, Cuoci A, et al. A wide range kinetic modeling study of pyrolysis and oxidation of benzene [J]. Combustion and Flame, 2013, 160(7): 1168-1190

[5] Yuan W H, Li Y Y, Dagaut P, et al. Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. I. Flow reactor pyrolysis and jet stirred reactor oxidation [J]. Combustion and Flame, 2015, 162(1): 3-21

[6] Yuan W H, Li Y Y, Dagaut P, et al. Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. II. A comprehensive kinetic modeling study [J]. Combustion and Flame, 2015, 162(1): 22-40

[7] Gaïl S, Dagaut P. Experimental kinetic study of the oxidation of p-xylene in a JSR and comprehensive detailed chemical kinetic modeling [J]. Combustion and Flame, 2005, 141(3): 281-

[8] Battin-Leclerc F, Bounaceur R, Belmekki N, et al. Experimental and modeling study of the oxidation of xylenes [J]. International Journal of Chemical Kinetics, 2006, 38(4): 284-302

[9] Gudiyella S, Malewicki T, Comandini A, et al. High pressure study of m-xylene oxidation [J]. Combustion and Flame, 2011, 158(4): 687-704

[10] Li Y Y, Cai J H, Zhang L D, et al. Experimental and modeling investigation on premixed ethylbenzene flames at low pressure [J]. Proceedings of the Combustion Institute, 2011, 33(1): 617-624

[11] Dagaut P, Karsenty F, Dayma G, et al. Experimental and detailed kinetic model for the oxidation of a Gas to Liquid (GtL) jet fuel [J]. Combustion and Flame 2014, 161(3): 835-847

[12] Roubaud A, Minetti R, Sochet L R. Oxidation and combustion of low alkylbenzenes at high pressure: comparative reactivity and auto-ignition [J]. Combustion and Flame, 2000, 121(3): 535-541

[13] Bikas G. Kinetic mechanisms for hydrocarbon ignition [D]. Aachen, Germany: RWTH Aachen University, 2001

[14] Hui X, Das A K, Kumar K, et al. Laminar flame speeds and extinction stretch rates of selected aromatic hydrocarbons [J]. Fuel, 2012, 97: 695-702

[15] Hui X, Sung C J. Laminar flame speeds of transportation-relevant hydrocarbons and jet fuels at elevated temperatures and pressures [J]. Fuel, 2013, 109: 191-200

[16] Won S H, Dooley S, Dryer F L, et al. Kinetic effects of aromatic molecular structures on diffusion flame extinction [J]. Proceedings of the Combustion Institute, 2011, 33(1): 1163-1170

[17] Weng J J, Liu Y X, Wang B Y, et al. Experimental and kinetic

investigation of 1,2,4-trimethylbenzene oxidation at low temperature [J]. Proceedings of the Combustion Institute, 2017: published online, http://dx.doi.org/10.1016/j.proci.2016.09.002

[18] Glarborg P, Kee R J, Grcar J F, et al. A fortran program for modelling well stirred reactors [R]. Albuquerque, USA: Sandia National Laboratories, 1986: Report No. SAND86-8209

[19] Diévart P, Kim H H, Won S H, et al. The combustion properties of 1,3,5-trimethylbenzene and a kinetic model [J]. Fuel, 2013, 109: 125-136

[20] Montgomery J A, Frisch M J, Ochterski J W, et al. A complete basis set model chemistry. VI. Use of density functional geometries and frequencies [J]. Journal of Chemical Physics, 1999, 110(6): 2822-2827

[21] Muller C, Michel V, Scacchi G, et al. A computer program for the evaluation of thermochemical data of molecules and free radicals in the gas phase [J]. Journal de Chimie Physique et de Physico-chimie Biologique, 1995, 92: 1154-1177

[22] Oehlschlaeger M A, Davidson D F, Hanson R K. Thermal decomposition of toluene: Overall rate and branching ratio [J]. Proceedings of the Combustion Institute, 2007, 31(1): 211-219

[23] Tian Z Y, Pitz W J, Fournet R, et al. A detailed kinetic modeling study of toluene oxidation in a premixed laminar flame [J]. Proceedings of the Combustion Institute, 2011, 33(1): 233-

[24] Brezinsky K, Litzinger T A, Glassman I. The high temperature oxidation of the methyl side chain of toluene [J]. International Journal of Chemical Kinetics, 1984, 16(9): 1053-

[25] Colket M B, Seery D J. Reaction mechanisms for toluene pyrolysis [J]. Proceedings of the Combustion Institute, 1994, 25(1): 883-891

[26] Tappe M, Schliephake V, Wagner H G. Reactions of benzene, toluene and ethylbenzene with atomic oxygen (o-3p) in the gas-phase [J]. Zeitschrift für Physikalische Chemie, 1989, 162: 129-145

[27] Baulch D L, Cobos C J, Cox R A, et al. Evaluated kinetic data for combustion modeling supplement-I [J]. Journal of Physical and Chemical Reference Data, 1994, 23(6): 847-1033

[28] Metcalfe W K, Dooley S, Dryer F L. Comprehensive detailed chemical kinetic modeling study of toluene oxidation [J]. Energy & Fuels, 2011, 25(11): 4915-4936