Fuel Processing Technology 92 (2011) 2030–2040

Contents lists available at ScienceDirect

Fuel Processing Technology

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

A kinetic modeling study of self-ignition of low alkylbenzenes at engine-relevant conditions

J.C.G. Andrae

J A Reaction Engineering, SE-183 32 Täby, Sweden

ARTICLE INFO

Article history:
Received 13 November 2010
Received in revised form 16 May 2011
Accepted 1 June 2011

Keywords:
Self-ignition
Auto-ignition
Low alkylbenzenes
Chemical kinetics

ABSTRACT

The self-ignition of low alkylbenzenes at engine-relevant conditions has been studied with kinetic modeling. A previously developed chemical kinetic model for gasoline surrogate fuels [J.C.G. Andrae, R.A. Head, *Combust Flame* 156 (2009) 842–51] was extended with chemistry for ethylbenzene and *m*-xylene resulting in an overall model consisting of 150 species and 759 reactions. In model validation, comparisons were made between model predictions and experimental data of ignition delay times measured behind reflected shock waves, laminar burning velocities collected at elevated temperature and pressure and species profiles in a high-pressure single pulse shock tube. Generally good agreement was found and the model is sensitive to changes in mixture strength, pressure and temperature. Shock tube ignition delay modeling results for ethylbenzene and *m*-xylene also compare well to the ones for toluene. The rate controlling step for the ignition of ethylbenzene in the current mechanism is the reaction with ethylphenyl radical and oxygen. Ignition delay time for *m*-xylene was found to be very sensitive to reactions involving hydrogen atom abstraction from fuel by hydroxyl and oxygen and to branching reactions where methylbenzyl reacts with oxygen and hydroperoxide. The validated mechanism was used to study fuel chemistry effects when blending ethylbenzene with the paraffinic fuels *iso*-octane and *n*-heptane. A sensitivity- and flow path analysis showed that a higher consumption of hydroperoxide by ethylphenyl than expected from the contribution of neat ethylbenzene in a fuel mixture with *iso*-octane inhibits both *iso*-octane and ethylbenzene ignition. This can explain the observed increase in ignition delay time and octane number for fuel mixtures compared to neat fuels.

1. Introduction

In order to reduce the emission of pollutants and toxic compounds, detailed modeling of combustion in engines is undertaken by engine makers. However, due to the high complexity of commercial fuels (gasoline, diesel, kerosene and jet), these models need kinetic reaction mechanisms for the combustion of simple surrogate fuels including representative hydrocarbons [1,2].

Aromatic hydrocarbons are important components of commercial gasoline, diesel, and jet fuels which according to a recent survey contain on average 25%, 33%, and 16% aromatics by volume respectively [3]. Among the aromatic hydrocarbons found in commercial fuels, alkylbenzenes in form of C_8H_{10} aromatics (xylenes and ethylbenzene) make up a substantial fraction, for example on average approximately 9% on a weight basis in gasoline [4], where they are used as octane-boosting additives with high research octane numbers (117.5 for 1,3-dimethylbenzene (*m*-xylene) and 116.4 for 1,4-dimethylbenzene (*p*-xylene)) [5]. Due to their relatively high concentrations in commercial fuels, aromatics have been proposed as components of surrogate mixtures for gasoline, diesel, and jet fuels [1,2,6–17]. In some of these surrogate mixtures xylenes have been proposed at concentrations as high as 20% [17].

Early studies of alkylbenzenes revealed that the length and number of alkyl side chains influenced the reactivity and that *o*-xylene (1,2-dimethylbenzene) was much more reactive with oxygen than *m*-xylene and *p*-xylene [18–20].

Reactions with oxygen and the three dimethylbenzene isomers and ethylbenzene were studied in an atmospheric flow reactor at high temperature (1060–1199 K) with diluted mixtures [21–23], and Roubaud et al. studied self-ignition of the fuels in a rapid compression machine at compressed temperatures between 600 and 900 K and compressed pressures up to 25 bar [24,25]. Gregory et al. [26] studied the chemical routes for the formation of exhaust hydrocarbons in a single-cylinder spark-ignition engine fueled with deuterium-labeled xylenes.

The oxidation (dilute conditions) of the three dimethylbenzenes also has been studied in jet-stirred reactor (JSR) at atmospheric pressure between 900–1400 K and comprehensive kinetic mechanisms were developed to describe the oxidation of the xylenes [27–29].

Battin-Leclerc et al. [30] performed shock tube ignition measurements for all three xylene isomers at reflected shock conditions of

---

E-mail address: joh1ana@gmail.com.

0378-3820/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.fuproc.2011.06.004

1330–1800 K, 6.7 to 9 bar, $\phi = 0.5$–2.0, and 92–98% argon dilution, observing no discernible difference in the reactivity of the three isomers at their conditions, and developed a comprehensive kinetic oxidation mechanism for all three xylene isomers.

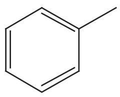
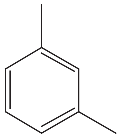
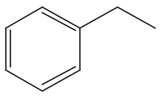
Except for the rapid compression machine data by Roubaud [24,25] most of the experiments described above are at atmospheric pressure. In a recent work, Shen and Oehlschlaeger [31] presented shock tube ignition delay time measurements for low alkylbenzenes (C_8H_{10}) at engine conditions (pressure 9–45 atm, temperature 941–1408 K and air as the oxidizer), the first data presented at the moderate-temperature elevated-pressure conditions. Narayanaswamy et al. [32] developed a consistent high-temperature kinetic mechanism for combustion of the substituted aromatic species toluene, styrene, *m*-xylene, ethylbenzene and 1-methylnaphthalene. The model was built on a detailed chemical mechanism for high temperature oxidation of smaller hydrocarbons developed by Blanquart et al. [33], and contained 158 species and 1049 reactions. The model was validated against a variety of data including plug flow reactors, ignition delay times, species profiles measured in shock tube and laminar flame speeds. Reasonable model prediction was found when compared to the shock tube data for ethylbenzene and *m*-xylene at engine like conditions in [31].

Ra and Reitz presented a compact chemical kinetic mechanism (113 species, 487 reactions) for internal combustion engine combustion simulations with multicomponent fuels [34]. Reduced chemistry for *n*-tetradecane, toluene, cyclohexane, dimethyl ether, ethanol and methyl butanoate were built and combined with a primary reference fuels mechanism to form a multi-surrogate fuel chemistry mechanism. Shock tube ignition delay time data and engine experiments were the principal targets for model validation.

However, smaller and numerically tractable chemical kinetic models that allows the self-ignition behavior to be modeled at engine conditions with realistic gasoline fuels containing low alkylbenzenes (except toluene), have not been presented. The purpose of this paper is therefore to present an extension of an existing chemical kinetic model developed for gasoline surrogate fuels [35,36] by the addition of chemical reactions for the fuels ethylbenzene and *m*-xylene. Table 1 shows information of these fuels together with toluene.

The principal target for validation of the kinetic model is the ignition delay time data by Shen and Oehlschlaeger measured in shock tube at engine conditions [31]. The model is also checked for validity against experimental data of laminar burning velocity and species profiles. Brute-force sensitivity analysis is conducted, and rate-limiting steps are deduced. The validated model is used to study fuel chemistry effects when blending aromatic and paraffinic fuels, and comparison to measured octane numbers is done. Sensitivity and rate-of-production analysis on the kinetic mechanism is used to analyze the results.

Table 1
Properties of low alkylbenzenes studied in this paper.

Fuel	Molecular formula	Chemical structure	Average concentration in gasoline (wt.%) [4]	RON [5]
Toluene	$C_6H_5CH_3$		12	120
m-xylene	$C_6H_4CH_3CH_3$		3.5	117.5
Ethylbenzene	$C_6H_5C_2H_5$		1.9	107.4

2. Chemical kinetic model and numerical solution method

The base mechanism for model development was a semi-detailed chemical reaction mechanism for gasoline surrogate fuels. It consists of a detailed reaction mechanism for toluene and ethanol, and a semi-detailed description of the chemistry for primary reference fuels *iso*-octane (2,2,4-trimethylpentane) and *n*-heptane. Overall the mechanism has 143 species and 672 reactions. More information of how the mechanism was constructed and validated can be found in [35,36]. No changes were made to the base mechanism (rate constants, thermo- and transport data).

Seven new species were introduced from the mechanism by Narayanaswamy et al [32]. They were $C_6H_5C_2H_2$ and $C_6H_5C_2H$ for ethylbenzene and $C_6H_4CH_3CH_3$, $C_6H_4CH_3CH_2$, $C_6H_4CH_3CHO$, $C_6H_4CHOCH_2$ and $C_6H_4CHOCHO$ for *m*-xylene with associated thermo- and transport data. Reactions with associated forward rate constants that were added to the base mechanism as a result of the introduction of new species are shown in Table 2 as 673–694 for ethylbenzene and 695–750 for *m*-xylene. Cross reactions (H atom abstraction reactions involving aromatic and aliphatic hydrocarbons) were also added to the model. They are shown in Table 2 as reaction 751–759.

No changes were made to rate constants in the ethylbenzene sub-set, but some of rate constants in the *m*-xylene sub-set were revised in this work in order to better predict shock tube ignition data. The source for thermodynamic data of smaller and larger species is different for the base mechanism in this work compared to Narayanaswamy et al [32]. A check of the impact on this uncertainty on the results for ethylbenzene and *m*-xylene was done by replacing some of the thermodata for the smaller and larger species in the mechanism by the Narayanaswamy et al data. Although a difference could be seen as a result of altering equilibrium constants, results did not deviate in a significant way. The chemical kinetic model is given in electronic format as supplementary material to the paper.

Simulations were performed with the Cantera software package [37,38]. When modeling shock tube ignition data, a homogeneous adiabatic reactor was assumed with the common constant internal energy, constant volume constraint. Ignition was assumed to be accomplished when the temperature had increased 400 K from the initial temperature. Similar ignition delay time is achieved when having an ignition criterion as the time when the hydroxyl radical (OH) reaches its maximum concentration.

3. Results and discussion

3.1. Model validation

The main purpose of the model is to be able to correctly describe self-ignition (or auto-ignition) at engine-like conditions for surrogates to transport fuels containing low alkyl-benzenes. Experiments conducted at those conditions (i.e. at high pressure) for the oxidation of C_8H_{10}-aromatic fuels are very limited. For this reason, the shock tube ignition delay data in [31] are the principal targets in the model construction and validation in this work.

Calculations of laminar burning velocity were also conducted as part of the model validation. Laminar burning velocity depends only on the mixture composition, temperature and pressure, making it an important target for combustion modeling.

Finally, the model was checked for validity against stable species data for toluene and *m*-xylene oxidation recently obtained in a high-pressure single pulse shock tube.

3.1.1. Ignition delay time in shock tubes

3.1.1.1. Ethylbenzene. Table 2 shows the reactions and associated rate constants specifically associated with the oxidation of ethylbenzene and *m*-xylene. The first three set of reactions for ethylbenzene (31,51–