A wide-range experimental and modeling study of oxidation and combustion of n-propylbenzene

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ABSTRACT

The oxidation of n-propylbenzene (NPB) was studied in a jet-stirred reactor (JSR) equipped with online GC and GC–MS for temperatures ranging between 700 and 1100 K, at $\varphi = 0.4$–2.0. In addition, laminar flame speeds were measured at $p = 1$, 3 and 6 bar at a preheat temperature of $T = 473$ K, and ignition delay times in a shock tube device behind reflected shock waves, for stoichiometric mixtures at around $p = 16$ bar. Mole fraction profiles of 25 intermediates including six species, namely 1-propenylbenzene, 2-propenylbenzene, α-methylstyrene, naphthalene, indene, and benzofuran were observed additionally. With φ increasing, NPB consumption shifts to higher temperatures, and the reaction temperature zone becomes broader. Based on the experimental measurements and on new calculations of the rate constants for the H-abstractions from NPB with OH, an updated kinetic model involving 292 species and 1919 reactions was developed with a reasonable agreement with the measured species profiles, flame speed values, and ignition delay times. Rate of production analysis reveals that NPB consumption is generally governed by C–H bond cleavage to form three $A1C_3H_6$ radicals, which mostly transform to styrene under rich condition and to benzaldehyde under lean condition. Compared to the aromatics formed in the oxidation of two other aromatic C9 fuels, 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene, NPB exhibits to be the most reactive fuel with the least aldehyde intermediates. Moreover, the present model gives a reasonable agreement with the literature-reported ignition delay times and JSR data. These results can improve the understanding of the oxidation and combustion of NPB as a surrogate fuel constituent for kerosene and diesel.

1. Introduction

In the past decades, the aviation industry experienced a rapid growth in both civilian and military areas. More and more attention has been paid to the combustion studies of aviation fuels, as the energy source of aircrafts, with respect to high efficiency and low pollutant emissions. Zheng et al. [1] identified the molecular class compositions of RP-3 aviation kerosene by gas chromatography–mass spectrometer (GC–MS) analysis as alkanes (53.0%), naphthenes (37.7%), aromatics (4.6%), and other minor species. Compositions of Jet-A POSF 4658 identified by Widegren and Bruno [2] applying GC–MS were alkanes (68.2%), aromatics (25.5%), naphthalenes (3.0%) and cycloalkanes (3.3%). Therefore, alkanes, cycloalkanes, and aromatics are the major components of all the aviation fuels certified today [3–5]. Due to the hundreds of components in aviation fuels, surrogate fuels have been commonly used to study the combustion of aviation fuels and make the modeling feasible.

NPB has been considered as an important component of surrogate model fuels in kerosene studies: NPB can yield more light hydrocarbons (e.g., methane, ethylene, and propene) and aromatics compared to other 1-ring aromatics, such as toluene, ethylbenzene, and xylene, with the advantage of a chemistry less complicated compared to the oxidation of butylbenzene resulting in much more isomers than NPB. For example, Dagaut et al. [6] used 74% n-decane and 26% NPB as surrogate model fuel of kerosene. For these reasons, it is worth investigating the oxidation of NPB in order to better understand the underlying mechanism process in NPB combustion.

The focus of most previous studies on NPB was put on species profiles, burning velocities (flame), and ignition (shock tube). In 2005, Johnston and Farrell [7] studied the laminar burning

velocities of NPB in a stainless steel vessel at 450 K and 304 kPa for equivalence ratios of 0.8–1.4. The study of NPB laminar flame speeds with both experiments and model was reported by Hui et al. [8,9] ($\varphi = 0.7$–1.4, 400 and 450 K, $p = 1$ atm); they also considered the influence of temperature and pressure ($\varphi = 0.7$–1.3, 350–470 K; $p = 1$–3 atm). In recent years, Ji et al. [10] and Mehl et al. [11] studied the laminar flame speed of NPB at atmospheric pressure, in a wide range of equivalence ratios. Studies of ignition delay times of NPB were first reported by Roubaud et al. [12] (600–900 K, $\varphi = 1.0$, 24.7 atm), and later on by Darcy et al. [13–15] ($\varphi = 0.29$–1.92, 1–50 atm, 800–1600 K). Gudiyella and Brezinsky [16,17] applied the shock tube technique to study mole fraction profiles by using standard GC-techniques during NPB oxidation and pyrolysis ($\varphi = 0.5$–1.9, 838–1678 K, 25 and 50 atm). Anderson et al. [18] reported on mole fraction profiles obtained by mass spectrometer when studying a non-premixed laminar flame of NPB doped with methane. Wang et al. [19] discussed the mole fraction profiles of reactants, intermediates and products measured in a fuel-rich ($\varphi = 1.79$) premixed low-pressure laminar flame of NPB by using synchrotron VUV photoionization mass spectrometry [20,21].

The oxidation data of mole fraction profiles of NPB are quite limited. Dagaut et al. [22] studied the oxidation of NPB in a JSR within 900-1250 K, 1 atm, and at variable equivalence ratios ($0.5 \leq \varphi \leq 1.5$). Mole fractions of 23 species were measured with GC. They proposed a comprehensive model to reproduce the experimental data. However, many aromatic species (soot precursors) were not measured. Thus, an investigation of the oxidation of NPB is desirable to reveal the reaction pathways and, moreover, to improve the NPB reaction model.

This work aims to identify and quantify intermediates and products of NPB oxidation as well as to measure its burning velocities and ignition delay times. Based on the experimental data set, the second goal is to develop a comprehensive reaction model involving the aromatic species newly detected in the present work. Rate of production (ROP) and sensitivity analyses were performed to identify the consumption pathways of NPB and the key reactions. Furthermore, the comparison of the oxidation of three C9 isomers, namely 1,3,5-trimethylbenzene (135TMB), 1,2,4-trimethylbenzene (124TMB) and NPB, was presented to reveal the differences among the major intermediates and consumption pathways. The updated mechanism will improve the understanding of the combustion characteristics of diesel and jet fuels, in particular with respect to the formation of soot precursors and aldehydes, pollutants being of pivotal role for local air quality.

2. Experiments

2.1. Oxidation

The experiments were carried out in a home-made JSR. The details of the setup and procedure can be found in our recent work [23,24], and only a brief description is given here. The JSR was equipped with online GC (7890B, Agilent) and GC–MS (7890B-5977A, Agilent) for gas analysis. The inlet concentration of NPB is 1.0 % and the equivalence ratios (φ) are from 0.4 over 1.0 to 2.0, as shown in Table S1 in the Supplemental Material (SM). Compared to the previously reported JSR work by Dagaut et al. [22] (0.1 % NPB, $\varphi = 0.5$-1.5), a higher concentration of NPB and a wider range of equivalence ratios were used in the present work in order to produce observable higher concentrations of intermediates. An estimate of the heat release is added in Section 1 of SM.

The flow rates of O_2 and Ar were regulated by MKS mass-flow controllers. The fuel was injected into a vaporization tank by a high-pressure infusion pump (FL2200, Fuli), then vaporized at 473 K and carried out by 450 sccm gas flow of Ar. All the tubes were kept at 473 K by heating belts before entering JSR to min-
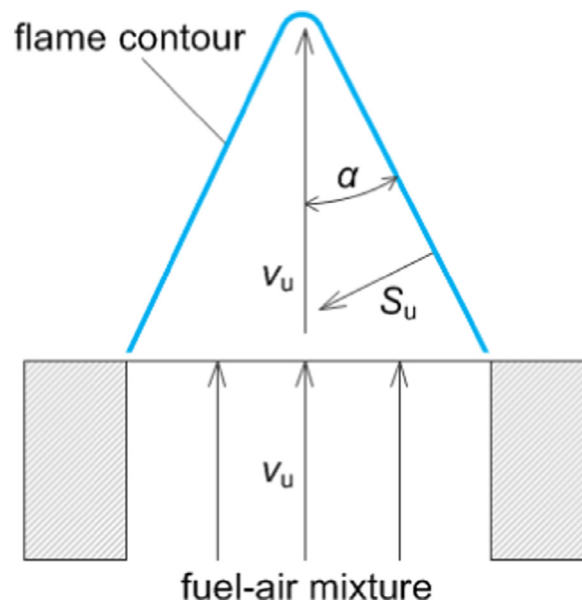

Fig. 1. Determination of the laminar burning velocity (S_u) using the cone angle method (α – cone angle, v_u – velocity of the unburned gas).

imize temperature gradients and after JSR to avoid condensation. The temperature range was 700–1100 K in the present work. The temperature ramp was 25 K between the data points. The temperature of JSR was controlled by a heating controller (HT60, Horst). The reaction temperature was measured by a K-type thermocouple located at the center of the sphere.

The GC and GC–MS techniques were used to quantify and qualify the products and intermediates. TCD was used to analyze H_2, CO, CO_2 and CH_4. The quantification of light hydrocarbons and aromatics was performed by FID with chromatographic columns of Al_2O_3-KCl and HP-INNOWax, respectively. The calibration was carried out by injecting known amounts of the standard gases. The newly detected intermediates without standard gas (e.g., $A1C_3H_5$) were quantified by using the effective carbon number method. The detection threshold of GC was about 0.1 ppm for FID and 10.0 ppm for TCD. The estimated uncertainty was about $\pm 5\%$ for major species and $\pm 15\%$ for intermediates. The experimental conditions and detailed analysis of methods are given in Section 2 in SM, followed by the original measured data (Tables S2–S7) in Section 3.

2.2. Laminar burning velocity

Values of the laminar burning velocity (S_u) were determined at a preheat temperature of $T = 473$ K, at pressures of 1, 3, and 6 bar within a wide range of φ by applying the cone angle method [25,26]. According to Fig. 1, S_u is calculated from the cone angle α of the flame and the velocity (v_u) of the unburned gas: $S_u = v_u \cdot \sin \alpha$. For the determination of the cone angle, premixed conical-shaped flames have been stabilized above a flame holder by the use of a coflow, either air for rich flames ($\varphi \geq 1.0$) or a mixture of 5% CH_4, 5% H_2 and 90% N_2 for lean flames ($\varphi \leq 1.0$). The used burner has been described in previous studies [27–30]. The fuel was first vaporized at temperatures between 473 and 560 K (depending on pressure), then mixed with a preheated N_2-stream (Linde, 99.999%), and adjusted to the setting temperature of 473 K. Finally, O_2 (Linde, 99.95%) was added so that the ratio between N_2 and O_2 matches their amounts in air (N_2:$O_2 = 79$:21). The liquid flow rate of NPB was controlled by a HPLC-pump (LC-20AD, Shimadzu) and the gas flows of N_2 and O_2 by mass flow controllers