DEVELOPMENT OF A KINETIC MECHANISM FOR NO$_x$ FUEL INTERACTION

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Abstract

This work introduces a newly developed reaction mechanism to predict fuel/NO$_x$ interaction in freely propagating, burner stabilized premixed flames, shock tubes, jet stirred reactors and plug flow reactors experiments. The study focuses on pure ammonia as fuel as well as H$_2$, H$_2$/CO, CH$_4$ doped with NO, NO$_2$ and N$_2$O. The kinetic scheme also focuses on the formation and consumption of nitrogen oxides at different experimental conditions. It is found that the doping with N$_2$O has almost no sensitivity on the H$_2$ chemistry, while small amount of NO$_2$ is enough to change the pressure dependence of H$_2$ auto ignition. The experiments with N$_2$O still show the significant influence of the chain breaking reaction H+O$_2$(+M)$\leftrightharpoons$HO$_2$(+M) on the H$_2$ ignition delay times, resulting in the crossing lines for the ignition delay times, which are moved at higher pressure to higher temperature. The concentration of HO$_2$ is decisive for the active reaction pathway in shock tube oxidation as well as in jet stirred and flow reactor. Reaction NO+HO$_2$$\leftrightharpoons$NO$_2$+OH and NO$_2$+H$\leftrightharpoons$NO+OH are very important because they strongly influence the inter conversion process of NO and NO$_2$ in jet stirred reactor and flow reactor for cases studied herein. The formation of NO in burner stabilized premixed flames is shown to demonstrate the capability of the mechanism to be integrated into mechanisms for hydrocarbon oxidation.

Introduction

Several NO$_x$ formation mechanisms have been developed in recent years, often dedicated to particular conditions of interest. Unlike hydrocarbons, there are not enough experimental or modelling studies for nitrogen related chemistry available. Still today we lack reliable rate parameter values, thermochemistry data and a sufficient experimental data base for validating NO$_x$ model. To support the engine development process by simulations, detailed mechanisms for the oxidation of ammonia (NH3) and the formation and the reduction of NO$_x$ are needed. This highly motivates the development of a detailed kinetic model in this work. The objective of our work is to develop the reliable kinetic model validated over a wide range of experimental data, i.e. laminar flame speeds, ignition delay times, speciation in jet stirred reactors (JSR), in plug flow reactors (PFR) and in burner stabilized flames (BSF) for pure fuels and mixtures. An updated kinetic mechanism for the H$_2$ and C$_1$ system along with NO$_x$ formation and consumption has been developed on the basis of an extensive literature review, including wide set of experimental data. The kinetic model has been developed on a hierarchical basis: first H$_2$ combustion, than H$_2$/CO and NH$_3$, NO, NO$_2$, N$_2$O and their mixtures. Further model is extended to include C$_1$ chemistry higher than CO.

H$_2$/CO/NH$_3$/NO$_x$ Kinetic model and validation

The detailed chemical kinetic mechanism of H$_2$ and CO is developed and validated extensively. The reaction rate parameter in this subset of mechanism in mostly based on the recommendations of Baulch et al. [1] and the uncertainty boundaries proposed by the authors. We refer Baulch et al. [1] because it is a comprehensive source, which provides reaction rate constants with their uncertainties. Alongside a NH$_3$/NO$_x$ mechanism is developed. Ammonia is discussed as a carbon-free alternative fuel produced by overpower from alternative

energy system [2]. Ammonia was also discussed as an internal measure in Diesel engines to recycle NO to form N_2. Most recently there has been various experimental studies on the NH_3 and H_2-NH_3 oxidation due to which the development and validation of NO_x model can be improved. The two key parameters for NH_3 combustion, laminar flame speed (see Fig 1 (a)) and ignition delay time (see Fig 1 (b)) are compared against the developed model. All simulations were performed using LOGEsoft 1.08.00 [3].
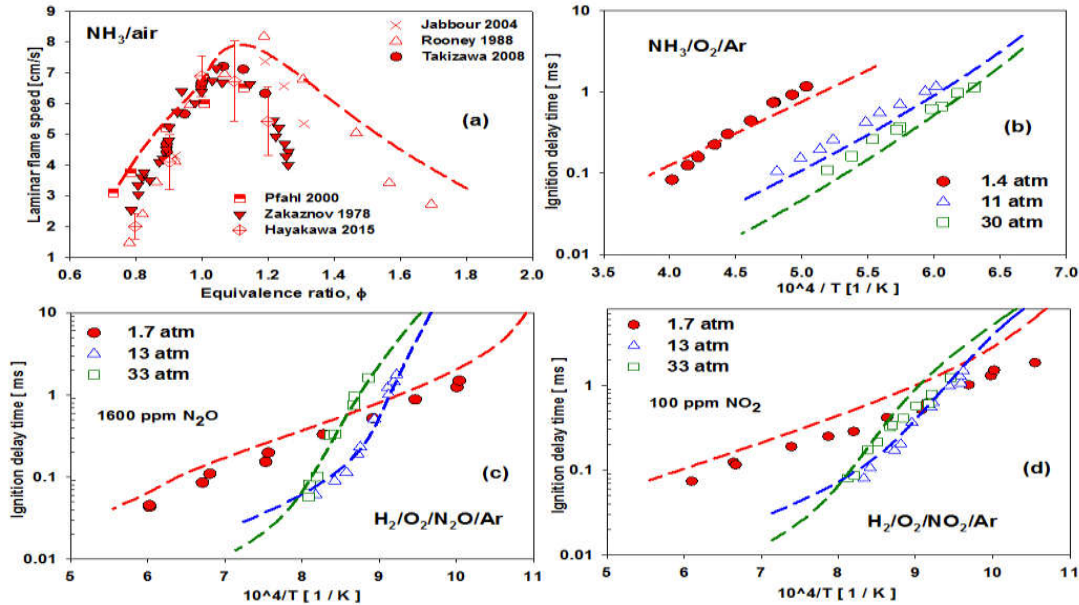

Figure 1. Comparison between model prediction and measurements. Symbols: Experimental data. Lines: model prediction. (a) laminar flame speed of NH_3/air at 298 K , 1 atm [3–7]; (b) ignition delay time of NH_3/O_2/Ar(99%),Φ=1.0 [9]; (c)H_2/N_2O(1600 ppm)/O_2/N_2 [11] and (d) H_2/NO_2(100 ppm)/O_2/N_2 [12] in shock tube respectively.

To develop the H_2/CO/NH_3/NO_x model various fuel mixtures at different conditions have been studied and validated against the wide set of experimental data available from literature. The laminar flame speed of NH_3/air mixture (at 298 K, 1atm, Fig. 1(a)) is very low compared to hydrocarbons and may not be well suited for internal combustion engines. As can be seen from Fig. 1 there is large discrepancies within the experimental data from literature which suggest that more accurate and reliable experimental data for ammonia laminar flame speed is required. However, the low laminar flame speed of NH_3 can be increased by the addition of H_2 as it is done for hydrocarbons which will promote the formation of H, O and OH radicals. The present model shows good agreement with published experimental data for NH_3/H_2/air laminar flame speed (not shown here).

Speciation of the NH_3-H_2 (Fig. 2 (c)), NH_3-H_2-NO (Fig. 2 (d)), NH_3-NO, H_2-N_2O and CO-N_2O system was studied in burner stabilized flames. Oxidation of H_2 in presence of NO and NO_2, H_2-CO system doped with NO was studied in JSRs. Further flow reactor experimental targets of H_2 oxidation in presence of NO and CO oxidation in presence of NO and NO_2 was also considered for model development and validation. In NH_3 and NH_3-H_2 flames NO formation is mainly controlled by $N+O_2 \rightleftharpoons NO+O$ and $N+OH \rightleftharpoons NO + H$ reactions. NH_3 subsequently decomposes to the Amidogen radical (NH_2) which, decomposes to the Imidogen radical (NH). Both are very reactive species and their reactions with H, O, OH, NO control the overall reactivity of the system. Overall good agreement between the model prediction and experimental data is observed. With the available published experimental data for the H_2-N_2O (Fig. 1(c)) and H_2-NO_2 (Fig. 1(d)) system in shock tubes the model was validated. H_2 oxidation in JSRs in presence of NO and NO_2 was also investigated (see Fig. 2 (a, b)). The conversion of NO to NO_2 is explained by the chain propagation reaction $NO+HO_2 \leftrightharpoons NO_2+OH$, which is accelerating the H_2 chemistry. As can be seen the highest NO_2 concentration occurs at 790 K. At

higher temperature the reaction progress of the H_2 oxidation reaches higher values, and NO_2 is reduced to NO via reaction $NO_2+H \leftrightarrows NO+OH$. It was found that in H_2-NO/NO_2 and CO-NO/NO_2 system reaction $NO+HO_2 \leftrightarrows NO_2+OH$ and $NO_2+H \leftrightarrows NO+OH$ are very important for inter conversion between NO and NO_2.
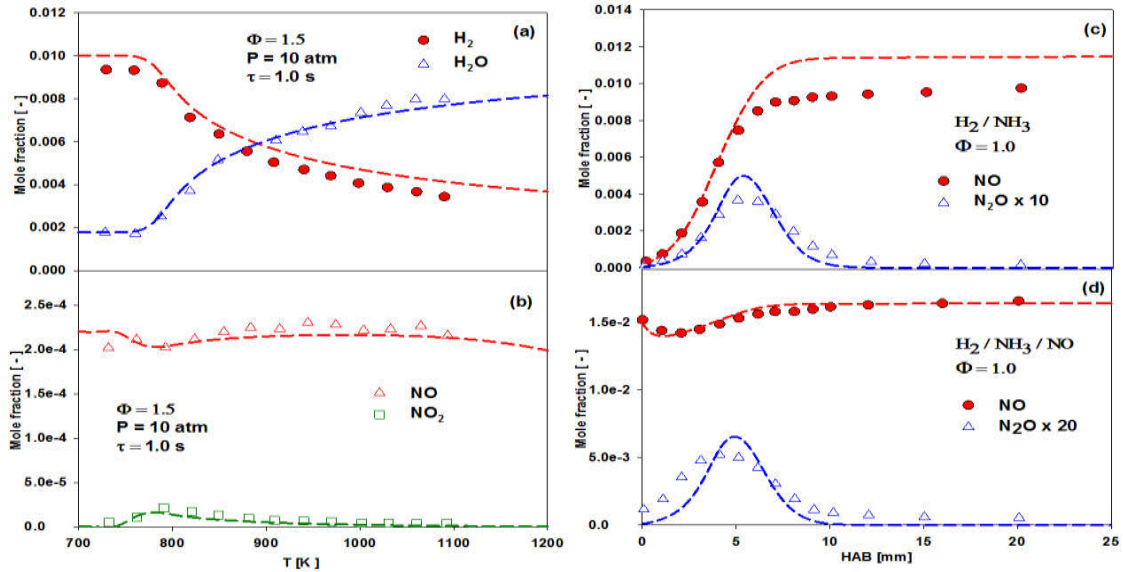

Figure 2. Comparison between experimental data and model prediction from this work. (a,b) $H_2(0.01)/O_2(0.00333)/NO(220 \text{ ppm})/N_2$ oxidation in JSR at $\Phi = 1.5$, p = 10 am and $\tau = 1.0$ s, symbols measurements from [10]. (c,d) Species profile comparison between measurements and model prediction(imposing experimental temperature profile) in burner stabilized premixed flame at 4.6 kPa, (c) $NH_3(0.03)/H_2 (0.209)/O_2 (0.127)/Ar (0.634)$; (d) $NH_3 (0.015)/H_2 (0.2315)/NO (0.015)/O_2 (0.1195)/Ar (0.6190)$, symbols measurements from [13].

$C_1 - NO_x$ Kinetic model and validation

The model for $H_2/CO/NH_3/NO_x$ was extended to include C_1 fuel chemistry. The updated model includes methane, methanol and formaldehyde as fuels and was validated against a wide set of experimental data available from literature.
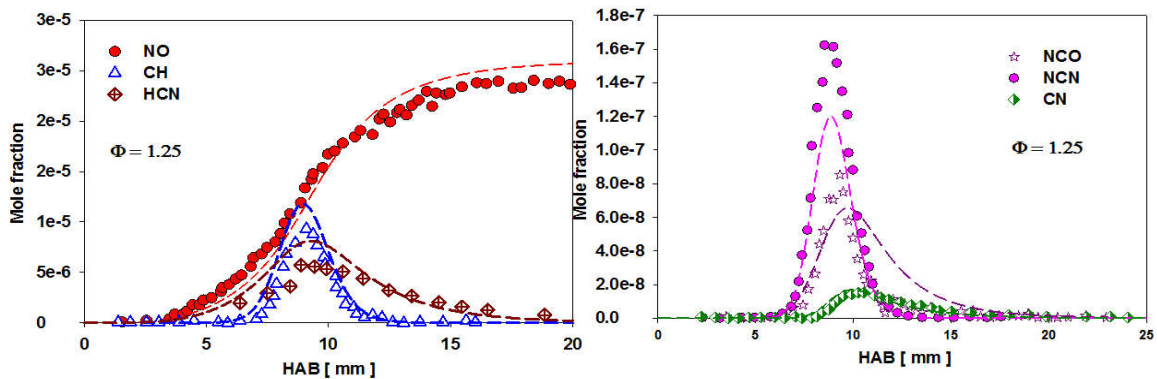

Figure 3. Speciation in premixed $CH_4/O_2/N_2$ flame at p = 5.3 kPa; T = 273.15 K; Φ=1.25. Symbols: measurements from Lamoureux et al. 2016 [20], lines: present model prediction imposing experimental temperature profile.

Special attention was paid for the formation and consumption of NO. In flames prompt-NO formation (see Fig. 3) results from the reaction between CH and N_2 yielding Cyanonitrene (NCN) and H. The NCN radicals reacts with H and O atoms yielding HCN+N and CN+NO, respectively. Beside NO profile other radicals (CH, NCN, CN, HCN and NCO) which are important in nitrogen chemistry (see Fig. 3) are also taken into consideration for the model development and validation.

The sensitivity of thermochemistry on NO_x prediction was investigated, especially for the NCN radical for which the enthalpy values reported in the literature varies by more than 10 kJ/mol (see Fig. 4(a) and Fig. 4(b)). Finally based on our study we choose the NCN thermochemistry from the theoretical study by Goos et.al. 2013 [14]. It was found that the rate parameter for the two main reactions (CH + N_2 ⇌ NCN + H and NCN + H ⇌ HCN + N) are important for the NO_x prediction in flames which was reviewed based on the experimental and theoretical study from literature [15–19]. The product branching ratio of the reaction NCN + H is also important which subsequently effects the NO_x prediction.

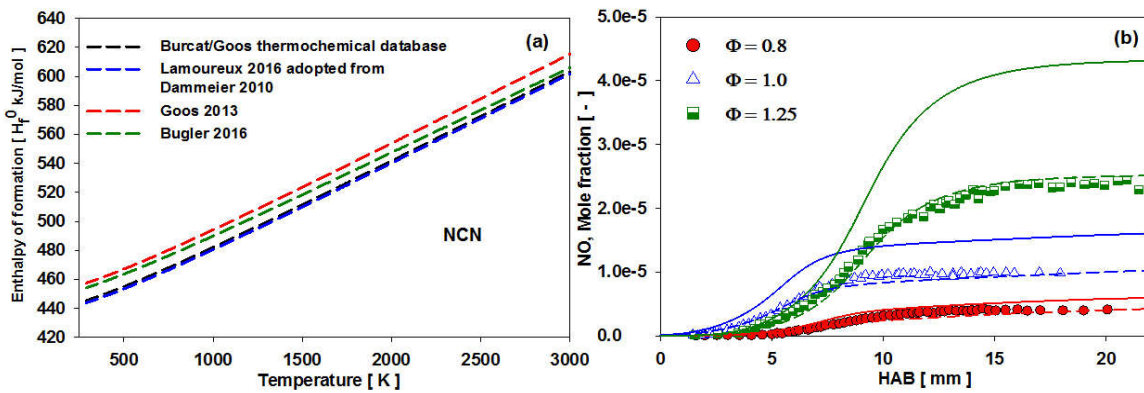**Figure 4.** (a), NCN Enthalpy comparison between different authors; black [21]:HF298=445.7 kJ/mol, blue [20]:HF298=444.1 kJ/mol, red [14]:HF298=457.8 kJ/mol and green [22]: HF298=454.52 kJ/mol. (b), Effect of NCN thermochemistry on NO prediction in $CH_4/O_2/N_2$ low pressure burner stabilized flame at p= 5.3 kPa, T=273 K at different equivalence ratio. Symbols: measurements from [20]. Continuous lines: prediction using the NCN thermochemistry of Lamoureux et.al. 2016 (HF298=444.1 kJ/mol) [20]; dash lines: prediction using NCN thermochemistry of Goos et.al. 2013 (HF298=457.8 kJ/mol) [14].
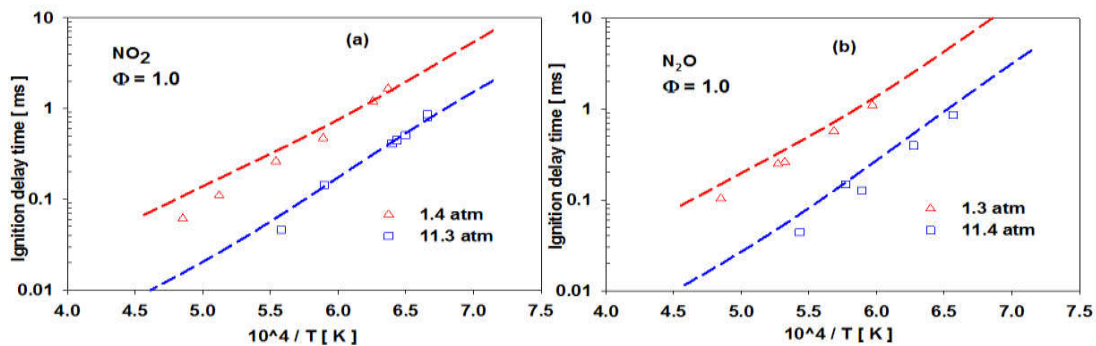

Figure 5. Ignition delay time comparison between experimental data from [27] and model prediction from this work. (a) CH_4 (0.83%)/O_2 (1.67%)/NO_2 (0.1383%)/Ar (b) CH_4 (0.83%)/O_2 (1.67%)/N_2O (0.1383%)/Ar.

Ignition delay time of CH_4/NO_2 and CH_4/N_2O mixtures in shock tube experiments (see Fig. 5) have also taken into account as model development target. In addition experiments dedicated to CH_4 oxidation in presence of NO in JSR [23] were also considered and model is well able to predict consumption and formation of NO_x.

Methanol oxidation in presence of NO in a JSR [24, 25] was also investigated and model performs well at those condition, too. Further experiments dedicated to HCN oxidation in a JSR [26] are also considered in model development targets.

Conclusion

In this work we developed a $H_2/C_1/NH_3/NO_x$ kinetic model which is validated over a wide range of experimental targets for pure fuels and mixtures. Overall there is a good agreement between the model prediction and measurements for broader range of experimental conditions obtained from published literature. We showed that the $H_2/CO/NH_3/NOx$ model was successfully extended to include C_1 chemistry and in future works this model can be further extended to include higher hydrocarbon. It was found that effect of NCN thermochemistry on prompt NO formation in premixed flames is significant. More accurate and reliable thermochemistry of NCN and other nitrogen related species are required to enhance the current understanding of NO_x chemistry and improve kinetic models. Rate parameters of reactions related to nitrogen chemistry are limited, future work should be dedicated for more reliable rate constant values at combustion condition from both experimental and theoretical side.

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