

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 H₂, H₂/CO, CH₄ doped with NO, NO₂ and N₂O. The kinetic scheme also focuses on the formation and consumption of nitrogen oxides at different experimental conditions. It is found that the doping with N₂O has almost no sensitivity on the H₂ chemistry, while small amount of NO₂ is enough to change the pressure dependence of H₂ auto ignition. The experiments with N₂O still show the significant influence of the chain breaking reaction $H+O_2(+M)\rightleftharpoons HO_2(+M)$ on the H₂ 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 HO₂ is decisive for the active reaction pathway in shock tube oxidation as well as in jet stirred and flow reactor. Reaction $NO+HO_2\rightleftharpoons NO_2+OH$ and $NO_2+H\rightleftharpoons NO+OH$ are very important because they strongly influence the inter conversion process of NO and NO₂ 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 H₂ and C₁ 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 H₂ combustion, than H₂/CO and NH₃, NO, NO₂, N₂O and their mixtures. Further model is extended to include C₁ chemistry higher than CO.

H₂/CO/NH₃/NO_x Kinetic model and validation

The detailed chemical kinetic mechanism of H₂ and CO is developed and validated extensively. The reaction rate parameter in this subset of mechanism is 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 NH₃/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 N₂. Most recently there has been various experimental studies on the NH₃ and H₂-NH₃ oxidation due to which the development and validation of NO_x model can be improved. The two key parameters for NH₃ 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].

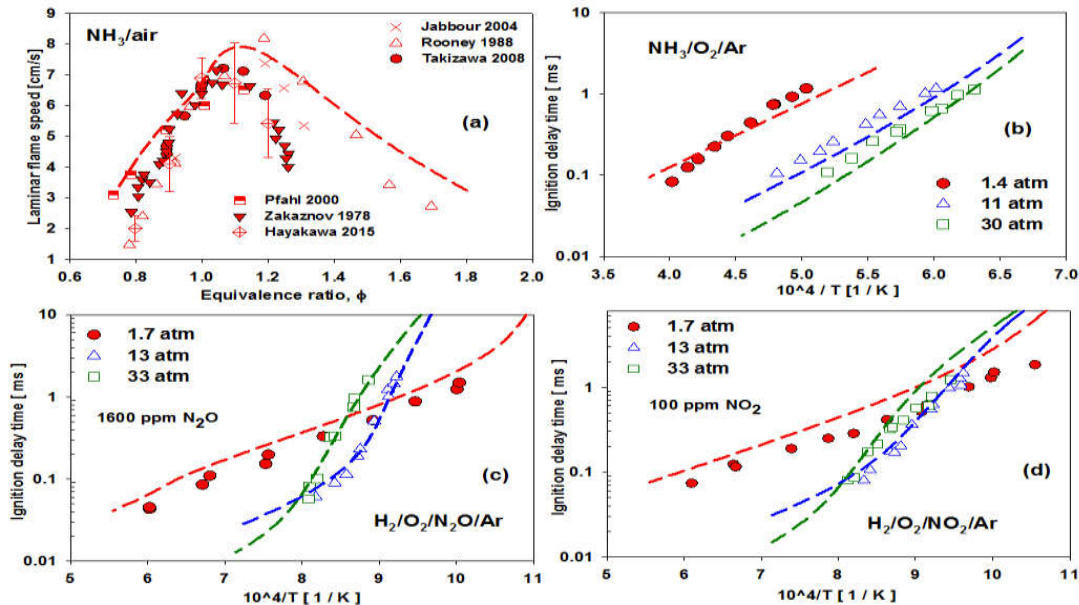


Figure 1. Comparison between model prediction and measurements. Symbols: Experimental data. Lines: model prediction. (a) laminar flame speed of NH₃/air at 298 K , 1 atm [3–7]; (b) ignition delay time of NH₃/O₂/Ar(99%), $\Phi=1.0$ [9]; (c)H₂/N₂O(1600 ppm)/O₂/N₂ [11] and (d) H₂/NO₂(100 ppm)/O₂/N₂ [12] in shock tube respectively.

To develop the H₂/CO/NH₃/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 NH₃/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 NH₃ can be increased by the addition of H₂ 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 NH₃/H₂/air laminar flame speed (not shown here).

Speciation of the NH₃-H₂ (Fig. 2 (c)), NH₃-H₂-NO (Fig. 2 (d)), NH₃-NO, H₂-N₂O and CO-N₂O system was studied in burner stabilized flames. Oxidation of H₂ in presence of NO and NO₂, H₂-CO system doped with NO was studied in JSRs. Further flow reactor experimental targets of H₂ oxidation in presence of NO and CO oxidation in presence of NO and NO₂ was also considered for model development and validation. In NH₃ and NH₃-H₂ flames NO formation is mainly controlled by N+O₂ \rightleftharpoons NO+O and N+OH \rightleftharpoons NO + H reactions. NH₃ subsequently decomposes to the Amidogen radical (NH₂) 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 H₂-N₂O (Fig. 1(c)) and H₂-NO₂ (Fig. 1(d)) system in shock tubes the model was validated. H₂ oxidation in JSRs in presence of NO and NO₂ was also investigated (see Fig. 2 (a, b)). The conversion of NO to NO₂ is explained by the chain propagation reaction NO+HO₂ \rightleftharpoons NO₂+OH, which is accelerating the H₂ chemistry. As can be seen the highest NO₂ 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 $NO_2+H\rightleftharpoons NO+OH$. It was found that in H_2 - NO/NO_2 and CO - NO/NO_2 system reaction $NO+HO_2\rightleftharpoons NO_2+OH$ and $NO_2+H\rightleftharpoons NO+OH$ are very important for inter conversion between NO and NO_2 .

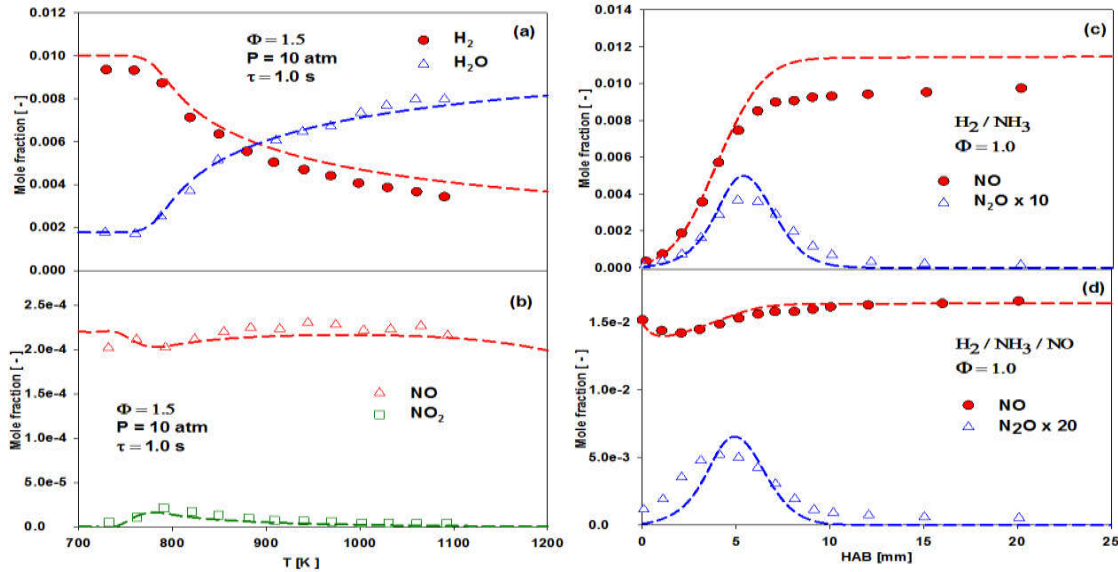


Figure 2. Comparison between experimental data and model prediction from this work. (a,b) $H_2(0.01)/O_2(0.00333)/NO(220 \text{ ppm})/N_2$ oxidation in JSR at $\Phi = 1.5$, $p = 10 \text{ atm}$ and $\tau = 1.0 \text{ s}$, symbols measurements from [10]. (c,d) Species profile comparison between measurements 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.

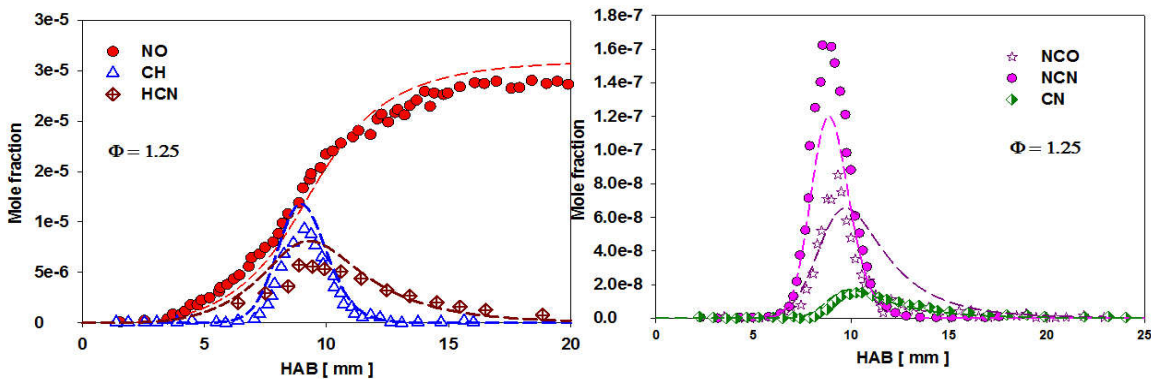


Figure 3. Speciation in premixed $CH_4/O_2/N_2$ flame at $p = 5.3 \text{ kPa}$; $T = 273.15 \text{ K}$; $\Phi = 1.25$. Symbols: measurements from Lamoureux et al. 2016 [20], lines: present model prediction imposing experimental temperature profile.

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 N₂ 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 + N₂ ⇌ 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.

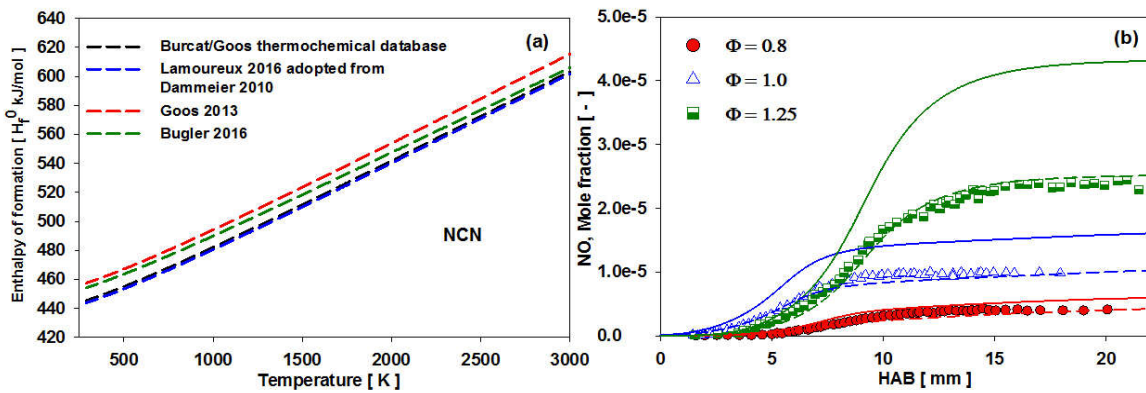


Figure 4. (a), NCN Enthalpy comparison between different authors; black [21]:HF298=445.7 kJ/mol, blue [20]:HF298=444.1 kJ/mol, red [14]:HF298=457.8 kJ/mol and green [22]: HF298=454.52 kJ/mol. (b), Effect of NCN thermochemistry on NO prediction in CH₄/O₂/N₂ low pressure burner stabilized flame at p= 5.3 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].

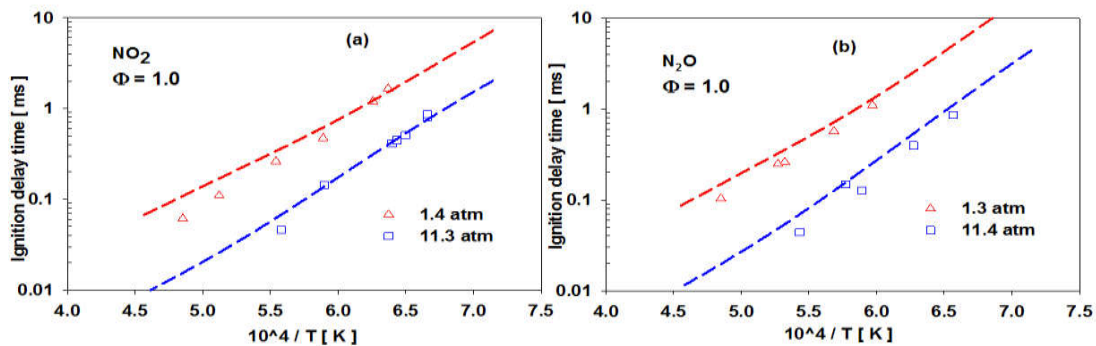


Figure 5. Ignition delay time comparison between experimental data from [27] and model prediction from this work. (a) CH₄ (0.83%)/O₂ (1.67%)/NO₂ (0.1383%)/Ar (b) CH₄ (0.83%)/O₂ (1.67%)/N₂O (0.1383%)/Ar.

Ignition delay time of CH₄/NO₂ and CH₄/N₂O mixtures in shock tube experiments (see Fig. 5) have also taken into account as model development target. In addition experiments dedicated to CH₄ 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 $H_2/CO/NH_3/NO_x$ 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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