Modeling for Nitromethane oxidation

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INTRODUCTION

The diminishing availability of conventional fuels and stricter regulations on pollution control and CO_2 emission targets have led scientist and engineers to look for alternative fuels. Recently nitromethane has slowly gained interest as alternative fuel over conventional fuel for internal combustion engines. In the past, it was mostly used as rocket propellant or as an explosives [1,2]. Nitromethane is an energetic compound with a wide variety of applications, including its use as a monopropellant, a liquid explosive, a solvent for chemical processing and analysis, and a high-performance fuel additive for internal combustion engines and pulsed detonation engines [3]. The chemical formula of nitromethane is CH_3NO_2. As the name suggests, the molecule is essentially methane with one of the four hydrogens replaced by a nitro group. In essence, it is the simplest of possible energetic CHON molecules that contain nitro groups, which is why it is often used in reaction studies as a prototype for more complex energetic materials. There is no reliable kinetic model for nitromethane combustion, which is validated over a wide range of experimental conditions. There are a few published studies [4–8] both numerically and experimentally focusing often on a single reactor at very specific conditions.

The aim of the present work is to extend our recently published mechanism [9] for syngas, methane and ammonia oxidation to include CH_3NO_2 as fuel and validate against the available experimental data from the literature. The development and compilation strategy for our mechanism is described in our recent work [9] and this study is conducted in a similar manner. Rates are taken mainly from [7,10–16]. This makes the kinetic model more robust and reliable for combustion modelling.

KINETIC MODEL AND VALIDATION

A detailed CH_3NO_2 kinetic model is developed and validated together with the NO_x chemistry. This mechanism also includes ammonia (NH_3) as a carbon-free alternative fuel producible by overpower from alternative energy systems. Most recently, there have been various experimental studies on the CH_3NO_2 due to which the development and validation of CH_3NO_2 models can be improved. To develop the C/H/N/O model various fuel mixtures at different conditions have been studied and validated against the wide set of experimental data available from the literature. All simulations were performed using LOGEresearch 1.10.00 [17].

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The ignition delay time of nitromethane obtained from shock tube experiments are compared against the developed model in Figure 1. The model agrees very well with the experimental data. The model follows the equivalence ratio dependency of ignition delay time (Figure 1(a)) and the pressure dependency (Figure 1(b)). The flame structure of the premixed nitromethane flame is studied numerically, which gives important information on emission formation from the fuel oxidation.
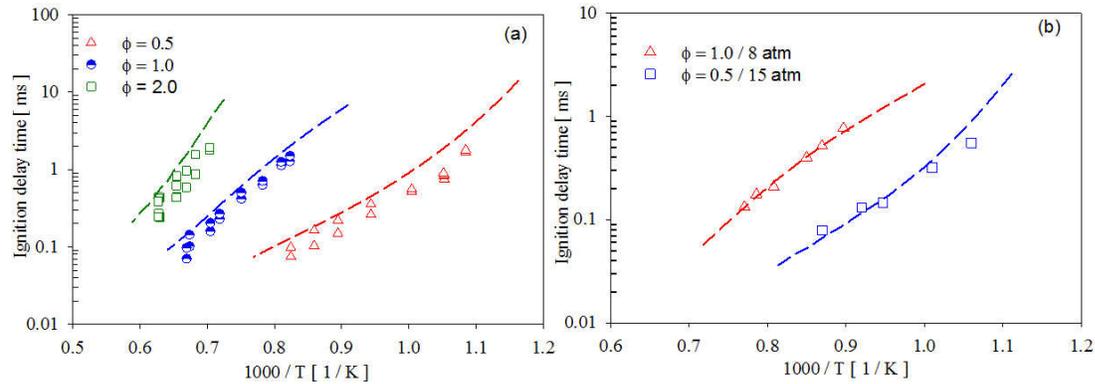

Figure 1: Ignition delay time comparison between experimental data and model prediction for CH₃NO₂/O₂/Ar in a shock tube. (a) Mathieu et al. [4] *, ϕ = 0.5, 4 % CH₃NO₂; ϕ = 1.0, 2.857 % CH₃NO₂; ϕ = 2.0, 1.455 % CH₃NO₂ at 2 atm (b) Nauclér et al.* [5] *ϕ = 1.0, 4 % CH₃NO₂, ϕ = 0.5, 2 % CH₃NO₂.*

Speciation of $CH_3NO_2/O_2/Ar$ premixed flames was studied in low-pressure burner stabilized flames for three different equivalence ratios by Zhang et al. [7]. Figure 2 shows the comparison between the model predictions against the experimental data from [7] for the stoichiometric condition. In this flame, 65 % of CH_3NO_2 is mainly decomposed to CH_3 and NO_2 via thermal decomposition and around 32 % of CH_3NO_2 reacts with radicals (H, OH, O, and CH_3) mainly forming CH_2NO_2. The formed CH_3 reacts with O radical and CH_2NO_2 undergoes thermal decomposition forming CH_2O+H and CH_2O+NO respectively. The NO_2 formed in the above process via thermal decomposition mainly forms NO via reaction NO_2+H⇋NO+OH (major channel) and reacts with CH_3 to form CH_3O+NO (minor channel). The formed NO further reacts with NCO and NH mainly forming N_2O. NO also reacts with the radicals CH_3, CH, CH_2-1 and CH_2-3 forming HCN as the main product. Overall, good agreement between the model prediction and experimental data is observed for major species while for intermediate nitrogenous species model under predicts the measurements. It should be noted that authors in their work [7] mentioned that uncertainty in the temperature profile is $\pm$100 K and for intermediate species, uncertainty can be as high as factor 2. Considering this information, we can say that model predictions for intermediate species are also within the mentioned uncertainty range. The influence of temperature uncertainty has not be analyzed yet, it is left for future work. For other rich mixtures (ϕ = 1.5 and 2) flame structure are not shown here and model predictions are in good agreement with experimental data.
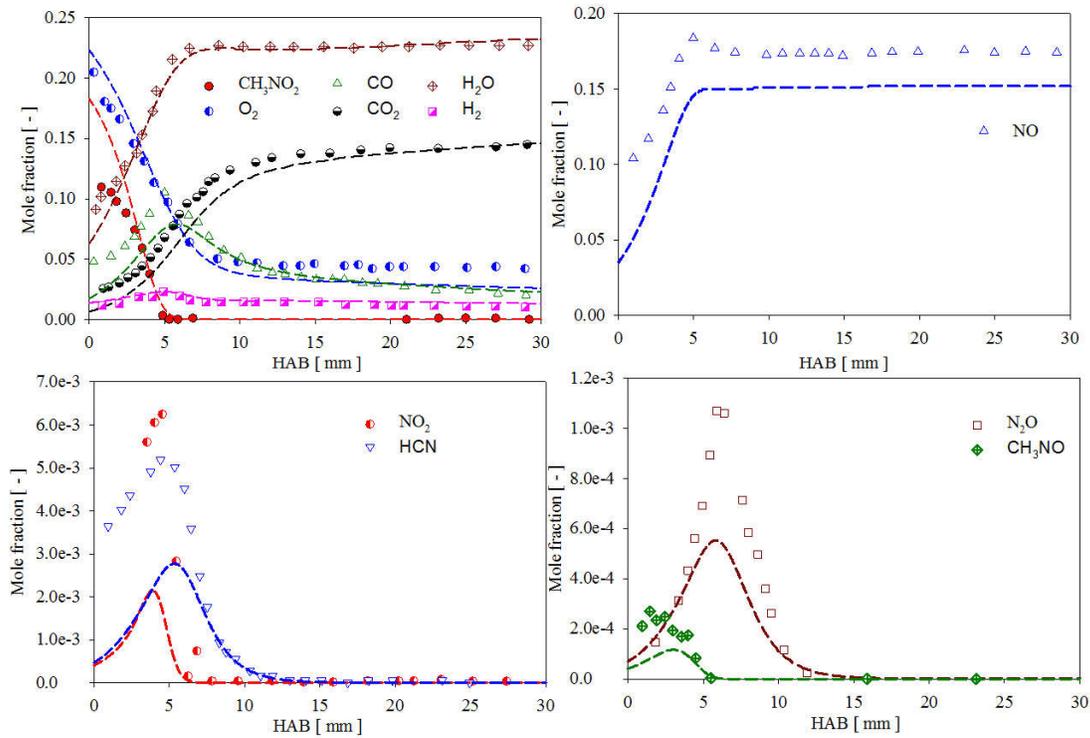
Figure 2: Speciation comparison between model prediction and measurements for CH₃NO₂/O₂/Ar (22.23/27.77/50 %) premixed flame at ϕ = 1.0, p = 4.665 kPa. Symbols: Experimental data [7]. *Lines: this work imposing the experimental temperature profile.*

CONCLUSION

A detailed nitromethane oxidation kinetic model was developed extending our recent work and overall there is good agreement between the model prediction and measurements for a range of experimental conditions investigated. More accurate and reliable thermochemistry of nitrogenous species is of importance to enhance the understanding of nitrogen chemistry and improve kinetic models. There is also the limited experimental data for nitromethane, so more experiments at combustion condition are required which can be used for model development. The knowledge about rate parameters of reactions related to nitromethane chemistry is limited, so future work should be dedicated towards more reliable rate constant values at combustion condition.

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