Shock-Induced Ignition of Methane Sensitized by NO_2 and N_2O

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1 Introduction

Nitrogen oxides, or NOx (NO, NO_2 and N_2O), are legislated pollutants that are produced during high-temperature oxidation. Without treatment, these species remain in the exhaust gases and can be recirculated in the combustion cycle of practical devices such as HCCI and gas turbine engines. Former research showed that even small NOx additions promote hydrocarbon combustion [1-5]. Hydrogen ignition was also shown to be very sensitive to NO_2 addition [6], but was less so with N_2O addition [7]. Therefore, the understanding of the interactions between NOx and hydrocarbons during combustion is of great interest for the design of practical devices. Although ignition delay time (τ_{ign}) is an important combustion parameter for gas turbine and HCCI engine operation [5], little research has been conducted to investigate the sensitizing effects of NO_2 addition to hydrocarbon/oxygen ignition.

Slack and Grillo [1] studied mixtures of $CH_4/O_2/Ar$ under fuel lean conditions (equivalence ratio (Φ) = 0.5 only) with varying concentrations of NO or NO_2. They observed that the addition of NO_2 reduced τ_{ign} over the pressure range investigated (1.8-3.6 atm). Gersen et al. [8] also investigated the sensitizing effects of NO_2 on methane ignition using a rapid compression machine at stoichiometric conditions and high pressure (25-50 atm). They showed that methane/ethane mixtures are sensitized by NO_2, but the effect decreases with increasing pressure or decreasing temperature. More recently, Herzler and Naumann [5] studied the influence of NO_2 on the ignition delay time of CH_4/C_2H_6 mixtures between Φ = 0.25 and 1.0 and at around 16 atm. To the best of the authors' knowledge, there is no study investigating the effect of N_2O addition on the ignition of hydrocarbons. Thus, the aim of this study was to extend the database for hydrocarbon/NOx interactions. Methane was selected as the hydrocarbon, and equivalence ratios of 0.5, 1.0, and 2.0 were investigated at around 1.4 and 11 atm, while the mixture at Φ = 0.5 was also investigated at around 30 atm. The baseline mixture was $CH_4/O_2/Ar$ (97.5% dilution), and NO_2 and N_2O were added to the baseline mixtures as 16.6% and 70.8% of the methane concentration by volume (the Argon concentration was decreased in the amount equal to the NO_2 or N_2O addition). Several NOx/HC mechanisms were tested in [5], where the authors therein found that predictions were all correct and that the differences between models were negligible. Based on this observation, only one NOx mechanism tested in [5] was used in this study. Results of the present study were compared to a detailed kinetics model combining the C0-C2

Correspondence to: epetersen@tamu.edu (E. L. Petersen) mechanism developed by Curran and coworkers [9] and the NOx mechanism produced by Sivaramakrishnan et al. [4] along with the modification recommended in [6]. Details on the experiments and the results are provided below.

2 Experimental Setup

Ignition delay times were measured in a stainless steel shock tube. The driver section is 2.46 m long (76.2 mm i.d.), and the driven section is 4.72 m long (152.4 mm i.d.). The measurement section is equipped with 5 pressure transducers (PCB P113A, equally spaced by 406 mm) mounted flush with the inner surface of the tube, the last one being 16 mm before the shock-tube end wall. The incident shock wave velocities were determined using signals delivered by these transducers and four Fluke PM-6666 timer/counter boxes. The incident wave speed at the end wall location was then determined using a curve fit of these four velocities extrapolated to the end wall. Post reflected-shock conditions were obtained using this extrapolated wave speed in conjunction with one dimensional shock relations and the initial conditions at the test region. In the same plane as the last pressure transducer, two CaF_2 windows (9.9 mm optical diameter and 9.8 mm thickness) are mounted across a photomultiplier (Hamamatsu 1P21) equipped with an interference filter centered at 307 ± 10 nm. Test pressure was monitored by one PCB 134A located at the end wall and one Kisler 603 B1 located at the sidewall. A scheme of the experimental setup is available in [7].

The shock tube and associated tubing are connected with a primary vacuum pumps and a Varian 551 Turbomolecular pump, which allow for the whole experimental setups to be vacuumed to 2×10^{-5} Torr or better before every run. The gases (CH_4 (99.97%), O_2 (99.999%), NO_2 (diluted at 1.02% with Ar (99.999%)), N_2O (99.5%) (all from Praxair) and Ar (Acetylene Oxygen Company, 99.999%)) were passed through a perforated stinger traversing the center of the mixing tank to allow for rapid, turbulent mixing. The mixtures were prepared in a mixing tank using the partial pressure method.

3 Results

Figure 1 shows the results for the fuel lean condition at 1.3, 11, and 30 atm for the NO_2 (a-c) and N_2O (d-f) cases. As can be seen, NOx addition reduces notably the ignition delay time over the range of condition investigated. This reduction in τ_{ign} seems to increase with the pressure, and one can see that the promoting effect is more important for NO_2 than for N_2O. In more detail, at around 1.3 atm, a 16.6% NO_2 addition shows a 65% reduction in τ_{ign} compared to the 0% experiments, and the 70.8% NO_2 mixture shows an 80% reduction (Fig.1 (a)). For the 11-atm case, 16.6% and 70.8% NO_2 mixtures, Fig. 1 (b), the results show a 60% and 90% reduction. At 30 atm, the 16.6% and 70.8% NO_2 mixtures data show a reduction in τ_{ign} by 75% and 91%, respectively (Fig. 1 (c)). For the N_2O additions at 1.3 atm, the 16.6% N_2O mixture indicates a 25% reduction, and the 70.8% mixture has a 60% reduction (Fig. 1 (d)). For the 11-atm case, the 16.6% and 70.8% N_2O mixtures (Fig. 1 (e)) show a 50% and 70% reduction, respectively. At 30 atm, the 16.6% and 70.8% N_2O additions reduce τ_{ign} by 50% and 75%, respectively (Fig. 1 (f)).

For the stoichiometric condition, Fig. 2, the NO_2 addition at low pressure (a) demonstrates a 51% reduction compared to the neat mixture. At around 11 atm, (Fig. 2 (b)) a 60% reduction in τ_{ign} is indicated. As for the fuel lean condition, the cases with N_2O addition showed smaller reductions in τ_{ign} at around 1.3 atm (Fig. 2 (c)) (31% reduction). However, the reduction in τ_{ign} is this time higher (67%) than for NO_2 at 11 atm (Fig. 2 (d)).

Finally, for the fuel rich condition, Fig. 3, a 50% reduction in τ_{ign} is observed at around 1.3 atm when NO_2 (a) or N_2O (c) are added to the mixture. At higher pressure, the reduction is 40% for NO_2 (b) and 50% with N_2O (d).

Overall, one can see that increasing the equivalence ratio at around 1.3 atm leads to a larger decrease in the ignition delay time with N_2O addition (25%, 31%, and 50% τ_{ign} reduction for Φ = 0.5, 1.0, and 2.0, respectively), whereas an opposite trend is observed for NO_2 (65%, 51%, and 50% τ_{ign} reduction for Φ = 0.5, 1.0, and 2.0, respectively). At around 11 atm, however, one can see that reductions in τ_{ign} are generally smaller at Φ = 2.0 than for the other equivalence ratios for NO_2 (60%, 60%, and 40% τ_{ign} reduction for Φ = 0.5, 1.0, and 2.0, respectively) and N_2O addition (50%, 67%, and 50% τ_{ign} reduction for Φ = 0.5, 1.0, and 2.0, respectively).

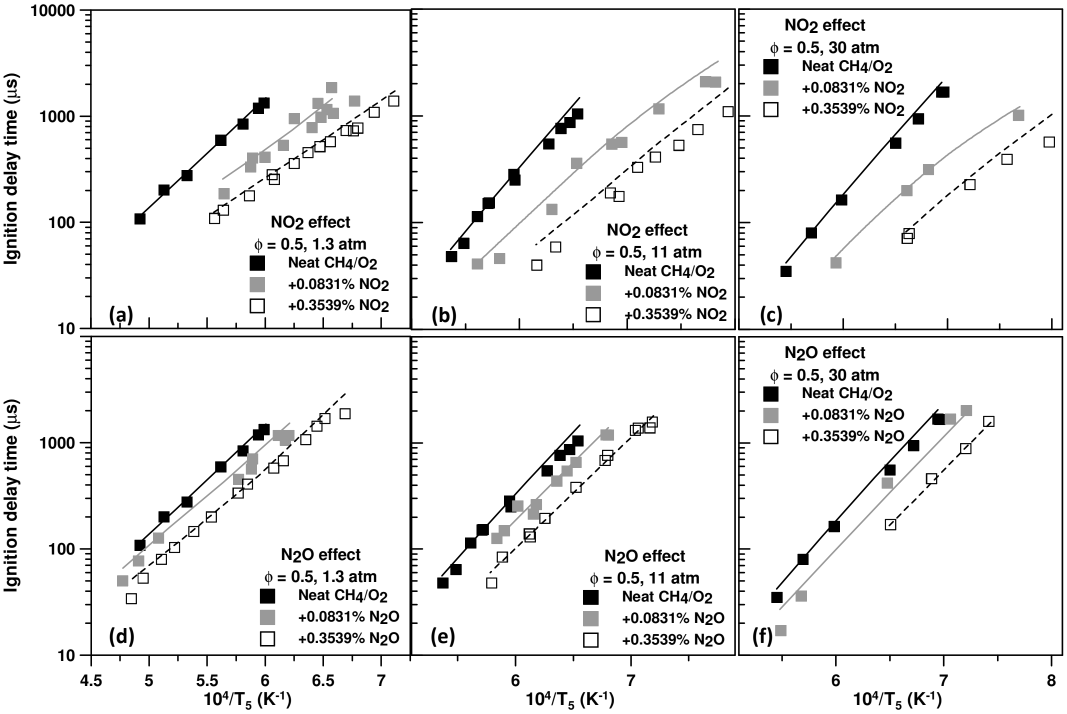

Figure 1: Comparison between the ignition delay times of a neat CH_4/O_2 mixture diluted in 97.5% Ar and the ignition delay times with NO_2 additions at around 1.3 atm (a), 11 atm (b), and 30 atm (c) and N_2O addition (1.3 atm (d), 11 atm (e), and 30 atm (f)) at Φ = 0.5. Lines correspond to the model.

The effect of pressure on the ignition delay time for the neat mixture and for the largest NO_2 and N_2O additions at Φ = 0.5 is visible in Fig. 4. As can be seen, an increase in the pressure leads to a substantial decrease in the ignition delay time, with or without NO_2 or N_2O. The greater effect on τ_{ign} of NO_2 over N_2O is also visible in this figure.

In general, the kinetics model when compared with the data demonstrates excellent agreement over all the conditions investigated. As can be seen in Figs. 1, 2, and 3 the pressure and equivalence ratio effects for the neat mixture are captured and accurately predicted. Predictions for the cases with NOx addition were also in very good agreement with the data. One can however notice that the reactivity is slightly too low for the NO_2 addition for pressures under 30 atm and for $\Phi = 0.5$, compared to the excellent agreement observed for the other conditions.

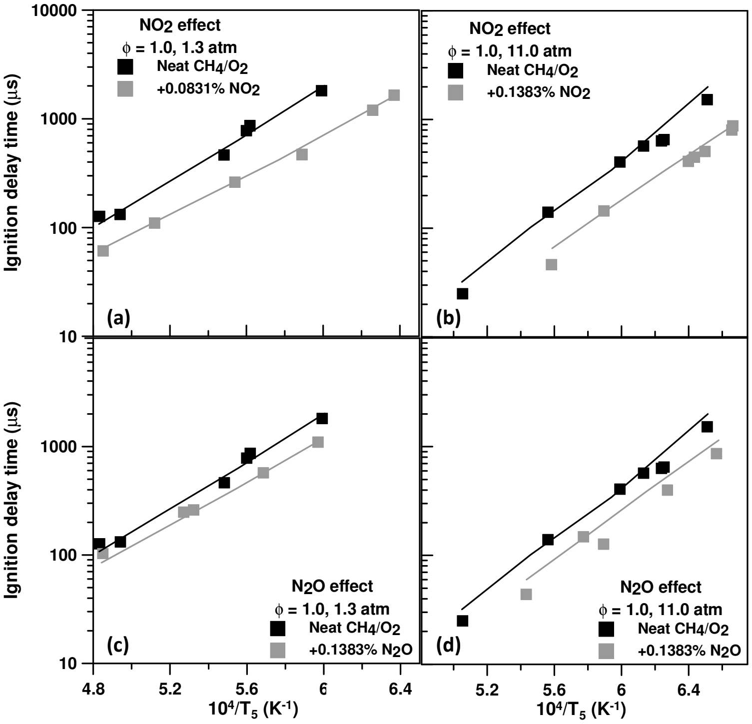

Figure 2: Comparison between the ignition delay times of a neat CH_4/O_2 mixture diluted in 97.5% Ar and the ignition delay times with NO_2 addition at around 1.3 atm (a) and 11 atm (b) and N_2O addition (1.3 atm (c), 11 atm (d)) at $\Phi = 1.0$. Lines correspond to the model.

4 Discussion

To explain the experimental results observed in Figs. 1-4, a sensitivity analysis was conducted on OH*, the species used to determine the ignition delay times in the experiment. For the NO_2 mixtures, the two most dominant reactions are $H+O_2 \rightleftarrows O+OH$ (r1) and $CH_3+NO_2 \rightleftarrows CH_3O+NO$ (r2). The last reaction was also identified in [4] as the key hydrocarbon-NOx reaction. This reaction (r2) produces CH_3O which is reactive and can participate in chain propagating reactions, speeding up ignition as observed experimentally. The two dominant reactions for the N_2O mixture are the reaction (r1) and the reverse of the N_2O formation: $O+N_2+M \rightleftarrows N_2O+M$ (r3). The reverse of (r3) is the decomposition of N_2O which produces the atomic oxygen. The O produced in this reaction can then speed up ignition by partaking in propagation reactions, which was also experimentally observed.

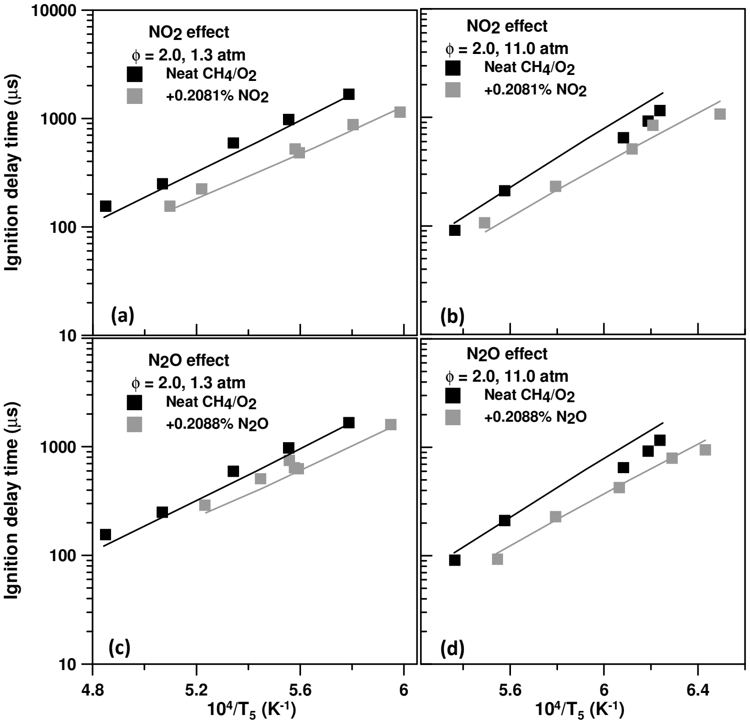

Figure 3: Comparison between the ignition delay times of a neat CH_4/O_2 mixture diluted in 97.5% Ar and the ignition delay times with NO_2 addition at around 1.3 atm (a) and 11 atm (b) and N_2O addition (1.3 atm (c), 11 atm (d)) at $\Phi = 2.0$. Lines correspond to the model.

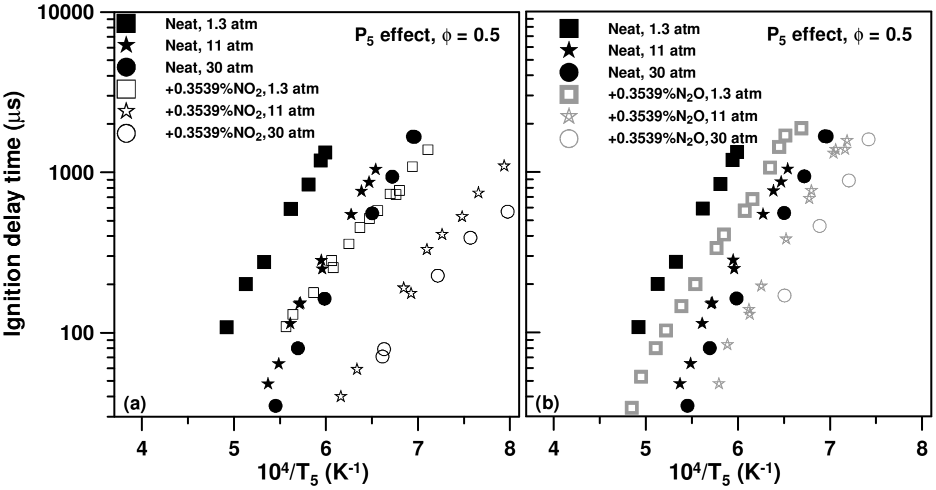

Figure 4: Effect of pressure on the ignition delay time of a CH_4/O_2 mixture diluted in 97.5% Ar and for addition of 0.3539% NO_2 (a) and N_2O (b) at $\Phi = 0.5$.

5 Conclusions

Several $CH_4/O_2/Ar$ mixtures were tested, and the effects of varying concentrations of NO_2 and N_2O were studied in conditions that have never been investigated heretofore. A reduction in τ_{ign} was observed for NO_2 and N_2O additions over the range of conditions investigated. An increase in the equivalence ratio at around 1.3 atm corresponds to a proportionally larger decrease in the ignition delay time with N_2O addition, whereas an opposite trend was observed for NO_2. However, reductions in τ_{ign} were generally smaller at $\Phi = 2.0$ than for the other equivalence ratios for NO_2 and N_2O addition at around 11 atm. The kinetics model used in this study shows a very good agreement with the data across the range of temperatures, pressures, and mixtures investigated. Sensitivity analysis showed that the reaction $CH_3+NO_2 \rightleftarrows CH_3O+NO$ is primarily responsible for the reduction in τ_{ign} when NO_2 is added. For N_2O additions, the increase in the reactivity is essentially due to the reaction $O+N_2+M \rightleftarrows N_2O+M$ (in reverse).

6 Acknowledgments

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