Shock Tube Study of the Influence of NO$_X$ on the Ignition Delay Times of Natural Gas at High Pressure

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1   Introduction

The influence of NO$_x$ on the combustion characteristics of natural gas is important for the modeling of gas turbines and HCCI engines [1] with exhaust gas recirculation, and of gas turbines with reheat combustion [2].

Even small amounts of nitrogen oxides lead to significantly shorter ignition delay times [3, 4] because NO and NO$_2$ are recycled in the hydrogen and hydrocarbon oxidation environment [5]. This was found for a variety of systems like H$_2$, CO, CH$_2$O, C$_1$, C$_2$ and higher hydrocarbons, see [5]. Only few studies were performed at high pressures, mainly by the group of Dagaut in a jet-stirred reactor [e.g. 1, 6], by Rasmussen et al. in a laminar flow reactor [5] and by Sivaramakrishnan et al. in a single-pulse shock tube [7].

There are no ignition delay time studies of natural gas in the presence of NO$_x$ at high pressures despite the importance of these data for modern combustion concepts. Therefore we performed studies at gas turbine relevant conditions.

2   Experimental Setup

The experiments were carried out in a high pressure shock tube with an internal diameter of 98.2 mm. It is divided by aluminium diaphragms into a driver section of 5.18 m and a driven section of 11.12 m in length. The driven section can be pumped down to pressures below 10^{-6} mbar by a turbomolecular pump. Gas mixtures were prepared manometrically in a stainless steel storage cylinder, which is evacuated using a separate turbomolecular pump to pressures below 10^{-6} mbar. The shock speed was measured over three 20 cm intervals using four piezo-electric pressure gauges. The temperature and pressure behind the reflected shock wave were computed from the measured incident shock speed and the speed attenuation using a one-dimensional shock model. The estimated uncertainty in reflected shock temperature is less than ±15 K in the temperature range of our measurements.

The ignition was observed by measuring pressure profiles with piezo-electric gauges (PCB$^{®}$ 113A24 and Kistler$^{®}$ 603B) located at a distance of 1 cm to the end flange. The PCB$^{®}$ gauge was shielded by 1 mm polyimide to reduce heat transfer. Also, the CH* emission at 431 nm at the same

position was selected by a narrow band pass filters (FWHM = 5 nm) and measured with a photomultiplier. All ignition delay time values shown in this paper were determined by measuring the time difference between the initiation of the system by the reflected shock wave and the occurrence of the CH* maximum because this allows a good comparability to simulations. The experimental setup allows measurements of ignition delay times for observation times up to 6.5 ms depending on the temperature.

3   Results

The ignition delay times of reference gas (92% methane, 8% ethane) – a natural gas model fuel – mixtures with NO$_2$ were determined at three different equivalence ratios. The fuel / oxygen / NO$_2$ / argon mixtures (Φ = 0.25, 0.5 and 1.0, [O$_2$] / [Ar] = 21 vol% / 79 vol%) were diluted with argon (50% mixture / 50% Ar, defined as dilution 1:2, 20% mixture / 80% Ar, defined as dilution 1:5). NO$_2$ concentrations of 20 – 251 ppm were used. NO$_2$ was used instead of NO because NO is rapidly oxidized by O$_2$ at room temperature [12]. The temperature range was 1000 K $\leq T \leq$ 1700 K at pressures of about 16 bar. A typical pressure and CH*-emission profile is shown in Fig. 1. The pressure signal of a reference gas / O$_2$ / NO$_2$ / Ar mixture (Φ = 1.0, dilution 1:5, 103 ppm NO$_2$) at T = 1264 K and p = 15.91 bar (black line) shows a two-step increase due to the incident and reflected shock wave (time zero) followed by a constant pressure for about 1500 µs, followed by a slow increase due to heat release of the reacting system and a steep rise at 2680 µs due to ignition. The CH* emission (red line) remains at zero level for 2680 µs, followed by a steep rise indicating ignition.

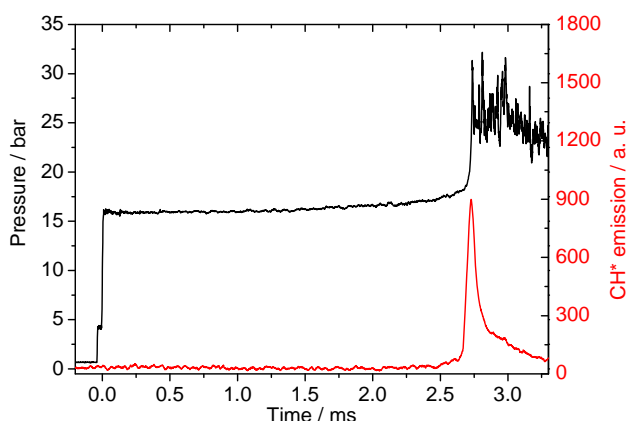Fig. 1:   Typical pressure (black line) and CH*-emission (red line) profiles indicating ignition delay in a lean, diluted (Φ = 1.0, dilution 1:5, 103 ppm NO$_2$) reference gas / Ar / NO$_2$ / O$_2$ mixture. Reaction conditions: T_5 = 1264 K, p_5 = 15.91 bar.

4   Discussion

The individual ignition delay times evaluated from the CH*-emission signals are summarized in Fig. 2. Even small amounts of NO$_2$ lead to significantly lower ignition delay times. The influence of NO$_2$ on ignition delay times is increasing with decreasing equivalence ratio.

The measured data were compared to MPFR-CHEMKIN II [8] predictions at constant initial conditions using the reaction mechanisms of Rasmussen et al. [5] and Sivaramakrishnan et al. [7]. Reactions leading to chemiluminescence like C$_2$H + O <=> CH* + CO, CH + O$_2$ <=> CO + OH*, and H + O <=> OH* and thermal and spectroscopic deexcitation reactions of CH* and OH* [9] were added to all mechanisms for comparison with the experimentally detected chemiluminescence maxima.
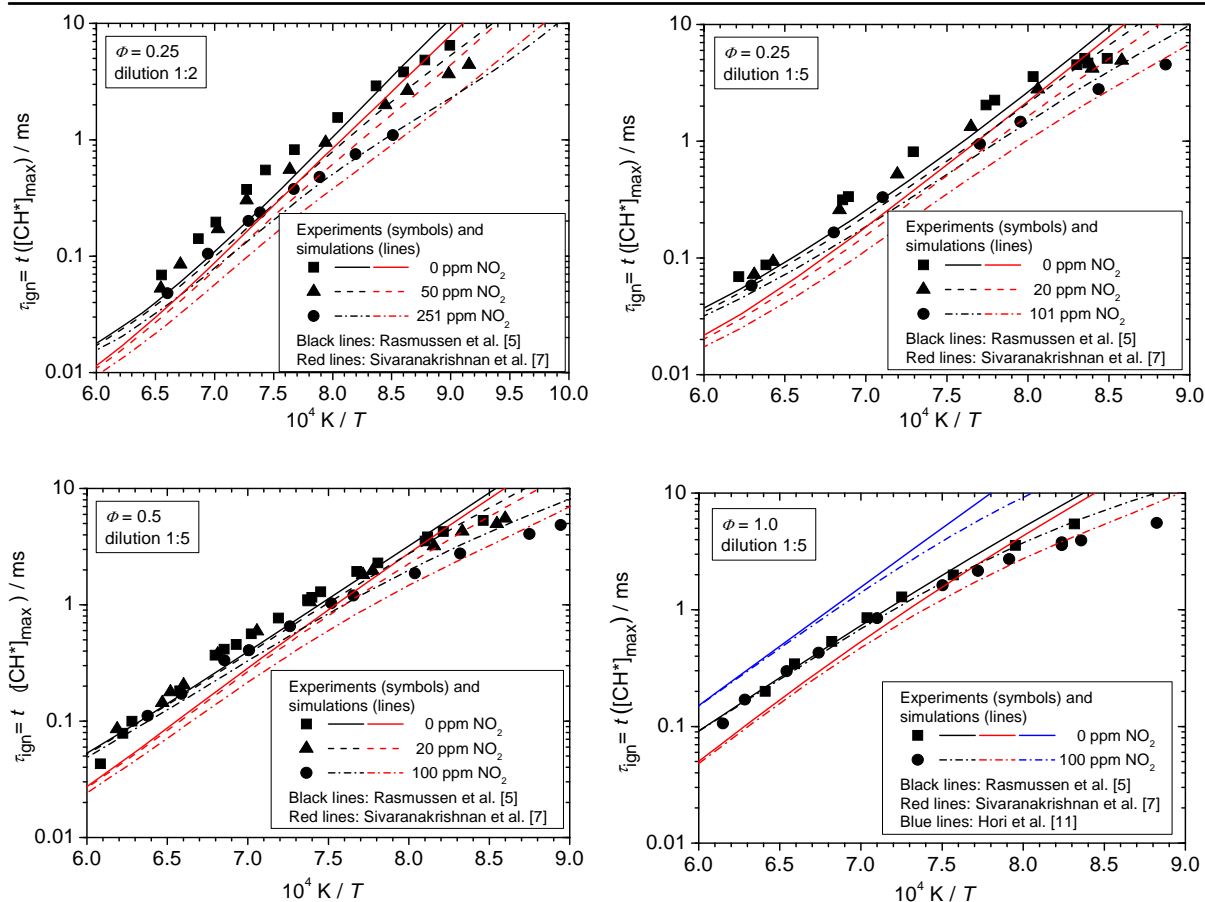
Fig. 2: Measured and calculated ignition delay times for mixtures of reference gas (92 vol% methane, 8 vol% ethane) / O$_2$ / (NO$_2$) / Ar at pressures of about 16 bar.

Simulations with the literature mechanisms of Rasmussen et al. [5] and Sivaramakrishnan et al. [7] show a good prediction of the shortening of the ignition delay times by NO$_2$, see Fig. 2. A comparison of both NO$_x$-submodels is quite difficult because the predictions of both mechanisms for the natural gas model fuel without NO$_x$ addition differ significantly. Therefore we combined the NO$_x$-submodels with our RD mechanism [8], which is based on the RAMEC mechanism of Petersen, Davidson and Hanson [10] with additions made at DLR Stuttgart concerning the C$_2$H$_5$, the formaldehyde, the acetaldehyde and the C$_2$H$_6$ system. The RD mechanism, which predicts the ignition delay times of the natural gas model fuel at all examined equivalence ratios and temperatures very well, is available on request. The results of the simulations with these mechanisms are shown in Fig. 3. It can be seen that that the shortening of the ignition delay times by NO$_2$ is very well predicted by both NO$_x$-submodels [5, 7]. The difference between the two models is negligible. The NO$_x$-submodel of Hori et al. [11] exhibits very similar results, see e.g. blue line in Fig. 3 for $\Phi = 1$. The model of Hori et al. [11] itself predicts too long ignition delay times for all conditions, see e.g. blue line in Fig. 2 for $\Phi = 1$. Deviations between the simulations with the RD hydrocarbon submechanism and the experiments occur only at long ignition delay times. Gasdynamic effects cause a slight pressure increase independent of the heat release of the reacting system during the experiments. By applying adiabatic isentropic conditions this pressure increase can be converted to a temperature increase of about 10 K at 2.5 ms and 30 K at 5 ms. MPFR-CHEMKIN II [8] simulations consider this temperature increase. The results of these simulations show that this temperature increase can be neglected for shorter ignition delay times and that the experiments at the longest ignition delay times are well reproduced contrary to the constant temperature simulations.
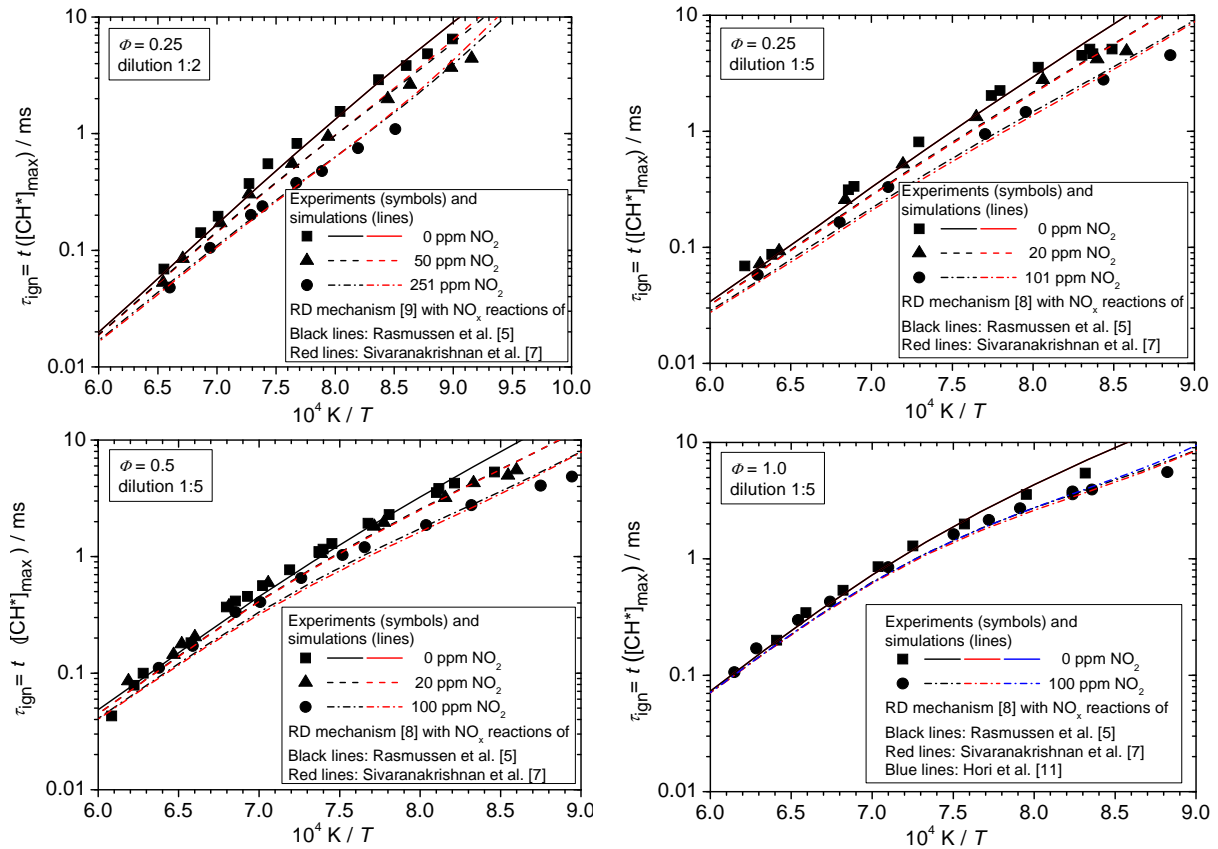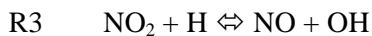
Fig. 3: Measured and calculated ignition delay times for mixtures of reference gas (92 vol% methane, 8 vol% ethane) / O$_2$ / (NO$_2$) / Ar at pressures of about 16 bar.

We performed sensitivity analyses at 1100 and 1300 K. The most important reactions describing the influence of NO$_x$ at our conditions characterized by high pressure and low NO$_x$ concentrations are shown in Fig. 4. The main reactions of NO$_x$ are

R1 $CH_3 + NO_2 \Leftrightarrow CH_3O + NO$ and

R2 $NO + HO_2 \Leftrightarrow NO_2 + OH$
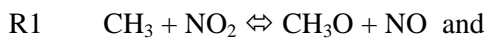
With increasing temperature

R3 $NO_2 + H \Leftrightarrow NO + OH$

gains importance.

NO and NO$_2$ lead to shorter ignition delay times by reactions R1 and R2. They are closely related by the cycle shown in Fig. 4. NO$_2$ is fast converted to NO by reaction R1 so that the mechanisms can only predict the catalytic effect of NO$_2$ as well as found in this work if the NO chemistry is also well described. Therefore they are very well suited for simulating natural gas / NO mixtures which are of interest because NO is the main NO$_x$ species which is formed during combustion. The calculated influence of NO on the ignition delay times of our natural gas model fuel is about half as strong as the one of NO$_2$, see Figs. 5 and 6. The different NO$_x$-submodels of Sivaramakrishnan et al. [7] and Hori et al. [11] show again very similar results whereas the model of Rasmussen et al. [5] predicts slightly longer ignition delay times especially at lower temperatures.
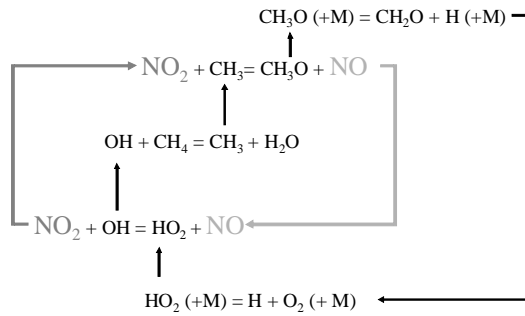
Fig. 4: Most important reactions of NO_x during natural gas oxidation at high pressures, intermediate temperatures and low NO_x concentrations.
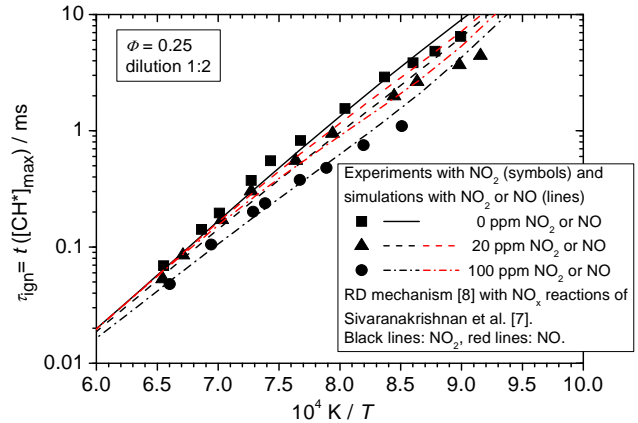

Fig. 5: Calculated and (measured) ignition delay times for mixtures of reference gas / O_2 / (NO_2) / (NO) / Ar at pressures of about 16 bar.
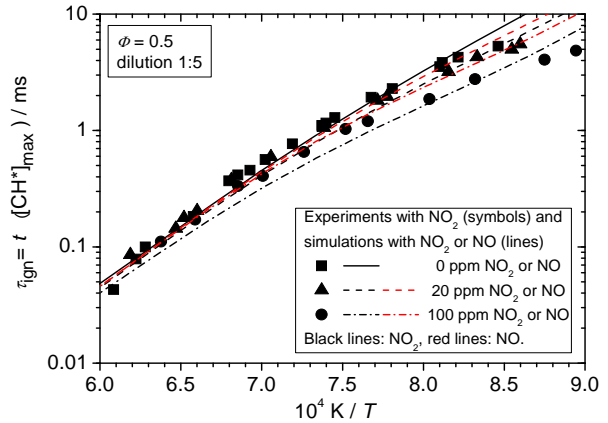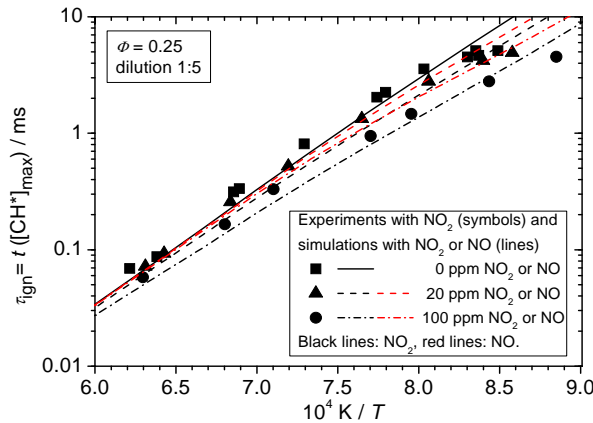

Fig. 6: Calculated and (measured) ignition delay times for mixtures of reference gas / O_2 / (NO_2) / (NO) / Ar at pressures of about 16 bar. Simulations were performed using the RD mechanism [8] with the NO_x chemistry of Sivaramakrishnan et al. [7].

4   Conclusions

The current work presents data at gas turbine relevant pressure and temperature conditions for ignition delay times of natural gas in the presence of NO_x, which are important for exhaust gas recirculation and for gas turbines with reheat combustion. It was shown that all tested mechanisms can predict well the influence of NO_x on the ignition delay times. Even small amounts of NO_x lead to significantly shorter ignition delay times, especially at lean conditions.

4   Acknowledgement

References

[1] P. Dagaut P, Nicolle A. (2005). Experimental study and detailed kinetic modeling of the effect of exhaust gas on fuel combustion: mutual sensitization of the oxidation of nitric oxide and methane over extended temperature and pressure ranges. Combust. Flame 140: 161.

[2] Güthe F, Hellat J, Flohr P. (2009). The Reheat Concept: The Proven Pathway to Ultralow Emissions and High Efficiency and Flexibility. J. Eng. Gas Turbines Power 131: 021503 1.

[3] Faravelli T, Frassoldati A, Ranzi E. (2003). Kinetic modeling of the interactions between NO and hydrocarbons in the oxidation of hydrocarbons at low temperatures. Combust. Flame 132: 188.

[4] Glarborg P. (2007). Hidden interactions - Trace species governing combustion and emissions. Proc. Combust. Inst. 31: 77.

[5] Rasmussen CL, Rasmussen AE, Glarborg P. (2008). Sensitizing effects of NO$_x$ on CH$_4$ oxidation at high pressure. Combust. Flame 154: 529.

[6] Dagaut P, Dayma G. (2006). Mutual sensitization of the oxidation of nitric oxide and a natural gas blend in a JSR at elevated pressure: Experimental and detailed kinetic modeling study. J. Phys. Chem. A 110: 6608.

[7] Sivaramakrishnan R, Brezinsky K, Dayma G, Dagaut P. (2007). High pressure effects on mutual sensitization of the oxidation of NO and CH$_4$-C$_2$H$_6$ blends. Phys. Chem. Chem. Phys. 9: 4230.

[8] Herzler J, Naumann C (2009). Shock-tube study of the ignition of methane/ethane/hydrogen mixtures with hydrogen contents from 0% to 100% at different pressures. Proc. Combust. Inst. 32: 213.

[9] Smith GP, Luque J, Chung P, Jeffries JB, Crosley DR. (2002). Low pressure flame determinations of rate constants for OH(A) and CH(A) chemiluminescence. Combust. Flame 131: 59.

[10] Petersen EL, Davidson DF, Hanson RK. (1999). Kinetics modeling of shock-induced ignition in low-dilution CH$_4$/O$_2$ mixtures at high pressures and intermediate temperatures. Combust. Flame 117: 272.

[11] Hori M, Matsunaga N, Marinov NM, Pitz WJ, Westbrook CK. (1998). An experimental and kinetic calculation of the promotion effect of hydrocarbons on the NO-NO$_2$ conversion in a flow reactor. Proc. Combust. Inst. 27: 389.

[12] Glasson WA, Tuesday CS (1963). The atmospheric thermal oxidation of nitric oxide. J. Am. Chem. Soc. 85: 2901.