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Shock-Tube Study of the Ignition of Methane / Ethane / Hydrogen Mixtures with Hydrogen Contents from 0 to 100% at Different Pressures

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Abstract

The ignition delay times of diluted hydrogen / reference gas (92% methane, 8% ethane) / O₂ / Ar mixtures with hydrogen contents of 0, 40, 80 and 100% were determined in a high-pressure shock tube at equivalence ratios $\phi = 0.5$ and 1.0 (dilution 1:5). The temperature range was $900 \text{ K} \leq T \leq 1800 \text{ K}$ at pressures of about 1, 4 and 16 bar.

The reference gas and the 40% hydrogen / 60% reference gas data showed typical characteristics of hydrocarbon systems and can be represented by:

$$\tau_{\text{ign}} / \mu\text{s} = 10^{-2.75 \pm 0.13} \exp(20450 \pm 442 \text{ K} / T) (p/\text{bar})^{-0.51 \pm 0.02} \phi^{0.59 \pm 0.06} \quad (\text{reference gas}) \text{ and}$$

$$\tau_{\text{ign}} / \mu\text{s} = 10^{-2.07 \pm 0.09} \exp(16350 \pm 299 \text{ K} / T) (p/\text{bar})^{-0.49 \pm 0.02} \phi^{0.75 \pm 0.06} \quad (40\% \text{ H}_2 / \text{reference gas}).$$

The pure hydrogen data exhibit a more complex pressure dependence with the 16 bar values having the slowest ignition delay times at lower temperatures and the fastest ignition delay times at higher temperatures. No dependence on the equivalence ratio was observed.

The 80% hydrogen / 20% reference gas data display characteristics of hydrocarbon and hydrogen systems.

The comparison of the measurements to MPFR-CHEMKIN II simulations with different mechanisms shows that the predictions of all tested mechanisms with the exception of the GRI3.0 agree well with the experimental values for reference gas, 40% hydrogen / 60% reference gas and partly for 80% hydrogen / 20% reference gas and 100% hydrogen. None of the mechanisms can represent the observed reduction of the activation energy at low

temperatures of pure hydrogen and of 80% hydrogen / 20% reference gas at $p \geq 4$ bar. Literature mechanisms which were developed for H₂ or for mixtures with a dominating H₂ subsystem cannot predict the observed reduction of the activation energies, either.

Keywords: hydrogen, methane, ethane, ignition, shock tube.

Introduction

Due to limited resources the use of good quality natural gas will decrease in the near future. It will be replaced by gasification products out of biogenic sources, waste, oil residues and coal or by low quality natural gas [1-3]. The use of biogenic sources offers the advantage of CO₂ neutrality. For the efficient use of biomass or coal the gasification can be combined with the power generation in one plant (IGCC: Integrated Gasification Combined Cycle). This concept which also offers low emissions and a cost-effective possibility of CO₂ capture for sequestration is currently under development and some demonstration plants already exist [4]. Main products of the gasification are H₂, CO, CO₂, CH₄ and C₂H₆ [5, 6].

There are only very few ignition delay studies of these mixtures at gas turbine relevant conditions. Therefore we studied fuel mixtures containing hydrogen and reference gas (92% methane, 8% ethane), a natural gas model fuel, with hydrogen contents of 0, 40, 80 and 100%. The data are important for the design of new gas turbine concepts which are necessary because the hydrogen content leads to high laminar flame speeds and combustion temperatures and to short ignition delay times. These can also cause safety problems due to self-ignition and flashback.

The data of pure hydrogen are also important because hydrogen is expected as a future fuel and for the understanding of the combustion characteristics of syngas (CO, H₂), which is also a main gasification product. Some recent studies at gas turbine relevant conditions showed that the ignition of syngas with more than 20% hydrogen is dominated by the H₂ subsystem and that current literature mechanisms are not able to predict the ignition delay times [7-11]. Therefore further studies of the H₂ kinetic systems at these conditions were necessary.

The ignition delay times of the hydrogen / reference gas mixtures were studied at 1, 4 and 16 bar because data at different pressures are necessary for the development of new gas turbine

concepts. The testing of the prototypes starts at atmospheric pressure. For the extrapolation to the real high pressure conditions of the technical use the pressure dependence of ignition delay times must be known. Contrary to hydrocarbon dominated systems which show a p^{-x} dependence hydrogen has a more complex behavior at intermediate temperatures. Because of the stabilization effect of the reaction $\text{H} + \text{O}_2 (+ \text{M}) \rightleftharpoons \text{HO}_2 (+ \text{M})$ at higher pressures, which reduces the chain branching by $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$, hydrogen shows a minimum of the ignition delay times as function of the pressure. The pressure value of minimum is dependent on the temperature due to the activation energy of the $\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$ reaction, the higher the temperature, the higher the pressure. This work examines if the hydrogen / reference gas mixtures show a similar behavior.

A good overview of literature studies of the ignition delay times of methane, natural gas and methane mixtures with higher hydrocarbons and hydrogen is given by de Vries and Petersen [9]. Hydrogen autoignition studies were compiled by Mittal et al. [8].

Experimental

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 and time range of our measurements. The purity of the used oxygen was better than 99.9999%, of argon better than 99.9999%, of hydrogen better than 99.999%, of methane better than 99.9995% and of ethane better than 99.95%.

The ignition was observed by measuring pressure profiles with piezo-electric gauges (PCB 113 A24 and Kistler 601B) 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 OH* emission at 307 nm and the CH* emission at 431 nm at the same position were selected by a narrow band pass filters (FWHM = 5 nm) and measured with a photomultiplier. All ignition delay time values shown in these report were determined by measuring the time difference between the initiation of the system by the reflected shock wave and the occurrence of the CH* or the OH* maximum because this allows a good comparability to the simulations. The OH* maximum was used for pure hydrogen whereas for all other fuels, the CH* maximum was used.

The experimental setup allows measurements of ignition delay times at constant pressure and temperature conditions for observation times < 4.5 ms.

The purity of the shock tube was tested by measuring the hydrogen atom background by H-ARAS (atomic resonance absorption spectroscopy). At the relevant temperature range of our ignition delay study the H atom background was below the detection limit of $2 \times 10^{10} \text{ cm}^{-3}$ [13]. This concentration is low enough so that the effect on the ignition delay times is negligible although the hydrogen system is very sensitive to hydrogen atom impurities.

Results

The ignition delay times of hydrogen / reference gas (92% methane, 8% ethane) mixtures with hydrogen contents of 0, 40, 80 and 100% were determined. The fuel / oxygen / argon

mixture ($\phi = 0.5$ and 1.0 , $[\text{O}_2] / [\text{Ar}] = 21\% / 79\%$) was diluted with argon (20% mixture / 80% Ar, defined as dilution 1:5). The composition of the used mixtures is given in table 1. The temperature range was $900 \text{ K} \leq T \leq 1800 \text{ K}$ at pressures of about 1, 4 and 16 bar. A typical pressure and CH^* emission profile is shown in Fig. 1. The pressure signal of a 40% hydrogen / 60% reference gas / O_2 / Ar mixture ($\phi = 0.5$, dilution 1:5) at $T = 1129 \text{ K}$ and 16.17 bar with an equivalence ratio $\phi = 0.5$ (black line) shows a two-step increase due to the incident and reflected shock wave (time zero) followed by a constant pressure for about 2000 μs , a slow increase due to heat release of the reacting system and a steep rise at 3600 μs . The CH^* emission (grey line) remains at zero level for 3600 μs , followed by a steep rise indicating ignition.

Discussion

The individual ignition delay times evaluated from the CH^* or OH^* (hydrogen experiments) emission signals are summarized in figs. 2-7. A list of all experimental results is given as supplemental material. It can be seen that for all conditions the ignition becomes faster with increasing hydrogen content.

Pressure and equivalence ratio dependence of the ignition delay times

The pressure dependence is shown in figs. 8-15. The data of reference gas and 40% hydrogen / 60% reference gas exhibit a pressure behavior which is typical for hydrocarbon systems. The ignition delays become shorter with increasing pressure with a factor of $p^{0.5}$ and with decreasing equivalence ratio with a factor $\phi^{0.59}$ (reference gas) and

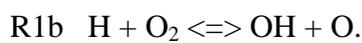
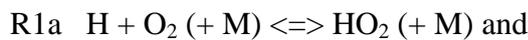
$\phi^{0.75}$ (40% hydrogen / 60% reference gas), respectively. The activation energy of the system with 40% hydrogen is considerably lower. The data can be fitted by:

$$\tau_{\text{ign}} / \mu\text{s} = 10^{-2.75 \pm 0.13} \exp(20450 \pm 442 \text{ K} / T) (p/\text{bar})^{-0.51 \pm 0.02} \phi^{0.59 \pm 0.06} \quad (\text{reference gas}) \text{ and}$$

$$\tau_{\text{ign}} / \mu\text{s} = 10^{-2.07 \pm 0.09} \exp(16350 \pm 299 \text{ K} / T) (p/\text{bar})^{-0.49 \pm 0.02} \phi^{0.75 \pm 0.06} \quad (40\% \text{ H}_2 / 60\% \text{ reference gas}),$$

see figs. 8-11. The only similarity of the 40% hydrogen / 60% reference gas mixture to hydrogen dominated systems can be seen for $\phi = 0.5$ and 16 bar at temperatures $T < 1170$ K. The ignition delay times for $p = 4$ and 16 bar and for $\phi = 0.5$ and 1.0 are almost identical for this temperature range.

The data of the mixtures with 80% hydrogen / 20% reference gas and of pure hydrogen have a more complex pressure behaviour. The ignition delay times of the H₂ subsystem are dominated by the two competing reactions:



R1a becomes dominant at higher pressures whereas R1b becomes dominant at higher temperatures because of its activation energy. If R1a is considerably faster as R1b, the ignition delay times are increased because less chain branching occurs by reaction R1b. Therefore the ignition of the pure hydrogen system at 16 bar and $T < 1100$ K is slower than at

4 and 1 bar because R1a, which is close to the low pressure limit [14], is about 4 or 16 times faster at the higher pressure, see figs. 12 and 13. This exceeds the effect of the higher absolute concentrations due to the higher pressure which dominates at higher temperatures and hydrocarbon systems. The crossing of the data at 4 and 1 bar is at a lower temperature (1000 K), respectively. The ignition delay times of hydrogen at $\phi = 0.5$ and 1.0 are almost identical at all pressures.

The mixture with 80% hydrogen / 20% reference gas exhibits characteristics of hydrocarbon and hydrogen systems. At $\phi = 1.0$, the data follow the trend $\tau_{\text{ign, 16 bar}} < \tau_{\text{ign, 4 bar}} < \tau_{\text{ign, 1 bar}}$, but for $T < 1200$ K, the data for $p = 4$ and 16 bar are almost identical, see fig. 15. At $\phi = 0.5$ the behavior of the ignition delay times is more dominated by the hydrogen system. There are 3 crossing points from slower to faster ignition times: at $T < \text{about } 1250$ K, the ignition becomes faster at $p = 4$ bar compared to $p = 16$ bar, at $T < 1100$ K, the ignition becomes faster at $p = 1$ bar compared to $p = 16$ bar and at $T < \text{about } 970$ K, the ignition becomes faster at $p = 1$ bar compared to $p = 16$ bar, see fig. 14. The data at $\phi = 0.5$ are considerably faster compared to the values at $\phi = 1.0$ for $p = 1$ and 4 bar. For $p = 16$ bar, the ignition delay times at both equivalence ratios are almost identical.

Simulation of the ignition delay times

The measured data were compared to MPFR-CHEMKIN II [15] predictions of literature mechanisms (GRI3.0 [16], LEEDS1.5 [17], Petrova and Williams [18], Petersen et al. [19]). Additional comparisons were made to the RD mechanism, which is based on the RAMEC mechanism of Petersen, Davidson and Hanson [20] with additions made at the DLR Stuttgart concerning the C_2H_5 , the formaldehyde, the acetaldehyde and the C_2H_6 system. Reactions

leading to chemiluminescence like $C_2H + O \rightleftharpoons CH^* + CO$, $CH + O_2 \rightleftharpoons CO + OH^*$, $H + O + M \rightleftharpoons OH^* + M$ and thermal and spectroscopic deexcitation reactions of CH^* and OH^* [18] were added to all mechanisms for comparability with the experimental results. The RD mechanism is available on request.

MPFR (Multiple Plug Flow Reactor) - CHEMKIN II characterises a programme developed at DLR Stuttgart to take into account gasdynamical effects causing pressure and temperature variations decoupled from effects of heat release combined with pressure relaxation effects along the axis due to the shock tube's 'open end' configuration. Thus the simulation assumes for the time of a PFR (25 μ s or shorter depending on the heat release ($\Delta T \leq 0.5\%$)) a constant pressure condition and takes into account the propagation of pressure increase by heat release within a PFR-time step along the shock tube axis. The correction of the gasdynamical effects is based on the measured pressure profiles of mixtures with similar acoustic properties but without heat release by chemical reactions. The temperature profiles are then calculated by applying adiabatic isentropic conditions. These temperature profiles can be used instead of constant initial temperatures for the simulation of experimental profiles with different chemical mechanisms. The pressure profiles of the mixtures without heat release showed only negligible pressure increases for observation times ≤ 4.5 ms so that gasdynamical effects could be neglected and the simulations could be performed based on constant initial temperatures.

The comparison between measured and simulated ignition delay times are shown in figs. 2 – 7 and in the supplemental material. The agreement of the different mechanisms is strongly dependent on the hydrogen content and the pressure. For 1 bar all mechanisms show a good agreement with the experiments for all fuels. The measured ignition delay times are predicted

well for reference gas and 40% hydrogen / reference gas at 4 bar by all mechanisms. The simulations of the 80% hydrogen / 20% reference gas and of pure hydrogen at 4 bar agree well with the experiments with the exception of the GRI 3.0 [16] mechanism. At temperatures below 1050 K for 80% hydrogen / 20% reference gas or below 990 K for pure hydrogen the mechanisms cannot reproduce the observed reduction of the activation energy. At 16 bar all mechanisms with the exception of the GRI 3.0 [16] reproduce the measured values quite well for reference gas and 40% hydrogen / 60% reference gas with the RD mechanism showing the best agreement for these fuels. The fuel mixtures with 80% hydrogen show a quite good agreement with all mechanisms except the GRI 3.0 [16] only for temperatures $T > 1100$ K at 16 bar. At lower temperatures all mechanisms predict too long ignition delay times. The experiments with pure hydrogen at 16 bar are predicted quite well only by the mechanisms of Petersen et al [19] and Petrova and Williams [18] and only for temperatures $T > 1100$ K. At lower temperatures all mechanisms predict too long ignition delay times.

Because of the relatively bad performance of the five used mechanisms for 100% hydrogen at higher pressures and low temperatures we simulated the data with other mechanisms (Davis et al. [22], Li et al. [23], and Jachimoski [24]) which were developed for H_2 or for mixtures with a dominating H_2 subsystem, see figs. 12 and 13. For $p = 16$ bar and $T < 1100$ K and $p = 4$ bar and $T < 1000$ K the H_2 mechanisms [22-24] like the other mechanisms [16-19] cannot predict the observed reduction of the activation energies and the deviations to the experiments become very high. In this experimental region the HO_2 and H_2O_2 chemistry is dominant and is obviously not well reproduced.

By replacing the H_2 kinetic and thermodynamic subsystem of the RD mechanism by the values of the Li et al. work [23] a better agreement between simulations and experiments could be achieved for a H_2 content $\geq 80\%$ for this mechanism. The predictions for pure

hydrogen are identical to the Li et al. mechanism [23], see discussion above. The simulations for 80% hydrogen content are shown in figs. 14 and 15. At 4 and 16 bar a good agreement of calculated and measured values is achieved at temperatures $T \geq 1100$ K (16 bar) and $T \geq 1050$ K (4 bar). At higher temperatures the simulations predict too long ignition delay times. The replacing of the H₂ subsystem leads also to reductions of the predicted values of up to 25 % for the pure reference gas and the 40 % hydrogen / 60 % reference gas fuel mixture, see supplemental material.

Conclusions

The current work offers a broad range of data at gas turbine relevant pressure and temperature conditions for the ignition delay of fuels which are typical products of the gasification of biomass or coal. It was shown that all tested mechanisms with the exception of the GRI3.0 can predict well the data at hydrogen contents $\leq 40\%$ for pressures from 1 to 16 bar. The data can also be represented by fit equations as function of temperature, pressure and equivalence ratio. The effect of the dilution can be determined with the validated mechanisms. These relations or reduced mechanisms on the basis of the tested mechanisms offer now the possibility of the CFD simulation of new combustor designs for this kind of fuel. The validation for a wide pressure range helps also in the extrapolation of atmospheric tests of newly developed turbine concepts to the real high pressure operating conditions. For fuels with very high hydrogen content or for pure hydrogen the existing mechanisms must still be improved to represent the observed reduction of the activation energy at high pressures and low temperatures.

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Table 1: Composition of the used mixtures.

| mixture | ϕ | CH ₄ | C ₂ H ₆ | H ₂ | O ₂ | Ar |
|--|--------|-----------------|-------------------------------|----------------|----------------|----------|
| 100% H ₂ | 0.5 | | | 0.034603 | 0.034900 | 0.930497 |
| 100% H ₂ | 1.0 | | | 0.058683 | 0.029470 | 0.911847 |
| 80% H ₂ / 20% reference gas | 0.5 | 0.004162 | 0.000356 | 0.018170 | 0.037399 | 0.939913 |
| 80% H ₂ / 20% reference gas | 1.0 | 0.007737 | 0.000651 | 0.032942 | 0.033823 | 0.924847 |
| 40% H ₂ / 60% reference gas | 0.5 | 0.007309 | 0.000645 | 0.005114 | 0.038957 | 0.947975 |
| 40% H ₂ / 60% reference gas | 1.0 | 0.013519 | 0.001175 | 0.009644 | 0.036070 | 0.939592 |
| 100% reference gas | 0.5 | 0.008589 | 0.000734 | | 0.039964 | 0.950713 |
| 100% reference gas | 1.0 | 0.016643 | 0.001414 | | 0.039226 | 0.942717 |

Figure Captions

Fig. 1: Typical pressure (black line) and CH*-emission (grey line) profiles indicating ignition delay in a lean, diluted ($\phi = 0.5$, dilution 1:5) hydrogen / reference gas (40% / 60%) / Ar / O₂ mixture. Reaction conditions: $T_5 = 1129$ K, $p_5 = 16.17$ bar.

Fig. 2: Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 16 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: RD-mechanism, grey lines: Leeds1.5 [17] mechanism. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

Fig. 3: Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 16 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: RD-mechanism, grey lines: Leeds1.5 [17] mechanism. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

Fig. 4: Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 4 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations:

black lines: RD-mechanism, grey lines: Leeds1.5 [17] mechanism. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

Fig. 5: Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 4 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: RD-mechanism, grey lines: Leeds1.5 [17] mechanism. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

Fig. 6: Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 1 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: RD-mechanism, grey lines: Leeds1.5 [17] mechanism. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

Fig. 7: Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 1 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: RD-mechanism, grey lines: Leeds1.5 [17] mechanism. Dashed-dotted line:

100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

Fig. 8: Measured and fitted ignition delay times for reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Experiments: squares: 16 bar, circles: 4 bar, triangles: 1bar. Lines: fit of the data ($\tau_{\text{ign}} / \mu\text{s} = 10^{-2.75 \pm 0.13} \exp(20450 \pm 442 \text{ K} / T) (p/\text{bar})^{-0.51 \pm 0.02} \phi^{0.59 \pm 0.06}$). Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Fig. 9: Measured and fitted ignition delay times for reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Experiments: squares: 16 bar, circles: 4 bar, triangles: 1bar. Lines: fit of the data ($\tau_{\text{ign}} / \mu\text{s} = 10^{-2.75 \pm 0.13} \exp(20450 \pm 442 \text{ K} / T) (p/\text{bar})^{-0.51 \pm 0.02} \phi^{0.59 \pm 0.06}$). Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Fig. 10: Measured and fitted ignition delay times for 40% hydrogen / 60% reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Experiments: squares: 16 bar, circles: 4 bar, triangles: 1bar. Lines: fit of the data ($\tau_{\text{ign}} / \mu\text{s} = 10^{-2.07 \pm 0.09} \exp(16350 \pm 299 \text{ K} / T) (p/\text{bar})^{-0.49 \pm 0.02} \phi^{0.75 \pm 0.06}$). Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Fig. 11: Measured and fitted ignition delay times for 40% hydrogen / 60% reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Experiments: squares: 16 bar, circles: 4 bar, triangles: 1bar. Lines: fit of the data ($\tau_{\text{ign}} / \mu\text{s} = 10^{-2.07 \pm 0.09} \exp(16350 \pm 299 \text{ K} / T) (p/\text{bar})^{-0.49 \pm 0.02} \phi^{0.75 \pm 0.06}$). Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Fig. 12: Measured and calculated ignition delay times for hydrogen / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Experiments: squares: 16 bar, circles: 4 bar, triangles: 1bar. MPFR-CHEMKIN II [15] simulations: black line: Davis et al. [22]

mechanism, grey lines: Li et al. [23] mechanism, lines with small circles: Jachimoski [24] mechanism. Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Fig. 13: Measured and calculated ignition delay times for hydrogen / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Experiments: squares: 16 bar, circles: 4 bar, triangles: 1bar. MPFR-CHEMKIN II [15] simulations: black line: Davis et al. [22] mechanism, grey lines: Li et al. [23] mechanism, lines with small circles: Jachimoski [24] mechanism. Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Fig. 14: Measured and calculated ignition delay times for 80% hydrogen / 20% reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Experiments: squares: 16 bar, circles: 4 bar, triangles: 1bar. Lines: MPFR-CHEMKIN II [15] simulations with RD mechanism with Li et al. [23] H₂ subsystem. Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Fig. 15: Measured and calculated ignition delay times for 80% hydrogen / 20% reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 1, 4 and 16 bar. Squares: 16 bar, circles: 4 bar, triangles: 1bar. Lines: MPFR-CHEMKIN II [15] simulations with RD mechanism with Li et al. [23] H₂ subsystem. Full line: 16 bar, dashed line: 4 bar, dotted line: 1bar.

Figure 1

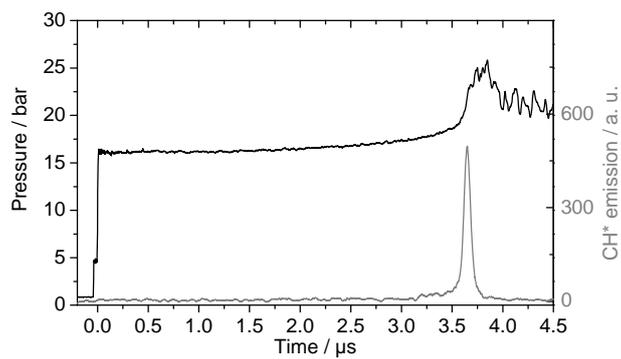


Figure 2

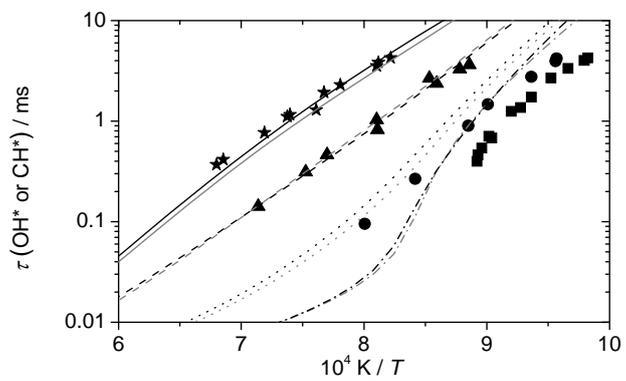


Figure 3

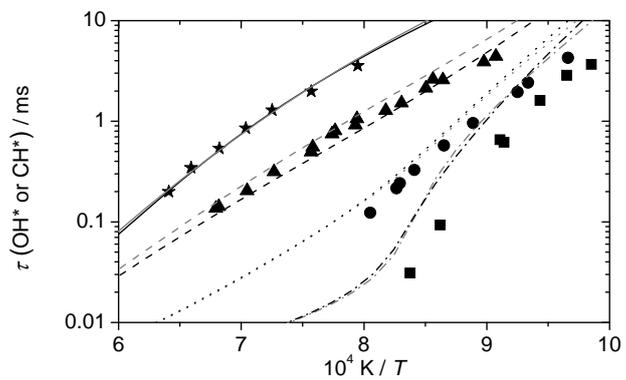


Figure 4

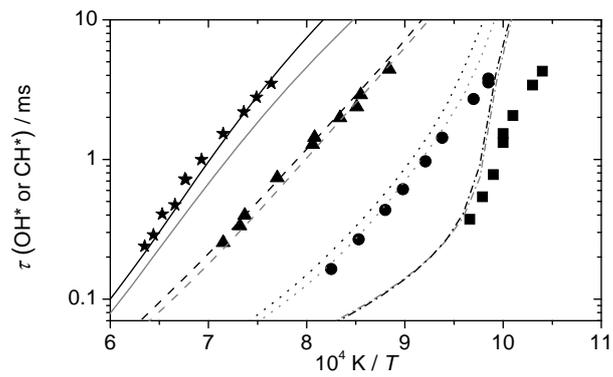


Figure 5

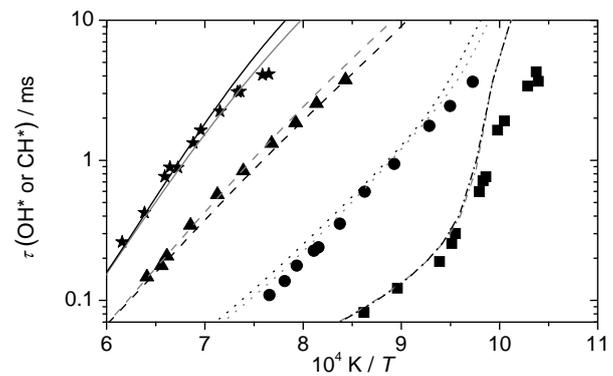


Figure 6

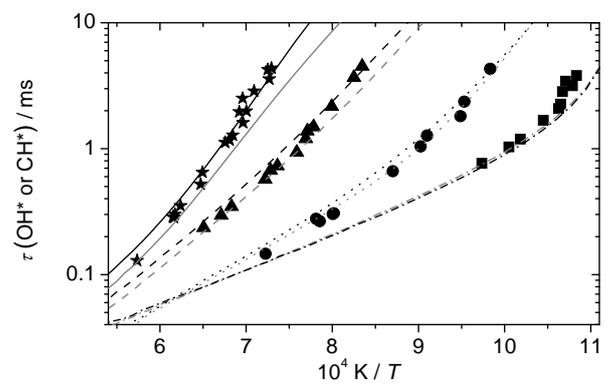


Figure 7

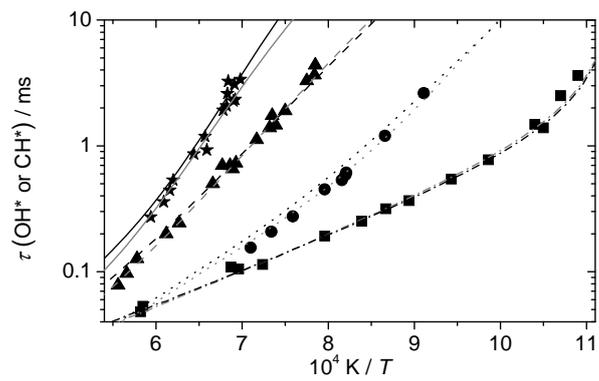


Figure 8

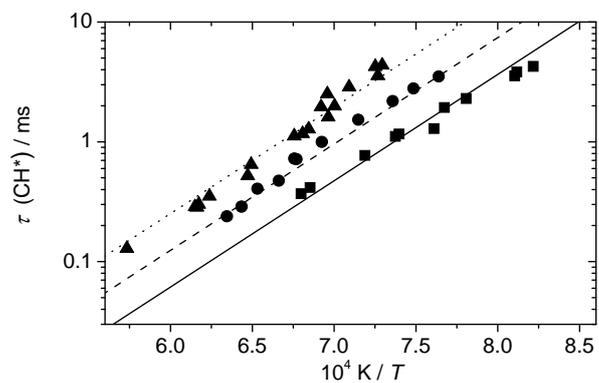


Figure 9

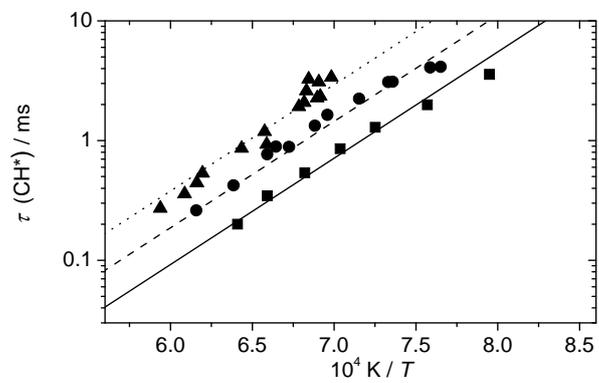


Figure 10

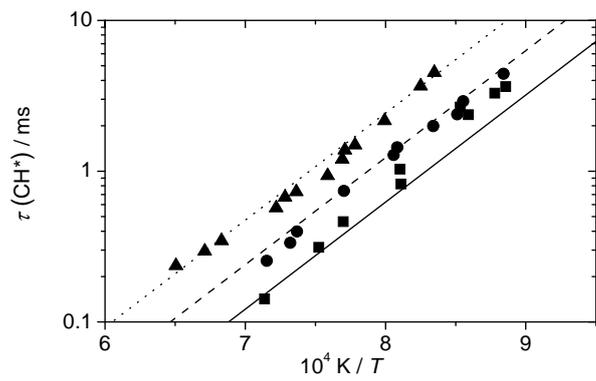


Figure 11

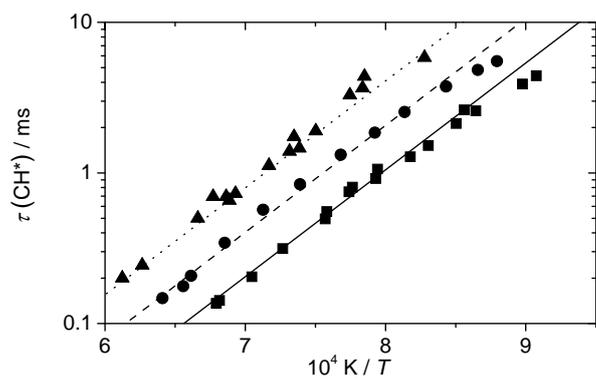


Figure 12

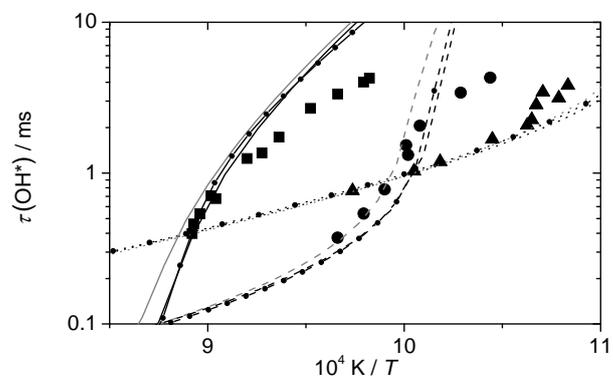


Figure 13

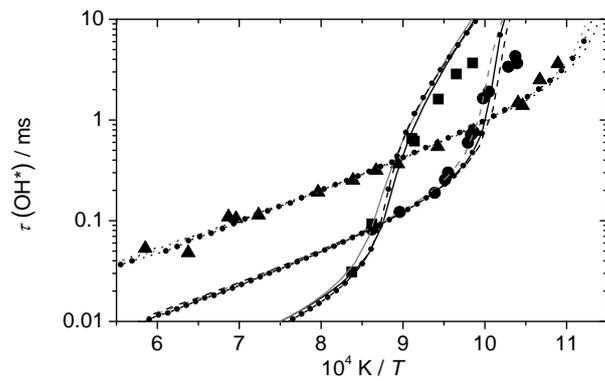


Figure 14

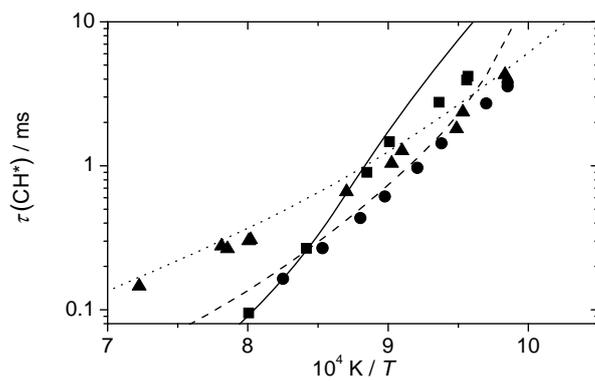
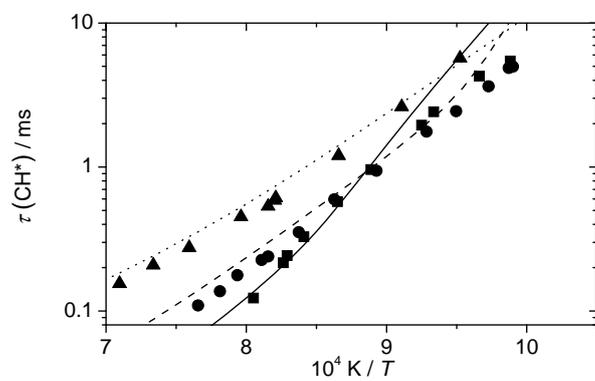


Figure 15



List of supplemental material:

Table S1: Experimental results

Figure S1 – S6: Comparison of experimental materials with simulations using the following mechanisms: GRI3.0 [16], Petrova and Williams [18], Petersen et al. [19], RD, RD with H₂ subsystem of Li et al. [23], Leeds1.5 [23].

Supplemental material

Table S1: Experimental results

| $\phi = 0.5, 100\% \text{ H}_2$ | | | $\phi = 1, 100\% \text{ H}_2$ | | |
|---------------------------------|------------------|----------------------|-------------------------------|------------------|----------------------|
| T / K | p / bar | $\tau / \mu\text{s}$ | T / K | p / bar | $\tau / \mu\text{s}$ |
| 1018 | 15.43 | 4250 | 1015 | 13.38 | 3680 |
| 1021 | 15.97 | 4010 | 1036 | 12.97 | 2860 |
| 1035 | 16.21 | 3340 | 1060 | 14.08 | 1610 |
| 1050 | 16.10 | 2680 | 1094 | 13.24 | 617 |
| 1068 | 16.09 | 1730 | 1098 | 13.36 | 654 |
| 1078 | 15.13 | 1360 | 1160 | 14.57 | 93 |
| 1087 | 15.73 | 1250 | 1194 | 16.67 | 31 |
| 1106 | 16.37 | 678 | 1207 | 15.38 | 12 |
| 1109 | 15.99 | 707 | 1238 | 17.07 | 10 |
| 1116 | 16.15 | 538 | 962 | 3.45 | 3660 |
| 1120 | 16.05 | 460 | 964 | 3.61 | 4290 |
| 1121 | 15.14 | 398 | 972 | 3.38 | 3380 |
| 958 | 3.93 | 4290 | 995 | 3.46 | 1910 |
| 972 | 3.95 | 3410 | 1002 | 3.50 | 1640 |
| 992 | 4.04 | 2060 | 1014 | 3.47 | 762 |
| 998 | 4.00 | 1320 | 1017 | 3.48 | 714 |
| 999 | 4.07 | 1530 | 1021 | 3.50 | 596 |
| 1010 | 4.09 | 779 | 1047 | 3.54 | 300 |
| 1021 | 4.04 | 539 | 1051 | 3.52 | 255 |
| 1035 | 3.78 | 373 | 1065 | 3.49 | 189 |
| 923 | 0.91 | 3810 | 1116 | 3.58 | 122 |
| 927 | 0.97 | 3150 | 1160 | 3.65 | 82 |
| 934 | 0.96 | 3440 | 918 | 0.90 | 3620 |
| 937 | 0.90 | 2830 | 937 | 0.90 | 2500 |
| 939 | 0.92 | 2260 | 956 | 0.83 | 1390 |
| 941 | 0.97 | 2080 | 961 | 0.89 | 1480 |
| 957 | 0.91 | 1680 | 1014 | 0.91 | 775 |
| 982 | 0.90 | 1190 | 1061 | 0.89 | 545 |
| 995 | 0.90 | 1030 | 1119 | 0.87 | 367 |
| 1027 | 0.92 | 764 | 1153 | 0.87 | 316 |
| | | | 1192 | 0.93 | 252 |
| | | | 1256 | 0.88 | 192 |
| | | | 1382 | 0.88 | 114 |

| | | | | |
|--|--|------|------|-----|
| | | 1437 | 0.85 | 105 |
| | | 1456 | 0.77 | 109 |
| | | 1709 | 0.99 | 53 |
| | | 1718 | 1.00 | 48 |
| | | | | |

| $\phi = 0.5$, 80% H ₂ , 20% reference gas | | | $\phi = 1.0$, 80% H ₂ , 20% reference gas | | |
|---|-------|------|---|-------|------|
| 1045 | 14.74 | 4190 | 1035 | 14.19 | 4270 |
| 1046 | 14.04 | 3940 | 1071 | 14.10 | 2420 |
| 1068 | 14.34 | 2760 | 1081 | 14.26 | 1950 |
| 1110 | 15.42 | 1470 | 1125 | 14.16 | 960 |
| 1130 | 13.12 | 900 | 1156 | 14.24 | 575 |
| 1188 | 14.06 | 267 | 1189 | 13.99 | 328 |
| 1249 | 14.46 | 95 | 1206 | 13.71 | 242 |
| 984 | 3.58 | 6060 | 1210 | 13.83 | 216 |
| 1000 | 3.61 | 4990 | 1242 | 14.12 | 123 |
| 1006 | 3.69 | 4820 | 1028 | 3.67 | 3630 |
| 1015 | 3.65 | 3560 | 1053 | 3.63 | 2440 |
| 1015 | 3.68 | 3790 | 1077 | 3.59 | 1760 |
| 1031 | 3.58 | 2710 | 1120 | 3.56 | 942 |
| 1066 | 3.66 | 1430 | 1159 | 3.51 | 596 |
| 1086 | 3.69 | 968 | 1194 | 3.41 | 352 |
| 1114 | 3.77 | 612 | 1226 | 3.49 | 239 |
| 1136 | 3.74 | 434 | 1233 | 3.46 | 226 |
| 1172 | 3.62 | 268 | 1260 | 3.52 | 177 |
| 1212 | 3.61 | 164 | 1280 | 3.52 | 137 |
| 1017 | 0.89 | 4300 | 1306 | 3.52 | 109 |
| 1049 | 0.91 | 2360 | 1098 | 0.86 | 2620 |
| 1054 | 0.88 | 1810 | 1155 | 0.86 | 1200 |
| 1099 | 0.79 | 1270 | 1218 | 0.91 | 611 |
| 1108 | 0.90 | 1040 | 1219 | 0.87 | 586 |
| 1149 | 0.87 | 661 | 1226 | 0.97 | 534 |
| 1247 | 0.95 | 307 | 1256 | 0.87 | 451 |
| 1249 | 0.87 | 302 | 1317 | 0.91 | 275 |
| 1273 | 0.87 | 265 | 1363 | 0.93 | 208 |
| 1280 | 0.83 | 277 | 1409 | 0.98 | 155 |

| $\phi = 0.5, 40\% \text{ H}_2, 60\% \text{ reference gas}$ | | | $\phi = 1.0, 40\% \text{ H}_2, 60\% \text{ reference gas}$ | | |
|--|-------|------|--|-------|------|
| 1129 | 14.33 | 3640 | 1102 | 15.73 | 4420 |
| 1139 | 14.03 | 3290 | 1114 | 15.47 | 3890 |
| 1164 | 13.76 | 2370 | 1157 | 16.12 | 2580 |
| 1172 | 17.70 | 2660 | 1168 | 13.33 | 2620 |
| 1233 | 13.93 | 823 | 1176 | 16.22 | 2130 |
| 1234 | 14.17 | 1030 | 1204 | 16.10 | 1520 |
| 1299 | 13.36 | 462 | 1223 | 15.88 | 1280 |
| 1329 | 15.99 | 312 | 1259 | 13.13 | 1060 |
| 1401 | 13.47 | 142 | 1261 | 15.36 | 918 |
| 1131 | 3.71 | 4430 | 1288 | 13.67 | 804 |
| 1169 | 3.69 | 2910 | 1292 | 13.30 | 749 |
| 1175 | 3.55 | 2380 | 1319 | 13.70 | 554 |
| 1199 | 3.61 | 1990 | 1321 | 14.93 | 495 |
| 1237 | 3.63 | 1440 | 1376 | 14.03 | 314 |
| 1241 | 3.74 | 1280 | 1419 | 13.86 | 204 |
| 1298 | 3.74 | 739 | 1467 | 13.87 | 142 |
| 1357 | 3.69 | 398 | 1472 | 13.87 | 136 |
| 1366 | 3.65 | 335 | 1186 | 3.56 | 3750 |
| 1398 | 3.59 | 254 | 1229 | 3.60 | 2540 |
| 1198 | 0.93 | 4510 | 1262 | 3.52 | 1850 |
| 1212 | 0.85 | 3670 | 1302 | 3.51 | 1320 |
| 1251 | 0.89 | 2160 | 1353 | 3.51 | 840 |
| 1285 | 0.93 | 1490 | 1403 | 3.48 | 569 |
| 1297 | 0.91 | 1380 | 1459 | 3.46 | 343 |
| 1300 | 0.89 | 1200 | 1512 | 3.35 | 207 |
| 1318 | 0.94 | 934 | 1525 | 3.38 | 177 |
| 1358 | 0.91 | 729 | 1560 | 3.51 | 147 |
| 1373 | 0.84 | 672 | 1274 | 1.01 | 4380 |
| 1385 | 0.89 | 570 | 1276 | 1.02 | 3660 |
| 1464 | 0.92 | 346 | 1291 | 0.96 | 3290 |
| 1490 | 0.89 | 295 | 1333 | 0.93 | 1900 |
| 1537 | 0.88 | 236 | 1354 | 1.03 | 1460 |
| | | | 1361 | 0.99 | 1740 |
| | | | 1367 | 0.88 | 1390 |
| | | | 1395 | 0.91 | 1120 |
| | | | 1443 | 0.97 | 729 |
| | | | 1452 | 0.91 | 657 |
| | | | 1457 | 0.84 | 697 |
| | | | 1477 | 0.75 | 697 |
| | | | 1501 | 0.84 | 500 |
| | | | 1596 | 0.77 | 244 |
| | | | 1633 | 0.90 | 200 |
| | | | 1731 | 0.82 | 127 |
| | | | 1767 | 0.86 | 97 |
| | | | 1800 | 0.97 | 78 |

| $\phi = 0.5$, 100% reference gas | | | $\phi = 1.0$, 0% , 100% reference gas | | |
|-----------------------------------|-------|------|--|-------|------|
| 1217 | 14.12 | 4260 | 1258 | 13.98 | 3570 |
| 1232 | 13.94 | 3830 | 1321 | 13.66 | 1990 |
| 1234 | 13.95 | 3550 | 1379 | 13.92 | 1290 |
| 1281 | 13.98 | 2300 | 1421 | 13.67 | 854 |
| 1303 | 14.50 | 1930 | 1466 | 13.55 | 537 |
| 1314 | 13.38 | 1290 | 1517 | 13.41 | 345 |
| 1352 | 14.67 | 1160 | 1560 | 13.52 | 200 |
| 1356 | 13.91 | 1110 | 1307 | 3.58 | 4130 |
| 1391 | 13.71 | 769 | 1318 | 3.64 | 4080 |
| 1459 | 14.01 | 415 | 1359 | 3.55 | 3100 |
| 1471 | 14.23 | 369 | 1364 | 3.67 | 3080 |
| 1309 | 3.60 | 3510 | 1398 | 3.54 | 2240 |
| 1336 | 3.59 | 2790 | 1437 | 3.54 | 1640 |
| 1359 | 3.59 | 2190 | 1453 | 3.49 | 1330 |
| 1399 | 3.46 | 1530 | 1487 | 3.37 | 887 |
| 1444 | 3.42 | 998 | 1505 | 3.41 | 891 |
| 1477 | 3.51 | 717 | 1517 | 3.46 | 767 |
| 1480 | 3.54 | 724 | 1566 | 3.31 | 423 |
| 1501 | 3.48 | 474 | 1624 | 3.31 | 261 |
| 1531 | 3.49 | 406 | 1432 | 0.85 | 3370 |
| 1554 | 3.44 | 288 | 1446 | 0.82 | 2340 |
| 1576 | 3.54 | 239 | 1448 | 0.86 | 3090 |
| 1371 | 0.84 | 4360 | 1450 | 0.89 | 2270 |
| 1376 | 0.89 | 3570 | 1461 | 0.94 | 3260 |
| 1379 | 0.82 | 4250 | 1464 | 0.88 | 2600 |
| 1410 | 0.89 | 2870 | 1467 | 0.80 | 2080 |
| 1428 | 0.80 | 1990 | 1474 | 0.82 | 1920 |
| 1436 | 0.84 | 1610 | 1518 | 0.86 | 928 |
| 1437 | 0.76 | 2510 | 1521 | 0.82 | 1190 |
| 1445 | 0.86 | 1960 | 1554 | 0.97 | 862 |
| 1461 | 0.84 | 1280 | 1614 | 0.83 | 534 |
| 1469 | 0.96 | 1170 | 1623 | 0.89 | 444 |
| 1480 | 0.93 | 1120 | 1643 | 0.82 | 359 |
| 1540 | 0.89 | 648 | 1684 | 0.88 | 272 |
| 1545 | 0.91 | 521 | | | |
| 1603 | 0.93 | 352 | | | |
| 1620 | 0.91 | 301 | | | |
| 1623 | 0.94 | 284 | | | |
| 1626 | 0.89 | 287 | | | |
| 1744 | 0.96 | 129 | | | |

Figure S1:

Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 16 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: GRI3.0-mechanism [16], red lines: mechanism of Petrova and Williams [18], blue lines: mechanism of Petersen et al. [19], cyan lines: RD mechanism, orange lines: RD mechanism with H₂ subsystem of Li et al. [23], green lines: Leeds1.5 mechanism[17]. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

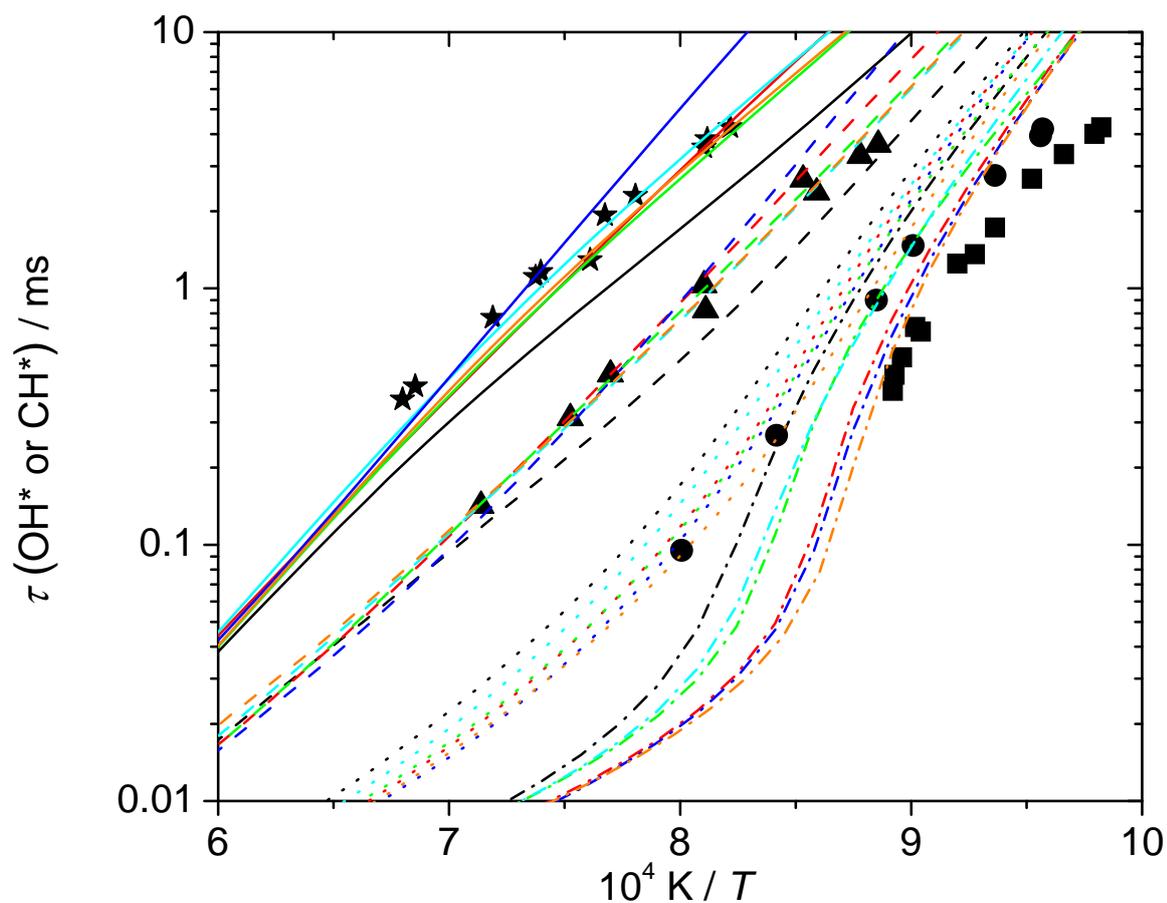


Figure S2:

Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 16 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: GRI3.0 mechanism [16], red lines: mechanism of Petrova and Williams [18], blue lines: mechanism of Petersen et al. [19], cyan lines: RD mechanism, orange lines: RD mechanism with H₂ subsystem of Li et al. [23], green lines: Leeds1.5 mechanism [17]. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

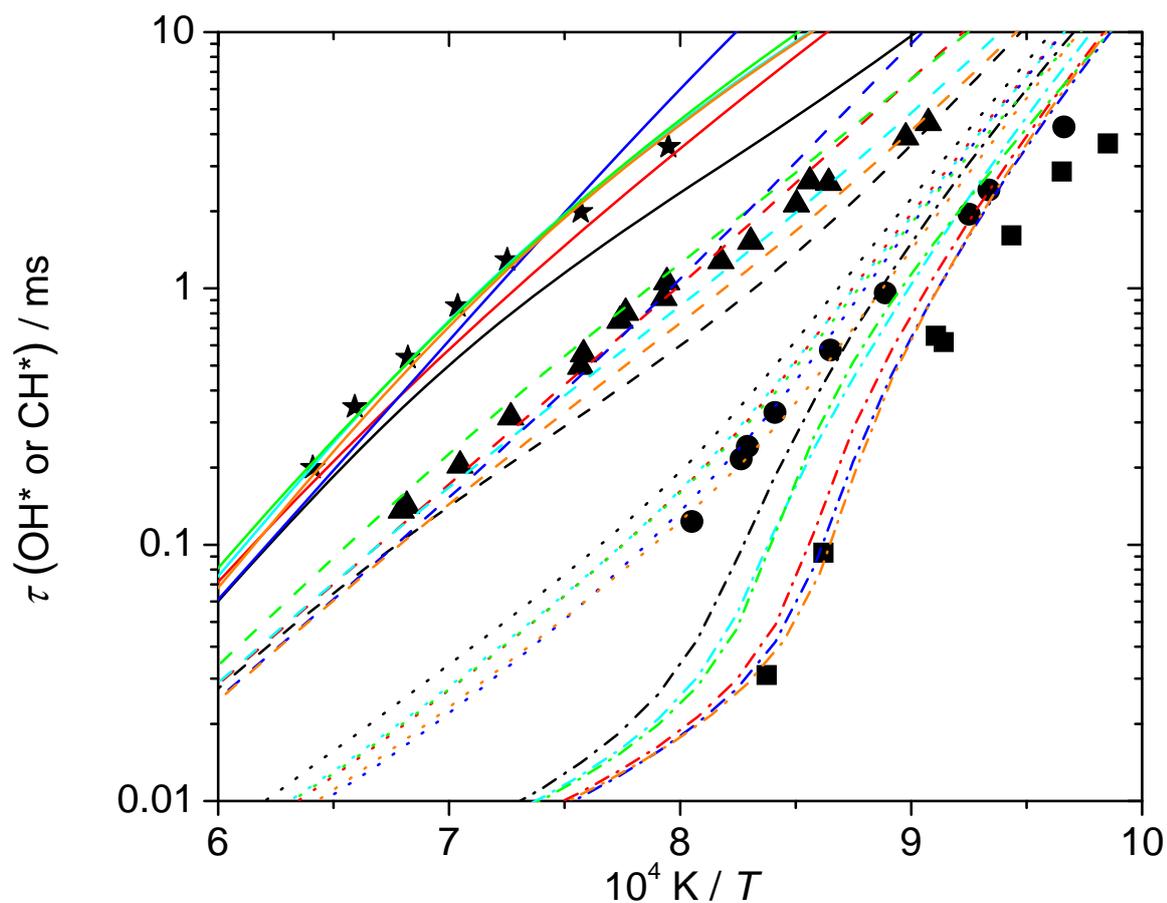


Figure S3:

Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 4 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: GRI3.0 mechanism [16], red lines: mechanism of Petrova and Williams [18], blue lines: mechanism of Petersen et al. [19], cyan lines: RD mechanism, orange lines: RD mechanism with H₂ subsystem of Li et al. [23], green lines: Leeds1.5 mechanism [17]. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

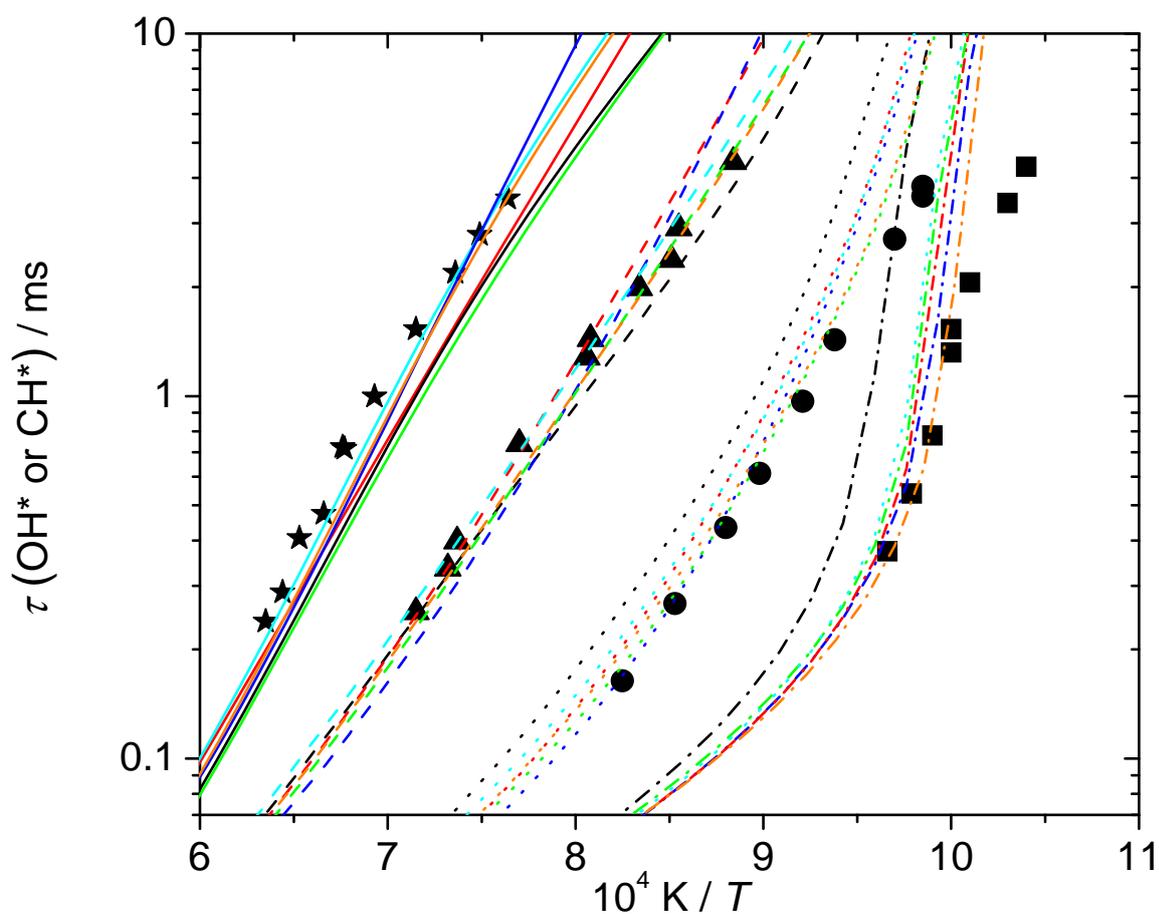


Figure S4:

Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 4 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: GRI3.0 mechanism [16], red lines: mechanism of Petrova and Williams [18], blue lines: mechanism of Petersen et al. [19], cyan lines: RD mechanism, orange lines: RD mechanism with H₂ subsystem of Li et al. [23], green lines: Leeds1.5 mechanism [17]. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

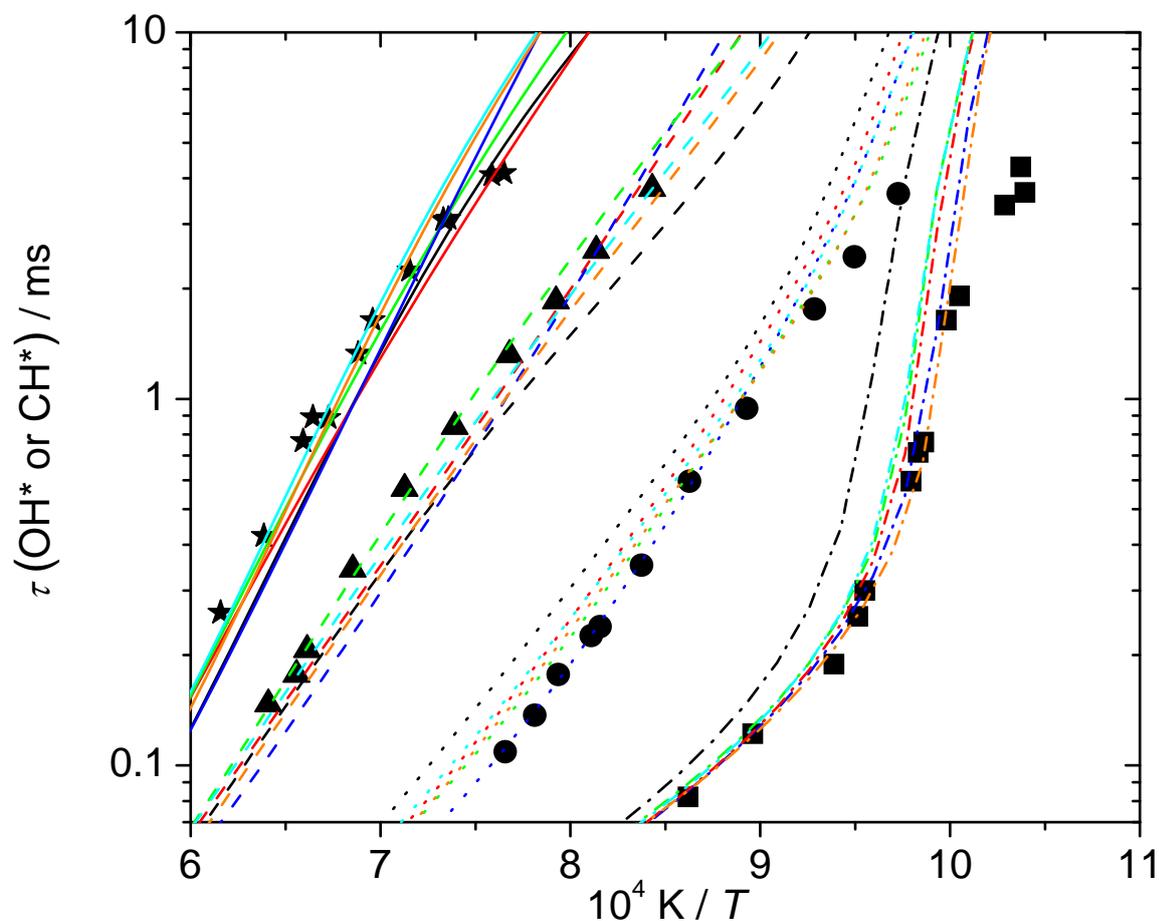


Figure S5:

Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 0.5$, dilution 1:5) at pressures of about 1 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: GRI3.0 mechanism [16], red lines: mechanism of Petrova and Williams [18], blue lines: mechanism of Petersen et al. [19], cyan lines: RD mechanism, orange lines: RD mechanism with H₂ subsystem of Li et al. [23], green lines: Leeds1.5 mechanism [17]. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

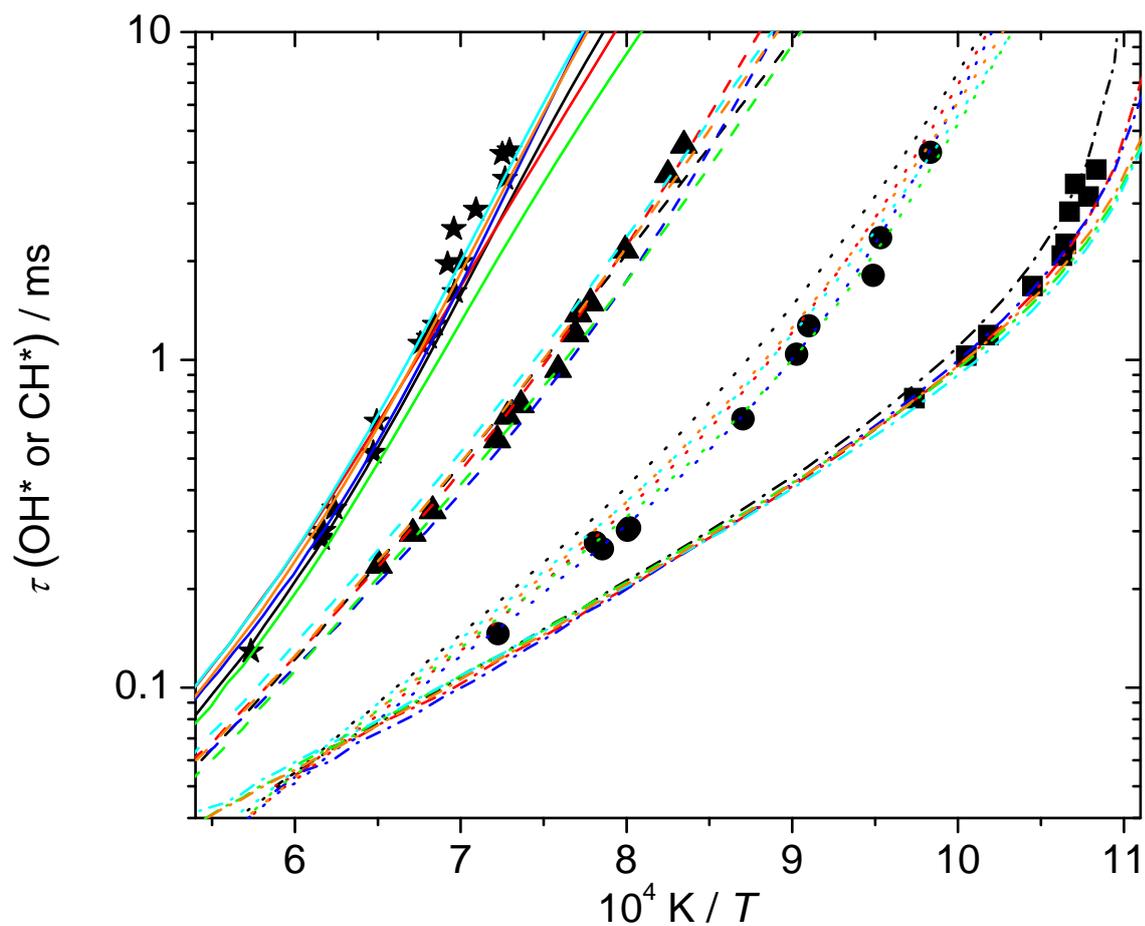


Figure S6:

Measured and calculated ignition delay times for mixtures of hydrogen / reference gas / O₂ / Ar ($\phi = 1.0$, dilution 1:5) at pressures of about 1 bar. Experiments: squares: 100% hydrogen, circles: 80% hydrogen / 20% reference gas, triangles: 40% hydrogen / 60% reference gas, stars: 100% reference gas. MPFR-CHEMKIN II [15] simulations: black lines: GRI3.0 mechanism [16], red lines: mechanism of Petrova and Williams [18], blue lines: mechanism of Petersen et al. [19], cyan lines: RD mechanism, orange lines: RD mechanism with H₂ subsystem of Li et al. [23], green lines: Leeds1.5 mechanism [17]. Dashed-dotted line: 100% hydrogen, dotted line: 80% hydrogen / 20% reference gas, dashed line: 40% hydrogen / 60% reference gas, full line: 100% reference gas.

