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Shock Tube Study of the Ignition of Lean CO/H₂ Fuel Blends at Intermediate Temperatures and High Pressure

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Abstract

The study of the combustion characteristics of H₂/CO fuel blends is of fundamental and technical interest because the H₂/CO system is very important in the hierarchical structure of oxidation models of hydrocarbon fuels and in advanced combustion technologies such as Integrated Gasification Combined Cycle (IGCC) which are currently developed allowing a reduction of the emissions of the power generation using biogenic sources and coal as fuel. Therefore, ignition delay times of 6 different H₂/CO/O₂/Ar-mixtures (fuel: 5% H₂ / 95 % CO and 50% H₂ / 50 % CO, $\Phi=0.5$) were measured at pressures of about 16 bar and temperatures between 1020 and 1260 K. The data were compared to predictions of different literature mechanisms.

1 Introduction

The study of the combustion characteristics of H₂/CO fuel blends is of fundamental and technical interest because the H₂/CO system is very important in the hierarchical structure of oxidation models of hydrocarbon fuels (Westbrook and Dryer, 1981) and in advanced combustion technologies such as Integrated Gasification Combined Cycle (IGCC) which are currently developed allowing a reduction of the emissions of the power generation using biogenic sources and coal as fuel (Mittal et. al., 2007). In the IGC cycle 'syngas', which contains mainly H₂ and CO, is produced by the gasification of coal, municipal waste or biomass. It is further processed by subsequent separation of pollutants and sequestration of CO₂ before its combustion in gas turbines. For the development of the 'syngas' combustors the characteristics of the H₂/CO systems must be understood. The exact knowledge of the kinetics of the combustion of CO/H₂ mixtures over very wide ranges of conditions is also necessary for risk and hazard assessments because of the safety problems of these mixtures due to their rapid flame propagation in high temperature combustion processes (Mittal et. al., 2007). Therefore there are some very recent studies of the CO/H₂ ignition at high pressures and intermediate temperatures between 780 and 1150 K (Mittal et. al., 2007, Petersen et al., 2007, Walton et al., 2007, Mittal et al., 2006) whereas older kinetic studies of the CO + H₂ system were performed at low pressures or high temperatures (see references in Mittal et al., 2007).

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 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% and of carbon monoxide better than 99.9997%.

The ignition was observed by measuring pressure profiles with piezo-electric gauges (PCB 113 A24) located at a distance of 1 cm from the end flange. Also, the OH* emission at 307 nm at the same position was selected by a narrow band pass filter (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 OH* maximum.

The experimental setup allows measurements of ignition delay times at constant pressure and temperature conditions for observation times < 4.5 ms, if no heat release of the chemical system occurs.

3 Results

The ignition delay times of 6 different H₂/CO/O₂/Ar-mixtures (fuel: 5% H₂ / 95% CO, $\Phi = 0.5$, dilution 1:2, 1:5, 1:10, fuel: 50% H₂ / 50% CO, $\Phi = 0.5$, dilution 1:2, 1:5, 1:10, see table 1) were measured at pressures of about 16 bar and temperatures between 1019 and 1259 K. Typical results are presented in Fig. 1, 2 and 3.

Figure 1 shows an experiment with 50% H₂ / 50% CO and a dilution of 1:10 at T = 1054 K and p = 15.59 bar. A strong increase of the pressure and the emission can be observed at about 4000 μ s. Similar characteristics of the signals are found for both H₂/CO mixtures at dilutions of 1:2 and 1:5 and for the 50% H₂ / 50% CO fuel blend at a dilution of 1:10 at temperatures lower than 1100 K with the pressure increase becoming weaker with increasing temperature for this mixture. A slow increase of the pressure and the emission before strong ignition could be observed only for the experiments with the 5% H₂ / 95% CO mixture at a dilution of 1:5, see fig. 2.

The 5% H₂ / 95% CO fuel blend at a dilution of 1:10 shows two emission maxima (see Fig. 3). The first one is increasing relatively to the second one with increasing temperatures. The pressure profiles feature a continuous small increase during the observation time beginning with the first maximum in the OH* emission but no steep increase and no maximum.

The experimental results are listed in table 2.

4 Discussion

The measured ignition delay times and comparisons to MPFR (Multiple Plug Flow Reactor)-CHEMKIN II (Kee et al., 1989) predictions of literature mechanisms (GRI3.0 (Smith et al., 1999), LEEDS1.5 (Hughes et al., 2001), USC Mech Version II (Wang et al., 2007), Li et al., 2007) are summarized in figs. 4 - 11. The reaction $\text{H} + \text{O} + \text{M} \rightleftharpoons \text{OH}^* + \text{M}$ and thermal and spectroscopic deexcitation reactions of OH^* (Smith et al., 2002) were added to the mechanisms for comparability with the experimental results. In agreement with the H_2/CO combustion mechanism of Davis et al. (2005), which is included in the USC Mech Version II, we changed the rate coefficients of the $\text{H} + \text{O}_2 (+\text{Ar} \text{ or } \text{H}_2\text{O}) \Rightarrow \text{HO}_2 (+\text{Ar} \text{ or } \text{H}_2\text{O})$ reaction. Instead of using only other collision efficiencies for Ar and H_2O like proposed in the USC Mech Version II we used the rate coefficients with slightly other activation energies like included in the H_2/CO mechanism by Davis et al. (2005) which are taken from the data evaluation of Baulch et al., 2005. Although the differences in the rate coefficients for the $\text{H} + \text{O}_2 (+\text{Ar}) \Rightarrow \text{HO}_2 (+\text{Ar})$ reaction are only up to about 10%, the differences in the predicted ignition delay times are very pronounced because of the high sensitivity of this reaction.

MPFR-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 μs or shorter depending on the heat release ($\Delta T = 0.5\%$)) 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. For the calculations of the experiments presented, gasdynamical

effects, which causes a pressure and temperature increase independent of the heat release of the chemical system, did not need to be considered within the observation period (see constant pressure signal of fig. 1).

The USC Mech Version II (Wang et al., 2007) agrees very well with the measurements of the 5% H₂ / 95% CO fuel blend in the upper temperature range of each dilution whereas at lower temperatures, too long ignition delays are predicted.. For the lowest dilution of 1:2 the simulations with the GRI3.0 (Smith et al., 1999) and the LEEDS1.5 (Hughes et al., 2001) mechanisms also reproduce very well the experimental results. For higher dilutions of 1:5 and 1:10 they predict clearly too long ignition delay times. The simulations with the model of Li et al. (2007) show generally too long ignition delay times, especially at lower temperatures. The pressure profile, the double peak structure and the very broad OH*-emission profiles of the 5% H₂/ 95% CO mixture with a dilution of 1:10 (see fig. 3) are qualitatively well described by all mechanisms used, see fig. 12. The OH*-maxima are caused by maxima in the H- and O-concentration profiles, leading to the production of OH* by the reaction of $O+H \Leftrightarrow OH^*$. The first maximum appears during the fast oxidation of the H₂, which initializes the CO oxidation causing a second OH*-maximum. For the less diluted mixtures the temperature increase by the H₂-oxidation is more pronounced so that the CO oxidation becomes faster and only one narrow peak (see fig. 1) can be observed. The time of the first maximum is best predicted by the Leeds1.5 mechanism (Hughes et al., 2001) whereas the simulated times of the USC Mech Version II (Wang et al. (2007)) and the Li et al. (2007) mechanism are about a factor of 2 too short. We did additional calculations for H₂/O₂/Ar mixtures replacing the CO of the 95% CO / 5% H₂ mixture by Ar. These predictions agree very well with the values for the 95% / 5% H₂ mixture confirming that the first OH* maximum is only caused by the H₂ subsystem. Differences between experiments and simulations are due to the failure of the

different mechanisms to reproduce the ignition in this very lean ($\Phi=0.025$) $\text{H}_2 / \text{O}_2 / \text{Ar}$ mixture. For the dilution 1:5, the first maximum at early reaction times predicted at the highest temperatures of this series could not be found in the experiments.

For the 50% H_2 / 50% CO mixture, the USC Mech Version II (Wang et al. 2007) shows a good agreement with the experiments only for temperatures higher than about 1075 K. For lower temperatures the simulated ignition delay times are up to a factor of 2 too long. The GRI3.0 (Smith et al., 1999) mechanism predicts up to a factor of 3 too long ignition delay times in the whole temperature range of the measurements. The model of Li et al. (2007) agrees well with the measured values for the higher temperatures of this study. For lower temperatures it predicts ignition delay times up to a factor of 2 too long.

Figure 13 shows a comparison of the CO/ H_2 ignition-delay measurements to H_2 data at the same dilution of 1:5 together with simulations with the Li et al. mechanism (Li et al., 2007). It can be seen that there is a good agreement of the experimental data for 50% H_2 / 50% CO and for 100% H_2 whereas the 5% H_2 / 95% CO data exhibit longer ignition delay times. This confirms the experimental results of Walton et al., 2007 and Mittal et al., 2007, that there are no differences between the ignition delay times of pure H_2 and H_2 /CO mixtures with up to 80% CO. The simulations feature no differences between the 50% H_2 / 50% CO and the 100% H_2 data, too, see e.g. fig. 13 for the mechanism of Li et al, 2007. This shows that the kinetic system for this mixture is dominated by the H_2 system and thus this kinetic subsystem must be improved for the conditions of this study to achieve a better agreement between the simulations and the experimental results.

We do not think that the deviations can be explained by 'mild ignition effects' which are used by Dryer and Chaos (2008) to explain the differences between experiments and predictions of ignition delay times of syngas and hydrogen at lower temperatures and high

pressures. The temperature of these study are slightly above the range where Petersen et. al. (2007) and Dryer and Chaos (2007) observe the 'mild ignition' effects, the dilutions, that were used, reduce these effects and the good reproducibility in the lower temperature range is not typical for the 'mild ignition' region.

Sensitivity analyses for the 5% H₂ / 95 % CO and the 50% H₂ / 50% CO mixtures confirm that the ignition delay times are determined by the H₂ subsystem for both mixtures, see fig. 14. The most sensitive reactions are $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ and $\text{H} + \text{O}_2 (+ \text{M}) \rightleftharpoons \text{HO}_2 (+\text{M})$. Other very sensitive reactions are $\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$ (only for the 5% CO / 95% H₂ mixture), $\text{CO} + \text{HO}_2 \rightleftharpoons \text{CO}_2 + \text{OH}$, $\text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H}$ and $\text{H}_2\text{O}_2 (+ \text{M}) \rightleftharpoons 2 \text{OH} (+\text{M})$. For almost all of these reactions the different mechanisms use different rate coefficients, only the rate coefficients for $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ of the USC Mech Version II (Wang et al. 2007) and the Leeds 1.5 (Hughes et al., 2001) mechanism and the value for $\text{CO} + \text{HO}_2 \rightleftharpoons \text{CO}_2 + \text{OH}$ of the GRI3.0 (Smith et al., 1999) and the Leeds1.5 mechanism are identical. The rate coefficient of $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$ of the Li et al. (2007) and the Leeds1.5 mechanism are quite similar to each other and to the recommended value of Baulch et al. (2005) whereas the GRI3.0 and the USC Mech Version II value are about 30% lower, differing very much from elementary kinetic measurements. For the reaction $\text{H} + \text{O}_2 (+ \text{Ar}) \rightleftharpoons \text{HO}_2 (+\text{Ar})$ all used mechanisms contain different rate coefficients which are up to 50% different at 1100 K. This leads to differences in the branching ratio of both reaction of about 10% in the measurement range of this study regarding only the USC Mech Version II, the Leeds1.5 and the Li et al. mechanism. The GRI3.0 predicts a branching ratio which is up to a factor of two higher favouring the HO₂ production.

5 Conclusions

The ignition delay times of 6 different H₂/CO/O₂/Ar-mixtures (fuel: 5% H₂ / 95% CO and 50% H₂ / 50% CO at an equivalence ratio $\Phi = 0.5$ and dilutions of 1:2, 1:5, 1:10) were measured at pressures of about 16 bar and temperatures between 1019 and 1259 K. The results were compared to MPFRCHEMKIN II (Kee et al, 1989) predictions using 4 different literature mechanisms (GRI3.0 (Smith et al., 1999), LEEDS1.5 (Hughes et al., 2001), USC Mech Version II (Wang et al., 20057), Li et al., 2007). None of the mechanisms can reproduce the experimental values very well. A comparison to data of pure H₂ shows that the 50% H₂ / 50% CO fuel blend has almost identical ignition delay times, whereas the 5% H₂ / 95% CO has longer ignition delay times so that we can conclude in agreement with Dryer and Chaos (2008) that the kinetic system of the 50% H₂ / 50% CO fuel blend is dominated by the H₂ kinetic subsystem. The failure of all used literature mechanisms to predict the ignition delay times of the 50% H₂ / 50% CO fuel blend in the whole temperature range can therefore be explained by the failure of these mechanisms to represent the H₂ system at high pressures and intermediate temperatures. The predictions of the H₂ data show the same deviations like the 50% H₂ / 50% CO data. Therefore, the H₂ kinetic system must be improved in order to get a good representation of the combustion characteristics of H₂ or H₂/CO fuel blends with high H₂ content at gas turbine relevant conditions.

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Figure captions:

Fig. 1: Typical pressure (black line) and OH* emission (grey line) profiles of a lean H₂ / CO / O₂ / Ar mixture ($\Phi = 0.5$, dilution 1:10, 50% H₂ / 50% CO) at $T_5 = 1054$ K, $p_5 = 15.59$ bar.

Fig. 2: Typical pressure (black line) and OH* emission (grey line) profiles of a lean H₂ / CO / O₂ / Ar mixture ($\Phi = 0.5$, dilution 1:10, 5% H₂ / 95% CO) at $T_5 = 1107$ K, $p_5 = 16.18$ bar.

Fig. 3: Typical pressure (black line) and OH* emission (grey line) profiles of a lean H₂ / CO / O₂ / Ar mixture ($\Phi = 0.5$, dilution 1:10, 5% H₂ / 95% CO) at $T_5 = 1223$ K and $p_5 = 16.04$ bar.

Fig. 4: Measured ignition delay times of 5% H₂ / 95% CO / O₂ / Ar ($\Phi=0.5$) mixtures. Circles: dilution 1:2, squares: dilution 1:5, stars: main ignition at a dilution of 1:10, triangles: first OH* maximum at a dilution of 1:10. The lines show the trends of the data.

Fig. 5: Measured ignition delay times of 50% H₂ / 50% CO / O₂ / Ar ($\Phi=0.5$) mixtures. Circles: dilution 1:2, squares: dilution 1:5, stars: dilution 1:10. The lines show the trends of the data.

Fig. 6: Measured and simulated ignition delay times of a 5% H₂ / 95% CO / O₂ / Ar ($\Phi=0.5$) mixture at a dilution of 1:2. Circles: experiments in the temperature range 1046 K $< T_5 < 1132$ K at pressures p_5 between 14.48 and 16.91 bar. The lines show CHEMKIN (Kee et al. 1989) predictions with the following mechanisms: full line: GRI3.0 (Smith et al., 1999), dashed line:

Leeds 1.5 (Hughes et al., 2001), dotted line: Davis et al, 2005, dashed-dotted line: Li et al., 2007.

Fig. 7: Measured and simulated ignition delay times of a 5% H₂ / 95% CO / O₂ / Ar ($\Phi=0.5$) mixture at a dilution of 1:5. Squares: experiments in the temperature range 1107 K < T_5 < 1206 K at pressures p_5 between 15.66 and 16.38 bar. The lines show CHEMKIN (Kee et al. 1989) predictions with the following mechanisms: full line: GRI3.0 (Smith et al., 1999), dashed line: Leeds 1.5 (Hughes et al., 2001), dotted line: Davis et al, 2005, dashed-dotted line: Li et al., 2007. Grey lines indicate time of first OH*-maximum predicted.

Fig. 8: Measured and simulated ignition delay times of a 5% H₂ / 95% CO / O₂ / Ar ($\Phi=0.5$) mixture at a dilution of 1:10. Stars: experiments in the temperature range 1165 K < T_5 < 1259 K at pressures p_5 between 15.88 and 16.42 bar, main ignition, triangles: first OH* maximum measured. The lines show CHEMKIN (Kee et al. 1989) predictions with the following mechanisms: full line: GRI3.0 (Smith et al., 1999), dashed line: Leeds 1.5 (Hughes et al., 2001), dotted line: Davis et al, 2005, dashed-dotted line: Li et al., 2007. Grey lines indicate time of first OH*-maximum predicted.

Fig. 9: Measured and simulated ignition delay times of a 50% H₂ / 50% CO / O₂ / Ar ($\Phi=0.5$) mixture at a dilution of 1:2. Circles: experiments in the temperature range 1019 K < T_5 < 1097 K at pressures p_5 between 14.11 and 15.84 bar. The lines show CHEMKIN (Kee et al. 1989) predictions with the following mechanisms: full line: GRI3.0 (Smith et al., 1999), dashed line: Leeds 1.5 (Hughes et al., 2001), dotted line: Davis et al, 2005, dashed-dotted line: Li et al., 2007.

Fig. 10: Measured and simulated ignition delay times of a 50% H₂ / 50% CO / O₂ / Ar ($\Phi=0.5$) mixture at a dilution of 1:5. Squares: experiments in the temperature range 1048 K < T_5 < 1128 K at pressures p_5 between 15.31 and 15.97 bar. The lines show CHEMKIN (Kee et al. 1989) predictions with the following mechanisms: full line: GRI3.0 (Smith et al., 1999), dashed line: Leeds 1.5 (Hughes et al., 2001), dotted line: Davis et al, 2005, dashed-dotted line: Li et al., 2007.

Fig. 11: Measured and simulated ignition delay times of a 50% H₂ / 50% CO / O₂ / Ar ($\Phi=0.5$) mixture at a dilution of 1:10. Stars: experiments in the temperature range 1054 K < T_5 < 1140 K at pressures p_5 between 15.59 and 15.87 bar. The lines show CHEMKIN (Kee et al. 1989) predictions with the following mechanisms: full line: GRI3.0 (Smith et al., 1999), dashed line: Leeds 1.5 (Hughes et al., 2001), dotted line: Davis et al, 2005, dashed-dotted line: Li et al., 2007.

Fig. 12: Calculated normalized concentrations of a 5% H₂ / 95% CO / O₂ / Ar mixture ($\Phi=0.5$, dilution 1:10) using the Leeds 1.5 mechanism (Hughes et al. 2001). The conditions (concentrations, $p_5 = 16.04$ bar, $T_5 = 1223$ K) are identical to fig. 3. Full line: H₂, short-dashed line: CO, dotted line: OH*, dashed-dotted line: H, long-dashed line: O, grey line: temperature.

Fig. 13: Comparison of the ignition delay times of lean CO/H₂/O₂/Ar mixtures with a H₂/O₂/Ar mixtures, all at an equivalence ratio $\Phi=0.5$, a dilution of 1:5 and pressures of about 16 bar. Circles: 5% H₂ / 95% CO, squares: 50% H₂ / 50% CO, stars: 100% H₂. The lines show

CHEMKIN (Kee et al. 1989) simulations with the mechanism of Li et al., 2007: full line: 5% H₂ / 95% CO, dashed line: 50% H₂ / 50% CO, dotted line: 100% H₂.

Fig. 14: Sensitivity analysis of the ignition delay times using the USC Mech VersionII (Wang et al. 2007).

Fig. 1

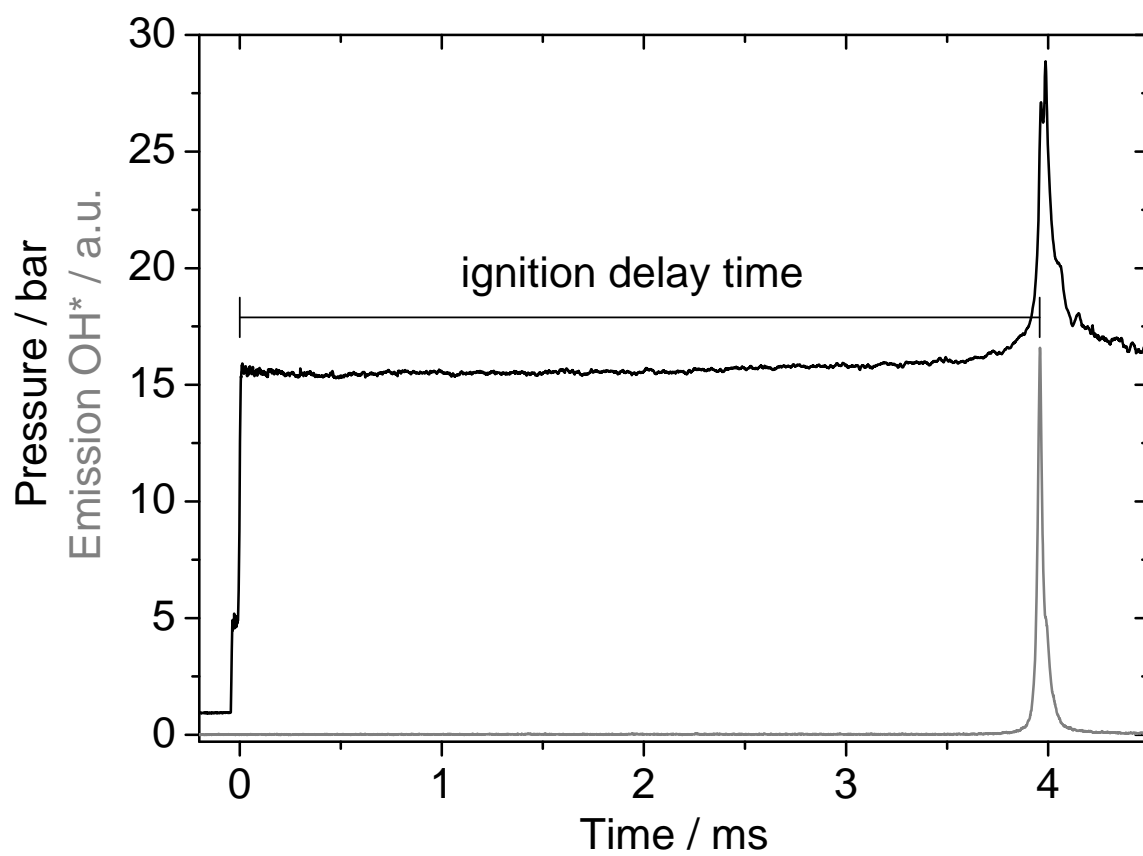


Fig. 2

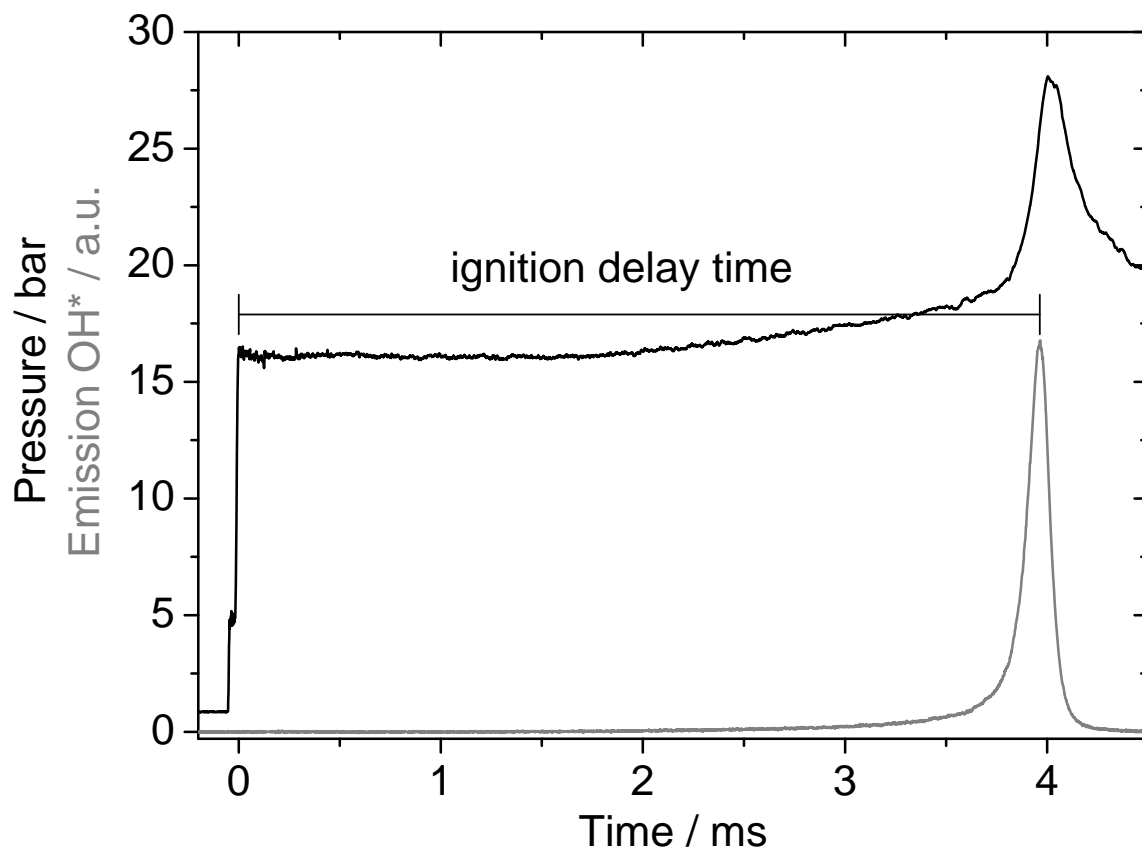


Fig. 3

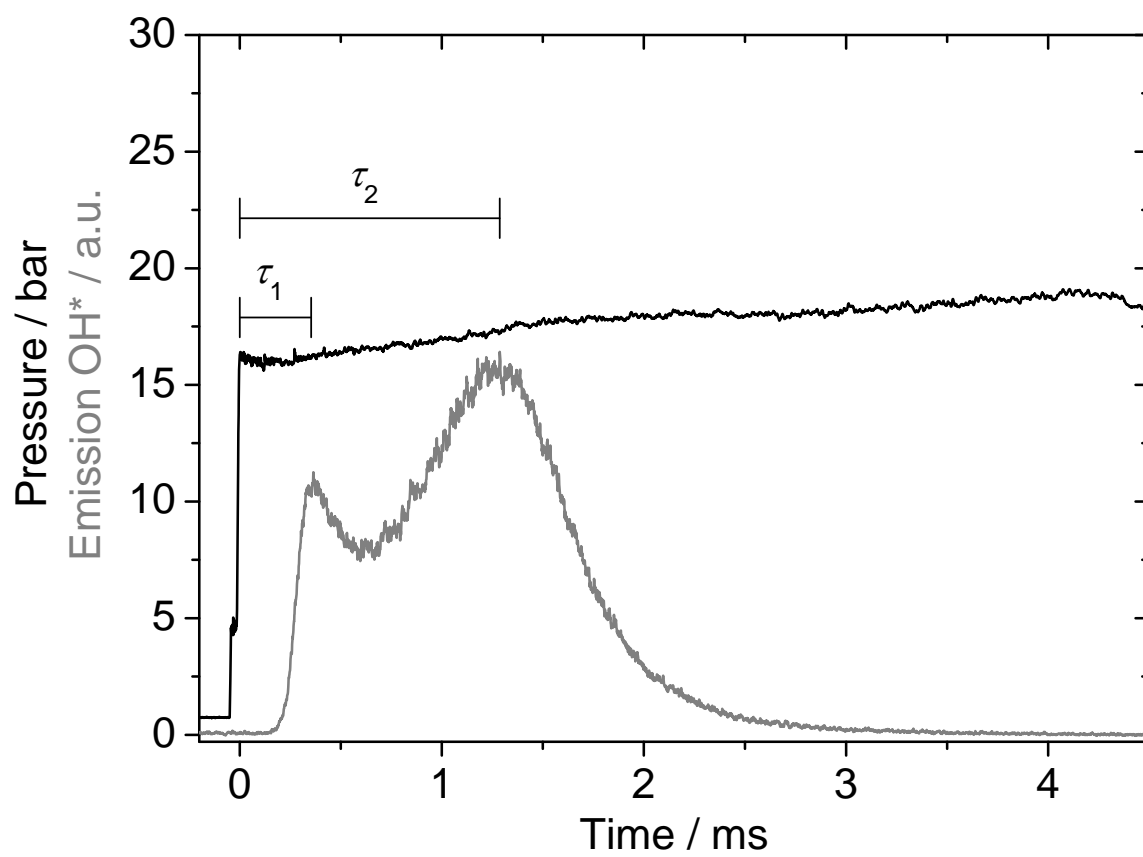


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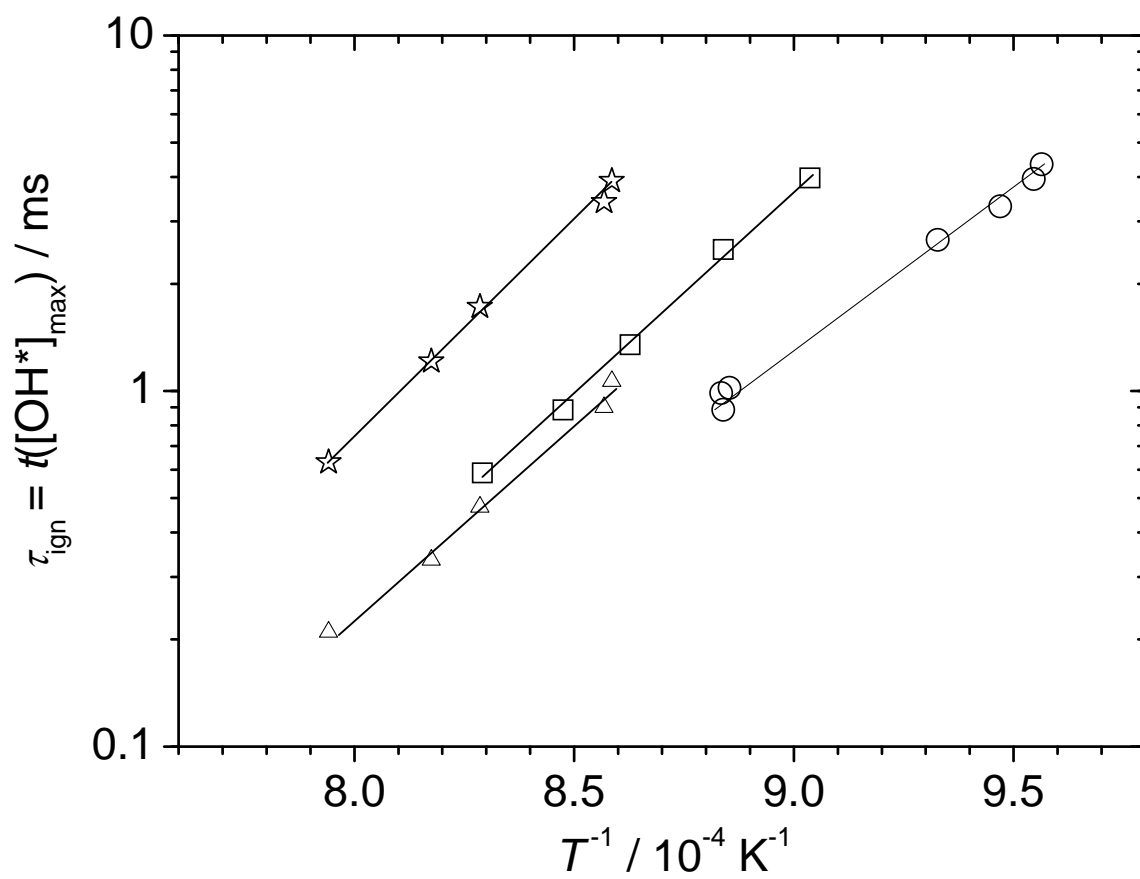


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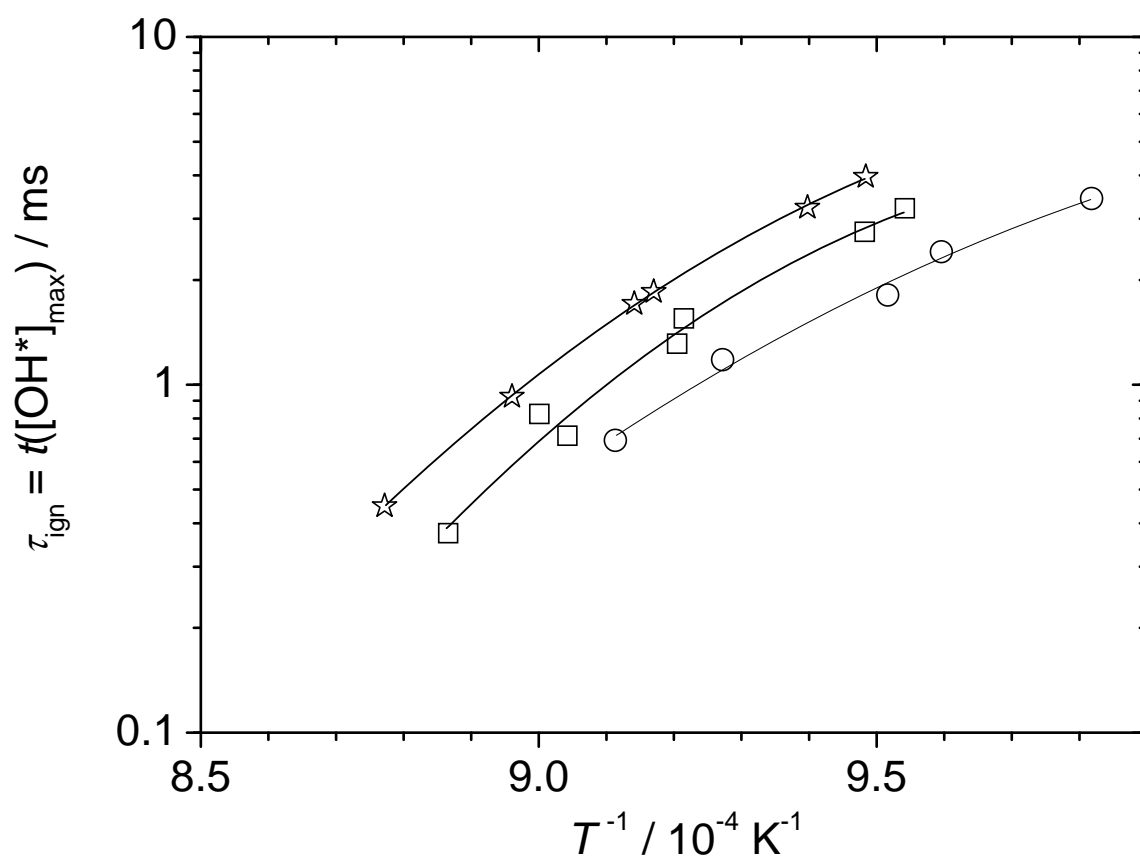


Fig. 6

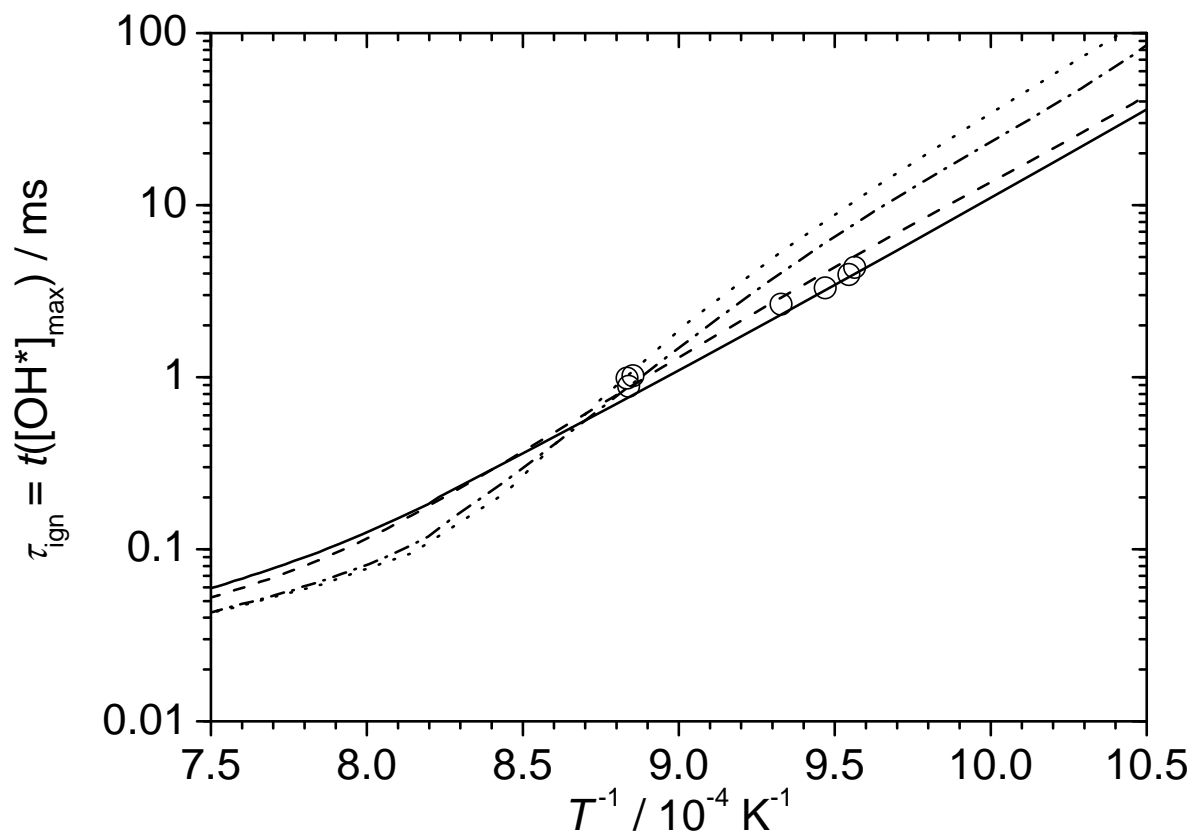


Fig. 7

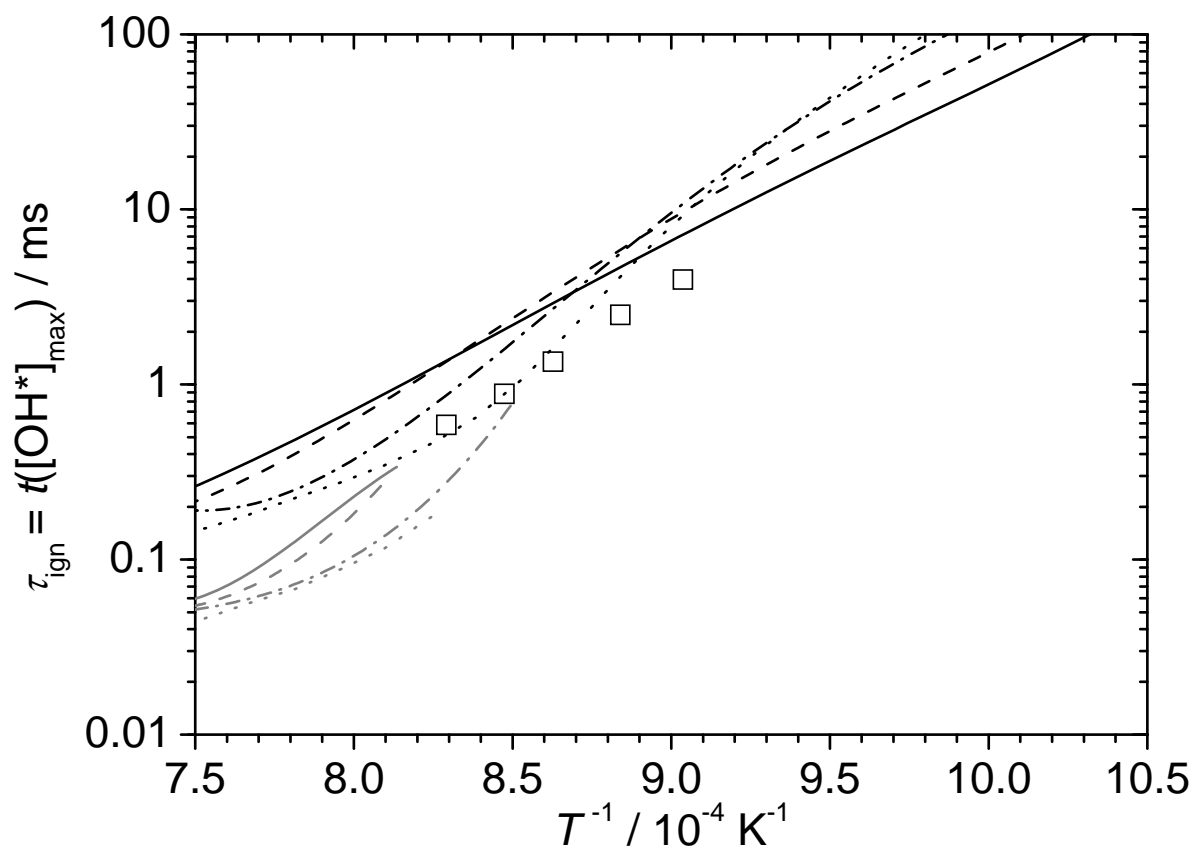


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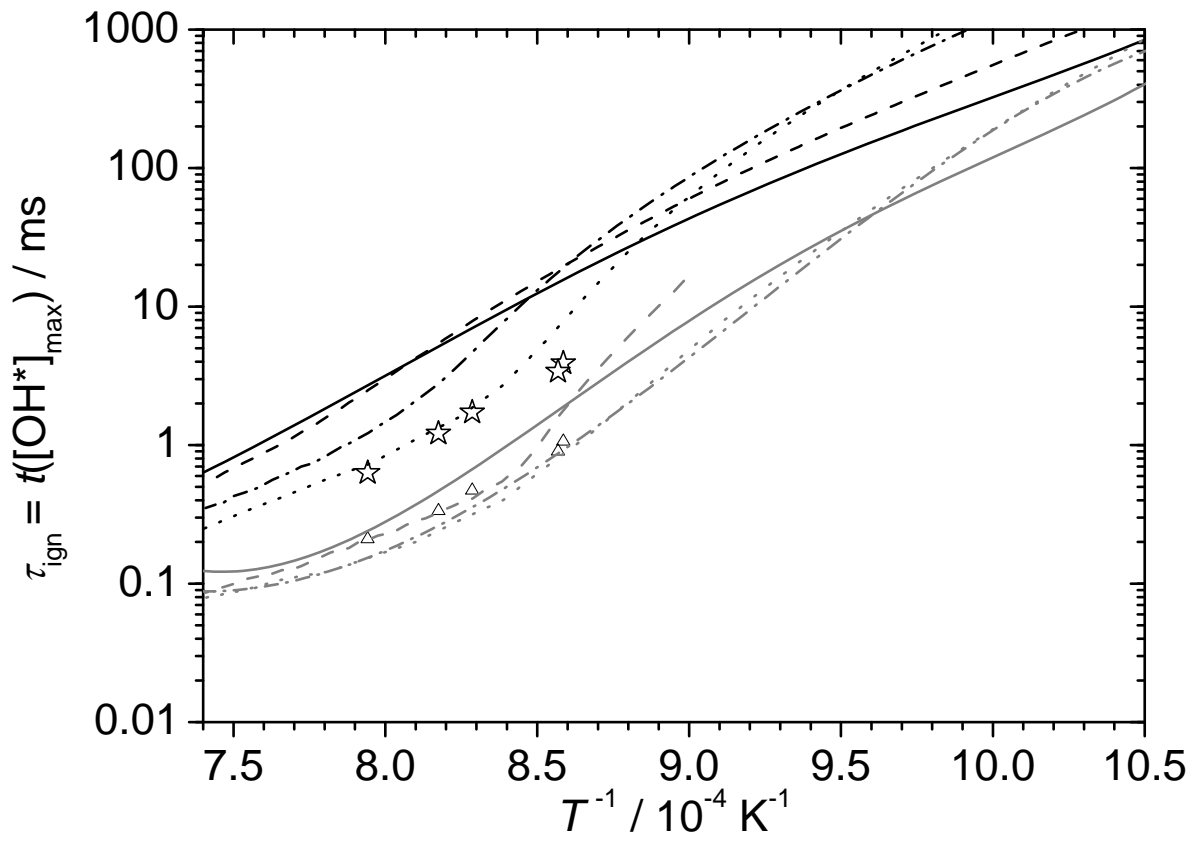


Fig. 9

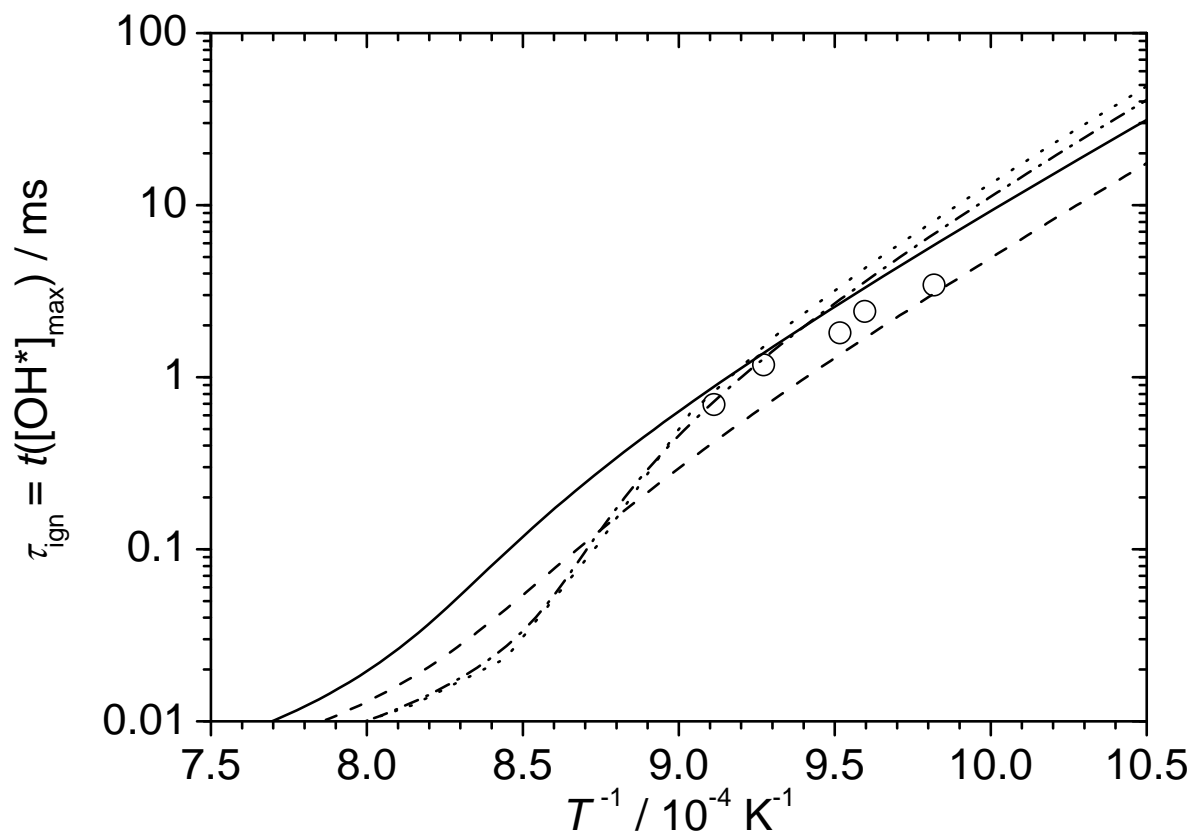


Fig. 10

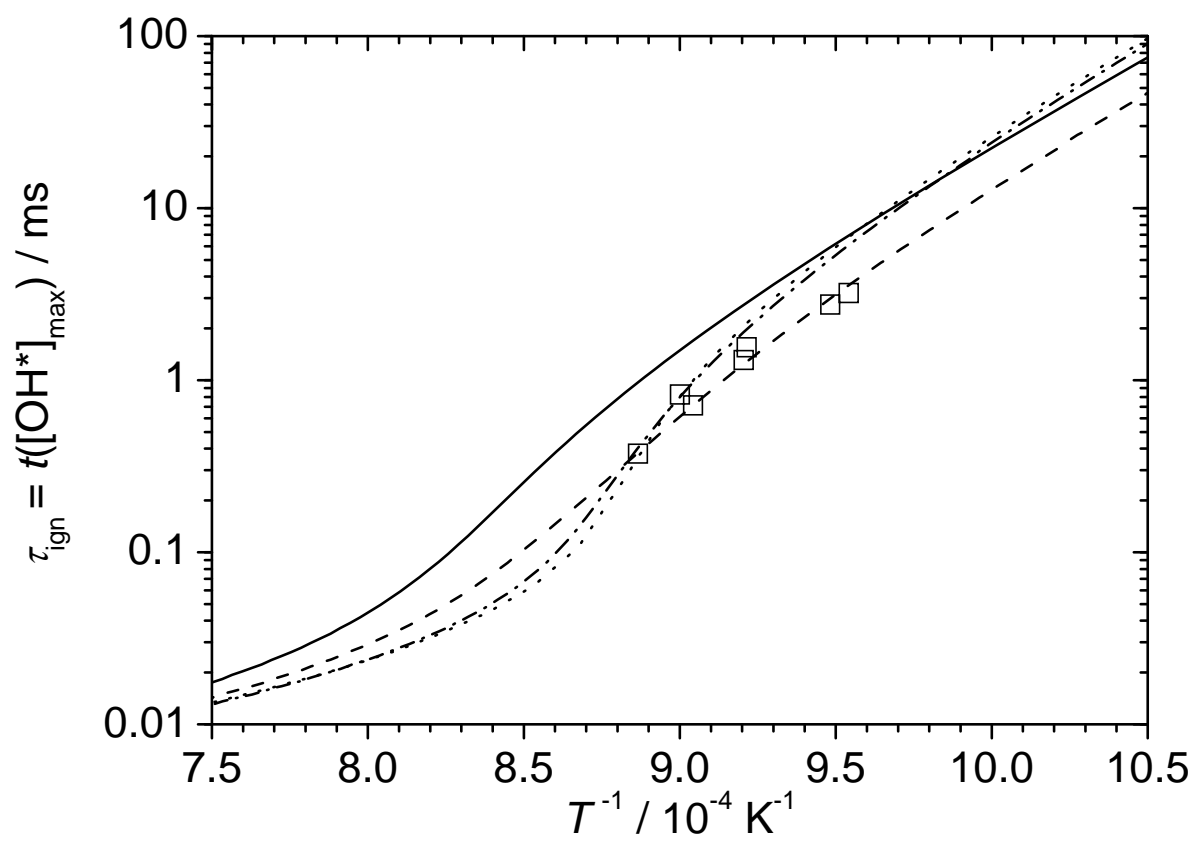


Fig. 11

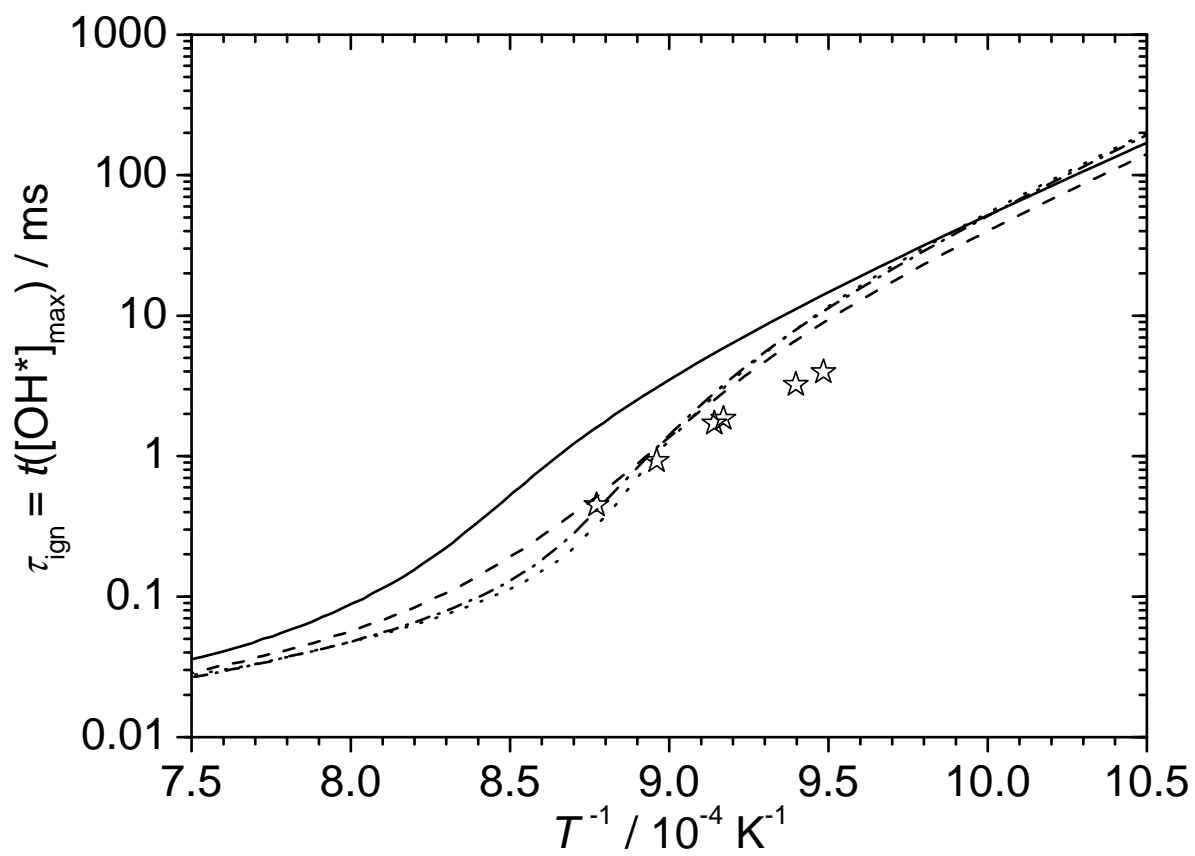


Fig. 12

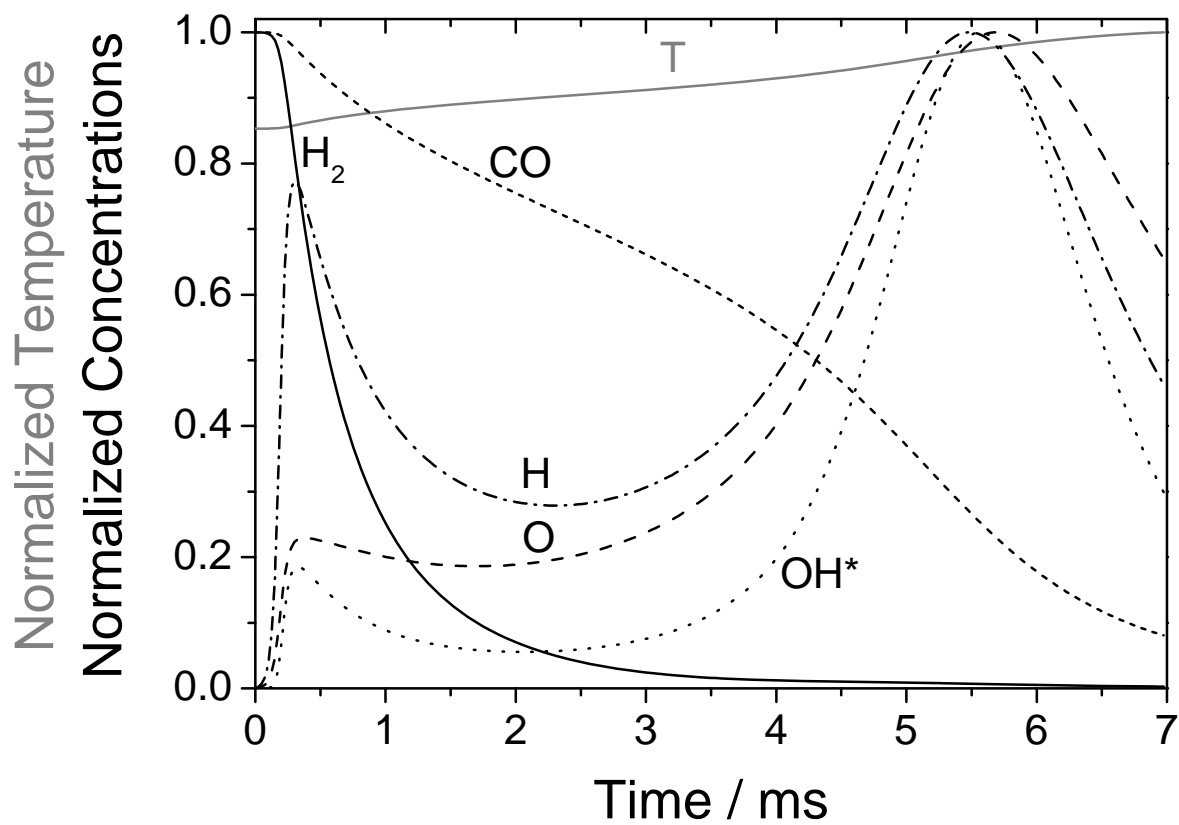


Fig. 13

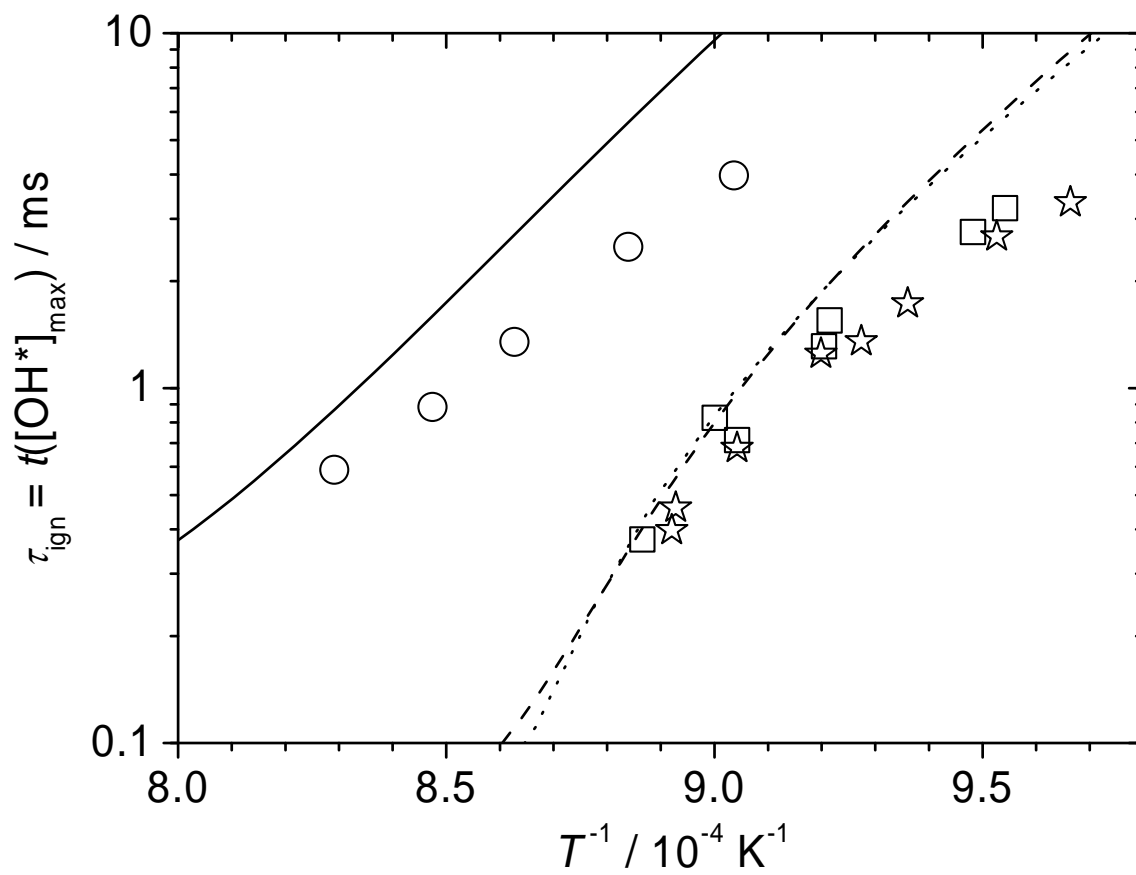


Fig. 14

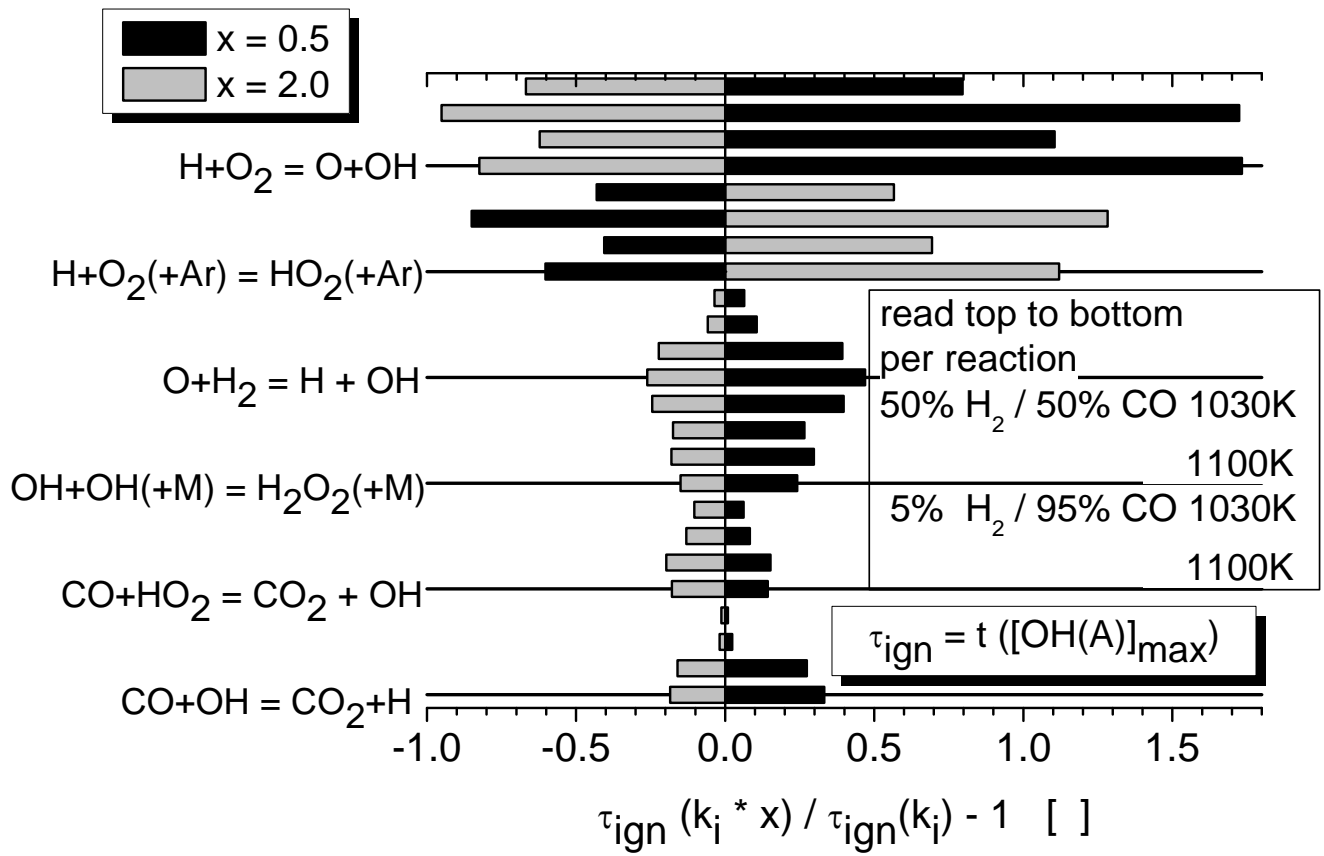


Table 1: List of the used mixtures.

5% H ₂ / 95% CO ($\Phi=0.5$)				
dilution	H ₂	CO	O ₂	Ar
1:2	0.436%	8.228%	8.657%	82.679%
1:5	0.175%	3.301%	3.473%	93.051%
1:10	0.088%	1.654%	1.740%	96.518%
50% H ₂ / 50% CO ($\Phi=0.5$)				
dilution	H ₂	CO	O ₂	Ar
1:2	4.364%	4.364%	8.718%	82.554%
1:5	1.770%	1.800%	3.559%	92.871%
1:10	0.858%	0.872%	1.725%	96.545%

Table 2: List of the measured ignition delay times.

5% H₂ / 95% CO		
Dilution 1:2		
Temperature / K	Pressure / bar	Ignition Delay Time / μ s
1046	16.80	4340
1048	16.24	3950
1056	14.48	3310
1072	15.76	2660
1130	16.91	1020
1131	14.77	886
1132	16.15	986
Dilution 1:5		
Temperature / K	Pressure / bar	Ignition Delay Time / μ s
1107	16.18	3970
1131	15.66	2500
1159	16.14	1350
1180	16.30	884
1206	16.38	588
Dilution 1:10		

Temperature / K	Pressure / bar	Ignition Delay Time / μs	
		τ_1	τ_2
1165	16.05	1070	3900
1167	16.03	900	3400
1207	16.42	470	1730
1223	16.04	335	1210
1259	15.88	210	630

50% H₂ / 50% CO

Dilution 1:2

Temperature / K	Pressure / bar	Ignition Delay Time / μs
1019	14.11	3430
1042	15.27	2410
1051	15.27	1810
1078	15.84	692
1097	15.56	470

Dilution 1:5

Temperature / K	Pressure / bar	Ignition Delay Time / μs
1048	15.97	3210

1055	15.77	2750
1085	15.93	1550
1086	15.53	1310
1106	15.31	714
1111	15.62	825
1128	15.53	374
Dilution 1:10		
Temperature / K	Pressure / bar	Ignition Delay Time / μ s
1054	15.59	3960
1064	15.69	3230
1090	15.82	1850
1094	15.50	1710
1116	15.79	925
1140	15.87	448