LLNL-CONF-469271

Detailed Chemical Kinetic Model for H2 and H2/CO (Syngas) Mixtures at Elevated Pressure

A. Keromnes, W. K. Metcalfe, N. Donohoe, H. J. Curran, W. J. Pitz

February 7, 2011

7th US National Technical Meeting of the Combustion Institute
Atlanta, GA, United States
March 20, 2011 through March 23, 2011

Disclaimer

7th US National Technical Meeting
of the Combustion Institute
Hosted by the Georgia Institute of Technology, Atlanta, GA
March 20-23, 2011

Detailed Chemical Kinetic Model for H_2 and H_2/CO (Syngas) Mixtures at Elevated Pressure

A. Kéromnès[1], W.K. Metcalfe[1], N. Donohoe[1], H.J. Curran[1], W.J. Pitz[2]

[1]Combustion Chemistry Centre, National University of Ireland, Galway
School of Chemistry, University Rd., Galway, Ireland
[2]Lawrence Livermore National Laboratory, Livermore, CA 94551

An improved detailed chemical kinetic mechanism for hydrogen and H_2/CO syngas mixtures has been developed to reflect new experimental information obtained at high pressures, and new rate constant values recently published in the literature. In the mechanism validation, particular emphasis is placed on reproducing behaviour at high pressures and temperatures which are important conditions for applications in internal combustion engines and gas turbines. The mechanism has been validated over a range of pressures of 1 to 50 atmospheres, 900–2500 K temperature and 0.1–4.0 equivalence ratios. Diluents included nitrogen, argon and helium. The detailed chemical kinetic model agrees well with ignition delay times up to 50 bar and with laminar flame speeds from 1 to 10 atmospheres. The reaction sequence $H_2 + HO_2 = H + H_2O_2$ followed by $H_2O_2 = OH + OH$ was found to play a key role for hydrogen ignition at high pressure. The rate constant for $H_2 + HO_2$ showed extreme sensitivity for high pressure ignition and has considerable uncertainty based on literature values. A rate constant for this reaction is recommended based on available literature values and our mechanism validation: $k = 2.15 \times 10^{10} T^{1.0} \exp(-6000 \text{ cal}/RT)$. Hydrogen oxidation was investigated experimentally and simulated with a revised chemical kinetic model. Ignition delay times for $H_2/O_2/N_2/Ar$ mixtures have been measured inside a rapid compression machine (RCM) at pressures from 8 to 32 bar, for a temperature range of 900–1050 K and equivalence ratio of 0.35 and 0.5. Results show a strong dependence of the ignition delays to compressed temperature and pressure. Ignition delays decrease with increasing temperature, pressure and equivalence ratio. Experimental results have been compared to our newly revised chemical kinetic mechanism and to literature mechanisms.

1. Introduction

Hydrogen and syngas (hydrogen and carbon monoxide) mixtures are subject to much attention because of their potential of producing energy with low CO_2 emissions. Therefore, the development of fuel flexible gas turbines able to operate with hydrogen rich fuels is of high interest to the gas turbine industry. Hydrogen can also be used with high efficiency in internal combustion engines to power transportation vehicles [1]. However, this fuel flexibility must not affect the reliability and the safety of the combustion devices. Consequently, their designs need accurate chemical kinetic mechanisms to predict the reactivity of the fuel mixtures in the practical combustion devices and in evaluating flammability issues with the hydrogen fuelling. Many hydrogen mechanisms are available in the literature, but none of them has been validated at such high pressures. Indeed, Mittal *et al.* [2] stated that improvements are needed for H_2/O_2 mechanism to achieve a good agreement with their ignition experiments in the rapid compression machine (RCM) at high temperature and intermediate temperature. The aim of the present study is to extend the validation of H_2/O_2 and $H_2/CO/O_2$ mechanism to such severe thermodynamic conditions.

Recently published experimental results [2-8] extend the knowledge of the hydrogen chemistry thanks to (i) new rate constant measurements and (ii) hydrogen and syngas combustion experiments. Moreover, hydrogen oxidation has been studied in the RCM over a pressure range of 8 to 32 bar and temperature range of 900 to 1050 K.

Because of these recent studies, we have updated and re-validated our $H_2/O_2/CO$ mechanism at high pressure and intermediate to high temperature. In the following, we first describe the improvements applied to the chemical kinetic mechanism. The updated mechanism is then validated against various experimental data and tested against our recent RCM experiments.

2. Chemical kinetic mechanism

The revised detailed kinetic mechanism for hydrogen is based on our previous mechanism [9] and is updated using more accurate rate constant measurements and calculations available in the recent literature [3,6,7,10]. The mechanism has been validated over a wide range of temperature (900–2500 K) and pressure (1–50 bar) using a variety of different experimental datasets, including ignition delay measurements from shock tubes and rapid compression machines, species concentration profiles measured in a flow reactor and laminar flame speeds. The validation mainly focused on ignition delay time prediction in both RCM and shock tubes. The hydrogen experiments from Mittal *et al*. [2] were used as a benchmark in order to test the sensitivity of the hydrogen mechanism to the recently published rate measurements discussed below. Moreover, recent data taken in an RCM at NUI Galway for H_2/O_2 mixtures was also used [11]. The Chemkin suite of programs [12] was used to perform all the simulations contained in this manuscript. In an attempt to accurately account for the physical conditions encountered in the RCM experiments, namely the temperature gradient due to heat loss after end of compression, an unreactive pressure profile was experimentally measured for every condition. This pressure profile was then converted to a volume profile and incorporated into Aurora, allowing the simulation of both the compression stroke and heat loss phenomenon, in the form of an adiabatic compression/expansion process.

2.1 H_2 / O_2 mechanism improvements

A sensitivity analysis has been performed for the fuel mixture tested by Mittal *et al.* for a temperature of 1000 K and pressures of 15 and 30 bar. Every reaction in turn is increased by a factor of two before calculating the ignition delay time. This is repeated by decreasing the reaction by a factor of two before defining the sensitivity coefficient (σ) based on the following equation:

$$\sigma = \log\left(\tau'/\tau''\right) \Big/ \log\left(2.0/0.5\right) \qquad (1)$$

where τ' is the calculated ignition delay with the reaction increased, and τ'' is the calculated ignition delay with the reaction decreased. The analysis is performed assuming ideal conditions, taking no account for heat losses encountered in the RCM.

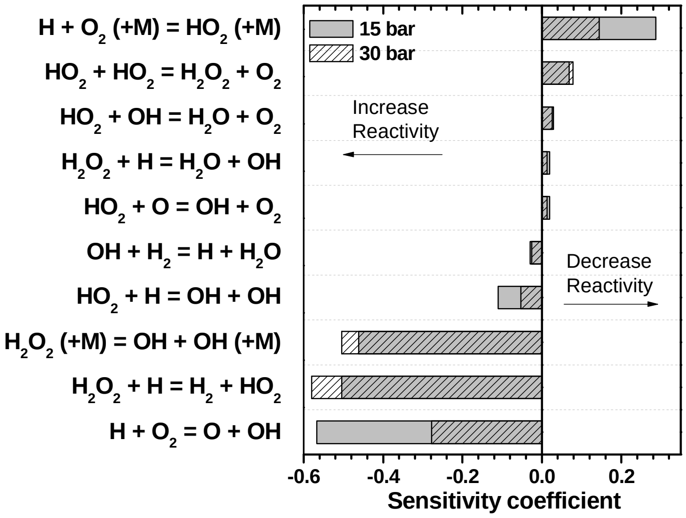
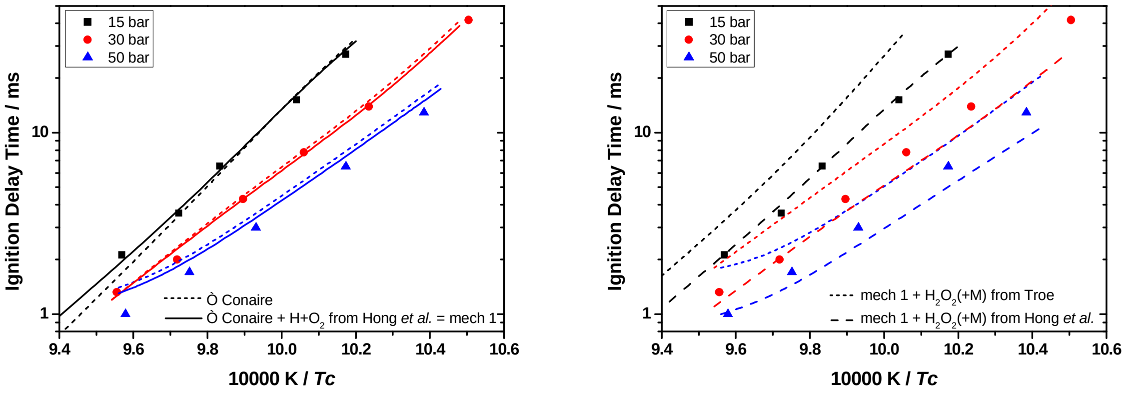
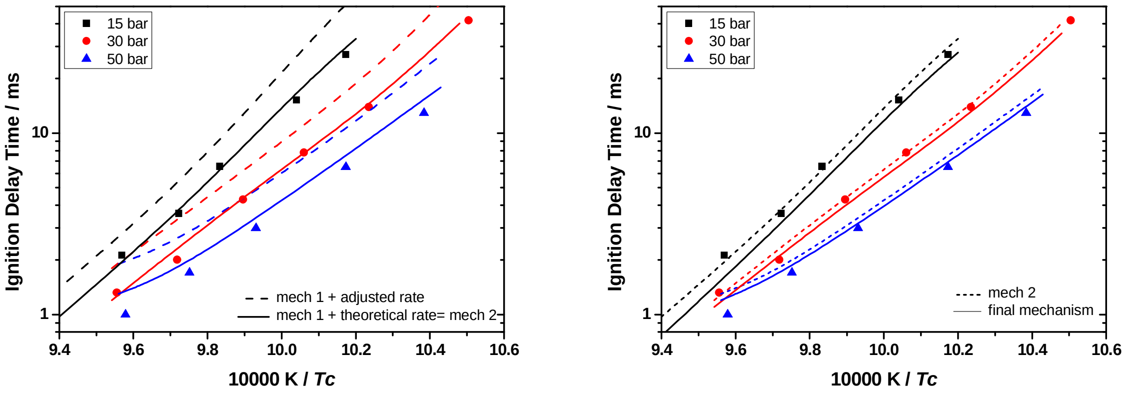


Figure 1: Sensitivity analysis highlighting the 10 most sensitive reactions for a mixture H_2 / O_2 / N_2 / Ar = 12.5 / 6.25 / 18.125 / 63.125 at 1000 K and at 15 bar and 30 bar

The ten most sensitive reactions are presented on Figure 1. The most sensitive reactions are H + O_2 = O + OH, H + O_2 (+M) = HO_2 (+M), H_2 + HO_2 = H_2O_2 + H and H_2O_2 (+M) = OH +OH (+M). These four reactions require particular attention and have been the subject of very recent studies, and their impact on the prediction of the ignition delay of the mechanism has been tested against the RCM results of Mittal *et al.* (Fig 2). Some other recently published rate constants have also been tested.


(a) H + O_2 = O + OH

(b) H_2O_2 (+M) = OH + OH (+M)


(c) H_2 + HO_2 = H_2O_2 + H

(d)

Figure 2: Mechanism evolution by testing different rate constants against Mittal *et al.* RCM data: (a) adoption of the H + O_2 = O + OH rate constant from Hong *et al.*; (b) test of the rate constant for H_2O_2 (+M) = OH + OH (+M) from Hong *et al.* and Troe; (c) addition of the rate for H_2 + HO_2 = H_2O_2 + H from Ellingson *et al.*; (d) comparison between mechanism 2 with the final mechanism

$H + O_2 = O + OH$

The reaction $H + O_2 = O + OH$ is not only extremely important in the hydrogen sub-mechanism (Fig 1) but also dominates/controls the oxidation of all fuels undergoing oxidation at high temperature (≥ 1000 K depending on the pressure). At temperatures below approximately 1000 K, this reaction competes with the propagation reaction $H + O_2$ (+M) = HO_2 (+M) which is inhibiting as it produces only one relatively unreactive radical and not two reactive radicals as in the chain branching reaction.

We have adopted the rate constant for $H + O_2 = O + OH$ recently measured by Hong *et al.* [6] to be $9.65\ x10^{14}\ T^{-0.3} exp(-16200\ cal/RT)\ cm^3\ mol^{-1}\ s^{-1}$ (±5%). This value is lower than our previous rate [13] and results in the prediction of slightly longer ignition times at intermediate temperatures and low-pressure and slightly shorter ignition times at higher pressures (Fig 2a).

$H + O_2\ (+M) = HO_2\ (+ M)$

For the reaction $H + O_2$ (+M) = HO_2 (+M), the new rate proposed by Fernandes [14] does not result in a major improvement in prediction at high pressure (50 bar) but results in the prediction of ignition times that are too fast at 15 bar. To obtain the best overall agreement, the high pressure limit proposed by Cobos *et al.* [15], which Ó Conaire *et al.* had previously used is retained, but the low pressure limit recommended by Mueller [16] has been employed. For shock tube experiments, the mechanism predicted the correct ignition delay times for experiments with nitrogen as the bath gas but under-predicted reactivity in argon. Therefore, in order to improve predictions without adversely affecting those in nitrogen, the low pressure limit from Bates *et al.* [17] has been employed for argon as the bath gas.

$H_2O_2\ (+M) = OH + OH\ (+ M)$

The second reaction whose rate affects the ignition delay times in the RCM at different pressures involves the initiation reaction H_2O_2 (+M) = OH + OH (+M). Pressure dependent rate expressions have recently been published by Hong *et al.* [7] and by Troe [18]. The former increases the pressure dependence of the system and results in the prediction of longer ignition times at low pressure and shorter ignition times at high pressure when compared to the RCM experiments of Mittal *et al.* (Fig 2b). The rates calculated by Troe reduce the overall reactivity and results in predicted ignition delays that are longer than experimentally measured (Fig 2b). The effect of third-body efficiencies was also examined and applied to both the Hong *et al.* [7] and the Troe [18] rate expressions but did not significantly affect predictions of ignition times for the Mittal *et al.* experiments. As a result, it was decided to retain our previous rate constant and associated efficiencies which come from Brouwer *et al.* [19] for the high pressure limit and Warnatz [20] for the low pressure limit as this combination reproduced the effect of pressure observed in the experiments.

$H_2 + HO_2 = H_2O_2 + H$

This reaction was found to exhibit a high sensitivity at the high pressures and low temperatures found in the RCM experiments (Fig 1). Ellingson *et al.* [3] published a theoretical study of the reaction $H_2 + HO_2 = H_2O_2 + H$, where they used *ab initio* methods to compute the rate constant as a function of temperature. However, the *ab initio* rate constant was too fast compared to experimental data from Baldwin *et al.* [e.g. [21,22] and they adjusted the barrier height to the upper theoretical limit to match Baldwin's experimental data. However in the RCM experiments, this adjustment results in a decrease of the reactivity and the model reproduces the RCM ignition delay data more precisely (Fig 2c) when using the unaltered theoretical rate, $k = 2.15 \times 10^{10}\ T^{1.0}\ exp(-6000\ cal/RT)\ cm^3\ mol^{-1}\ s^{-1}$.

$H_2O_2 + OH = H_2O + HO_2$

This reaction requires the sum of two rate expressions to accurately reproduce its temperature dependence. The summed rate constant expression for $H_2O_2 + OH = H_2O + HO_2$ published by Hong *et al.* [7] have been compared with the two previously used. These rate constant expressions have been tested by combination with and without the rate constant proposed for H_2O_2 decomposition by Hong *et al.* and by Troe. We observe a low sensitivity of the mechanism to the rate constant of $H_2O_2 + OH = H_2O + HO_2$ under the conditions of Fig. 1(not shown), and have adopted the recent summed rate expression of Hong *et al.*

The performance of the resulting updated mechanism is presented in Fig 2(d). It will be use as a basis for the H_2/CO mechanism.

2.2 H_2 / O_2 / CO mechanism improvements

$CO + O_2 = CO_2 + O$

The CO reactions initially come from the previous mechanism [23] and have been updated with recently published rates. The rate for the reaction $CO + O_2 = CO_2 + O$, $k = 1.05 \times 10^{12}\ exp(-42540\ cal/RT)\ cm^3\ mol^{-1}\ s^{-1}$, is a new fit from the authors to the available data in the NIST database [24].

$CO + OH = CO_2 + H$

The rate constant used in our mechanism for the reaction between CO and OH was initially taken from Li *et al.* [25]. As stated by Li *et al*,. based on the work from Zhao et al. [26], the laminar flame speed prediction is highly sensitive to the reactions $CO + OH = CO_2 + H$ and $HCO + M = H + CO + M$. To obtain better agreement with flame speed measurements for syngas mixtures, the Zhao et al. reaction rate for the former reaction was reduced by 30% in order to reduce predicted flames speed, resulting in $k = 1.78 \times 10^5\ T^{1.9}\ exp\ (1158\ cal/RT)\ cm^3\ mol^{-1}\ s^{-1}$, whereas the latter was retained as defined by Li *et al.* [25].

$CO + HO_2 = CO_2 + OH$

The rate constant used for $CO + HO_2 = CO_2 + OH$ was updated taking the rate recently published by You *et al.* [10]. According to many authors [27-29], this rate considerably improves the prediction of RCM results published by Mittal *et al.* [2].

2.3 Validation of the mechanism

The updated mechanism has been validated against various types of combustion experiments including RCM and shock tubes for ignition delay time measurements, species profiles measured in flow reactors and flame speed measurements. It has been tested for various types of fuel mixtures (from 100% H_2 to 5% H_2 + 95% CO) for a wide range of temperature (900–2500 K) and pressure (1–50 bar). The performance of the present mechanism has been compared to previously published mechanism: Ó Conaire *et al.*[9], Li *et al.* [25] and Hong *et al.*[30], referred respectively as Ó Conaire, Li and Hong.

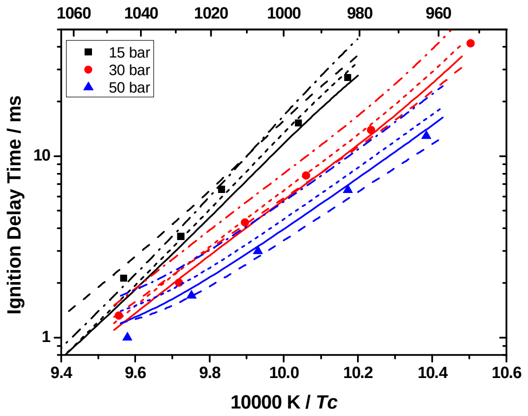


Figure 3: Comparison between the experimental data for hydrogen from Mittal et al. [2] (symbols) and different mechanisms: – this study, -- Ó Conaire, -.- Li, – – Hong

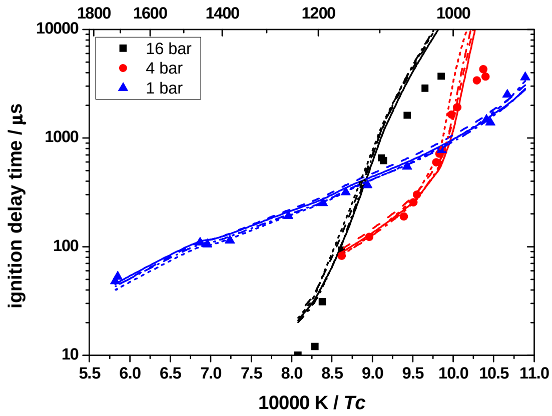


Figure 4: Comparison between the experimental data for hydrogen from Herzler et al. [5] (symbols) and different mechanisms: – this study, -- Ó Conaire, -.- Li, – – Hong

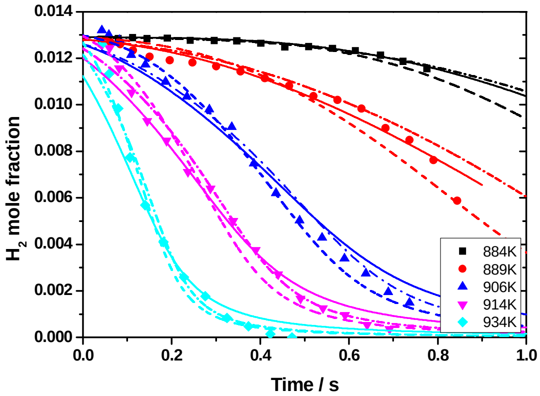


Figure 5: Comparison between flow reactor hydrogen profiles from Mueller et al. [31] and different mechanisms: – this study, -- Ó Conaire, -.- Li, – – Hong

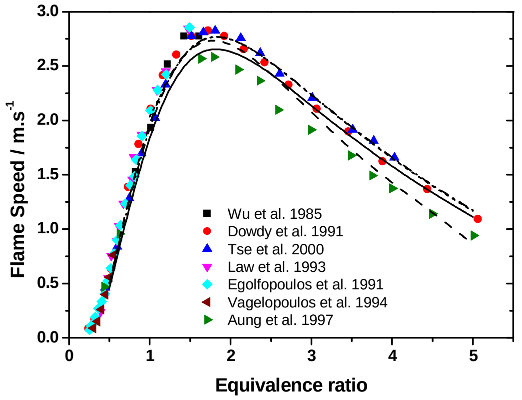


Figure 6: Comparison between hydrogen flame speed experiments in air and different mechanisms: – this study, -- Ó Conaire, -.- Li, – – Hong

The updated mechanism shows excellent agreement with previously published hydrogen experiments for various experimental setups (Figs 3-6). The predictions of the mechanism are especially very accurate for ignition time measurement at both low temperature conditions in the RCM (Fig. 3) and at high temperature in the shock tube (Fig. 4). The pressure dependence is well reproduced in both experimental setups for a pressure range from 1 to 50 bar. However, a disagreement appears at low temperature for the shock tube experiments at 4 and 16 bar. The longer prediction of the ignition time is due to a pre-ignition pressure rise during the experiments. This phenomenon is not taken into account in the modelling. Heat losses encountered in the experiments of Mittal *et al.* have been considered in the form of volume profiles supplied in that work.

Flow reactors provide species vs. time profiles at intermediate temperature. Therefore, it is important to reproduce this type of data. The mechanism accurately predicts the hydrogen concentration profile and the temperature dependence of the profile. As far as flame speed is concerned, the mechanism predicts a slightly slower maximum flame speed than the data. The experimental data presented in Fig. 6 were obtained before experimentalists were aware that linear flame stretch corrections were inaccurate and resulted in flame speeds that were too high compared to more accurate nonlinear corrections [32]. Thus, a slight under-prediction by the mechanism of these experimental data is to be expected. To obtain more accurate validation of hydrogen mechanisms at atmospheric pressure, modern experimental data are needed with nonlinear corrections for flame stretch.

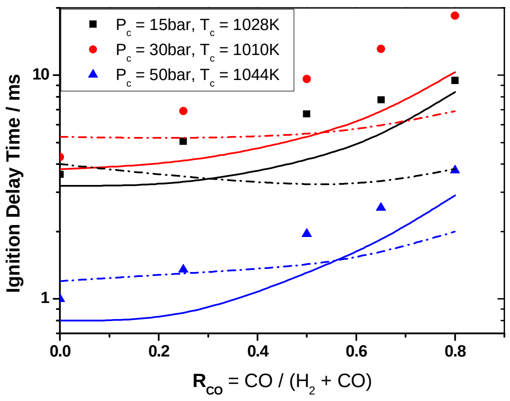


Figure 7: Comparison between the experimental data from Mittal et al. [2] (symbols) and two mechanisms: – this study, -.- Li.

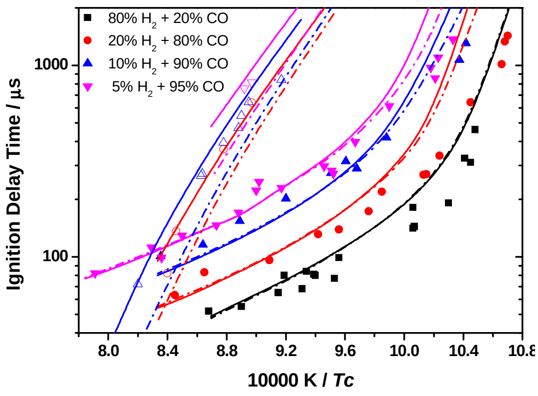


Figure 8: Comparison between the experimental data from Kalitan et al. [8] (solid symbols: 1.1atm, open symbols 15atm) and two mechanisms: – this study, -.- Li.

The updated mechanism has been tested against the H_2/CO RCM experiments from Mittal *et al.* (Fig. 7), where predicted ignition delays are shorter than those measured experimentally. However, the trend as a function of R_{CO}, pressure and temperature is well reproduced. The effect of the CO has also been studied by Kalitan *et al.* [8], Fig. 8, where it can be seen that the mechanism reproduces these experiments accurately at high temperature at both pressures, but is too slow for the low temperature experiments at 1.1 atm. The Li mechanism shows the same trend against the shock tube experiments but does not reproduce the trends for the RCM experiments.

3. New RCM results for hydrogen

Some experiments were conducted in the RCM at the National University of Ireland, Galway (NUIG) for hydrogen oxidation [11]. The RCM is a horizontally opposed twin piston device which has been widely described in previous publications [33,34]. The symmetry of the system associated with the creviced pistons generates a homogeneous temperature field at the end of the compression stroke [35]. The creviced pistons capture the piston corner vortex and thus maximize the homogeneity of the temperature field. Therefore, both temperature and mixture homogeneity are achieved at the end of the compression stroke.

Thermodynamic conditions of pressure and temperature relevant to those in gas turbines are achieved in the RCM due to a very rapid adiabatic compression process completed within ~16 ms. After compression, the pistons are locked in place to ensure constant volume conditions until ignition occurs. The experiments were carried out over a compressed temperature range of 900–1100 K at pressures of 8, 16 and 32 bar. The different compressed temperatures and pressures are achieved by changing the initial temperature and pressure, respectively. Fuel-oxidizer mixtures were prepared manometrically in stainless steel tanks with gases with a purity of 99.9% or higher. The oxidizer is mixture of 21% oxygen, 39.5% nitrogen and 39.5% argon. Two equivalence ratios have been studied $\phi = 0.35$ and 0.5.

During the experiments, the piston position and the pressure profile are recorded by a digital oscilloscope. The compressed temperature is calculated from the initial temperature T_i, and pressure p_i, the compressed pressure p_c and the mixture composition while assuming an adiabatic compression process and frozen chemistry. The ignition delay time is defined as the time between the end compression and the maximum of the heat release rate.

In order to take the heat loss phenomenon into account in model, non reactive experiments are performed by replacing oxygen by nitrogen. The recorded pressure profiles are then post processed, assuming adiabatic compression/expansion process, in volume profiles which will be used as inputs for the modelling.

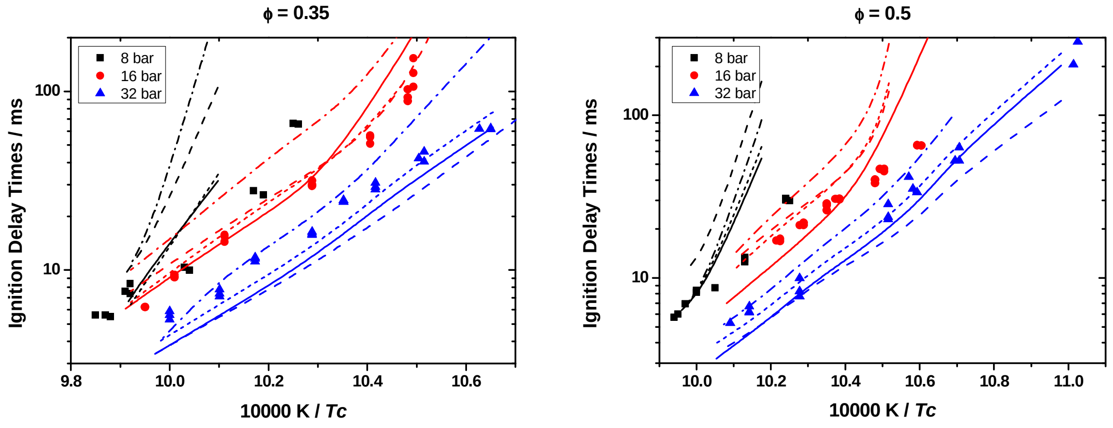


Figure 9: Comparison between experimental (symbols) results and modelling (– this study, -- Ó Conaire, -.- Li, – – Hong) for pure H_2 at Φ=0.35 and 0.5

The ignition times show a strong dependence on the temperature and pressure and decrease with increasing temperature, pressure and equivalence ratio. All these effects are qualitatively well reproduced by the updated mechanism. However, the quantitative agreement needs further improvements. The Hong mechanism shows a too high pressure dependence which may come from the rate for the H_2O_2 decomposition. As a result, the predicted ignition delays are too long at low pressure and too short at high pressure. The Li mechanism predicts ignition delays which are always too long compared to the experimental results. The results of Ó Conaire mechanism are slightly slower than the updated mechanism.

4. Conclusion

Our previously published mechanism for hydrogen [9] has been updated with recently published reaction rate constants and extended to $H_2/CO/O_2$ in order to enable the prediction of high interest syngas behaviour at high pressure and intermediate to high temperature. It has been validated for a wide range of pressure (1–50 bar), temperature (900–2500 K) and equivalence ratios (0.1–4.0) against various type of experimental results: ignition delay times, species concentration profiles and flame speed.

Moreover, some new RCM ignition times have been presented for hydrogen at compressed pressure of 8, 16 and 32 bar for a temperature of 900–1050 K.

Acknowledgments

The NUIG work is part of the European Project H_2-IGCC funded by the European Commission the Science Foundation Ireland and funding is gratefully acknowledged. The LNLL work is performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

[1] White, C.M., et al., *International Journal of Hydrogen Energy*, 2006. 31(10): p. 1292-1305.
[2] Mittal, G., et al., *International Journal of Chemical Kinetics*, 2006. 38(8): p. 516-529.
[3] Ellingson, B.A., et al., *Journal of Physical Chemistry A*, 2007. 111(51): p. 13554-13566.
[4] Herzler, J., et al., *Combustion Science and Technology*, 2008. 180(10-11): p. 2015-2028.
[5] Herzler, J., et al., *Proceedings of the Combustion Institute*, 2009. 32: p. 213-220.
[6] Hong, Z., et al., *Proceedings of the Combustion Institute*, 2011. 33(1): p. 309-316.
[7] Hong, Z.K., et al., *Journal of Physical Chemistry A*, 2010. 114(18): p. 5718-5727.
[8] Kalitan, D.M., et al., *Journal of Propulsion and Power*, 2007. 23(6): p. 1291-1303.
[9] Ó Conaire, M., et al., *International Journal of Chemical Kinetics*, 2004. 36(11): p. 603-622.
[10] You, X., et al., *The Journal of Physical Chemistry A*, 2007. 111(19): p. 4031-4042.
[11] Keromnes, A., et al. in *5th International Gas Turbine Conference*. 2010. Brussels, Belgium.
[12] Kee, R.J., et al., *Chemkin Collection, Release 3.7.1*. 2003, Reaction Design, Inc.
[13] Hessler, J.P., *The Journal of Physical Chemistry A*, 1998. 102(24): p. 4517-4526.
[14] Fernandes, R.X., et al., *Physical Chemistry Chemical Physics*, 2008. 10(29): p. 4313-4321.
[15] Cobos, C.J., et al., *The Journal of Physical Chemistry*, 1985. 89(2): p. 342-349.
[16] Mueller, M.A., et al., *Symposium (International) on Combustion*, 1998. 27(1): p. 177-184.
[17] Bates, R.W., et al., *Physical Chemistry Chemical Physics*, 2001. 3(12): p. 2337-2342.
[18] Troe, J., *Combustion and Flame*. In Press, Corrected Proof.
[19] Brouwer, L., et al., *The Journal of Chemical Physics*, 1987. 86(11): p. 6171-6182.
[20] Warnatz, J., ed. W.C. Gardiner. 1985, New York: Springer-Verlag.
[21] Baldwin, R.R., et al., *Combustion and Flame*, 1970. 15(2): p. 133-&.
[22] Baldwin, R.R., et al., *Journal of the Chemical Society-Faraday Transactions I*, 1979. 75: p. 140-154.
[23] Ó Conaire, M. (2005) PhD Thesis, National University of Ireland, Galway
[24] NIST. Standard Reference Database 17-2Q98.
[25] Li, J., et al., *International Journal of Chemical Kinetics*, 2007. 39(3): p. 109-136.
[26] Zhao, Z.W., et al., *International Journal of Chemical Kinetics*, 2005. 37(5): p. 282-295.
[27] Sung, C.J., et al., *Combustion Science and Technology*, 2008. 180(6): p. 1097-1116.
[28] Chaos, M., et al., *Combustion Science and Technology*, 2008. 180(6): p. 1053-1096.
[29] Rasmussen, C.L., et al., *International Journal of Chemical Kinetics*, 2008. 40(8): p. 454-480.
[30] Hong, Z., et al., *Combustion and Flame*. In Press, Corrected Proof.
[31] Mueller, M.A., et al., *International Journal of Chemical Kinetics*, 1999. 31(2): p. 113-125.
[32] Wang, Y.L., et al., *Proceedings of the Combustion Institute*, 2009. 32(1): p. 1035-1042.
[33] Brett, L., et al., *Combustion and Flame*, 2001. 124(1-2): p. 326-329.
[34] Gallagher, S.M., et al., *Combustion and Flame*, 2008. 153(1-2): p. 316-333.
[35] Würmel, J., et al., *Combustion and Flame*, 2005. 141: p. 417–430.