Ignition delay of ultra-lean hydrogen/air mixtures

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1 Introduction

Hydrogen is increasingly being used as a fuel for energy sources everywhere. The issues of safe production, transportation and storage of hydrogen are very important. In the case of a leakage hydrogen mixes with surrounding air and create a combustible mixture at atmospheric pressure in a very wide concentration range. Besides, without accidental leakage, hydrogen is released into the containment of nuclear power plants even during its normal operation mode. This is why the problem of spontaneous ignition of ultra-lean hydrogen-air mixtures under normal pressure is relevant nowadays.

In present study, the autoignition of ultra-lean (φ=0.15 and φ=0.25, where φ – stoichiometric ratio) hydrogen-air mixtures under normal shock wave reflection was studied. Experimental results were compared with theoretical one, calculated using several detailed kinetic mechanisms.

2 Experimental setup

To obtain the most reliable data the experiments were carried out using two shock tubes simultaneously: 76 mm in inner diameter, 6.5 meter in length and 50 mm in inner diameter, 7.1 meter in length correspondingly. The measuring sections of the both tubes were the same, equipped with PCB Piezotronics 113B24 pressure transducers and ion current sensors installed along the tube axis. The reflection walls (flanges) were transparent, made from plexiglass, also were equipped with pressure transducers and ion current sensors. Ignition delay time measurements were carried out behind reflected shock waves, using three ways simultaneously: analyzing pressure profiles, ion current profiles and self-luminescence through transparent flange registered by photomultiplier equipped with narrowband optic filters. The photoluminescence of the OH radical transition ($A^2\Sigma - X^2\Pi$) at a wavelength of λ = 308-309 nm were registered in our tests.

Two mixtures: 9,5% H_2 + 19 %O_2 + 71,5 %N_2 (hydrogen-air, φ=0.25) and 5,93 % H_2 + 19,76 %O_2 + 74,31 %N_2 (hydrogen-air, φ=0.15) were used in tests. Mixtures were prepared from commercially grade pure hydrogen, oxygen and nitrogen by method of partial pressures in separate vessels and kept at least one day before use.

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3 Results and discussion

Figure 1 presents ignition delay time vs. reciprocal temperature for two studied mixtures in temperature range 902-1630 K and 1 atm pressure. For each of the shock tubes, measurements of ignition delay by luminescence and ionization current are presented. Measurement data on pressure oscillograms were used for monitoring and are not presented on the graphs. It is clearly seen that the data obtained from the two experimental setups coincide very well. This indicates that the experiments were carried out qualitatively, the methodology of measurement was chosen correctly and the results are reliable.

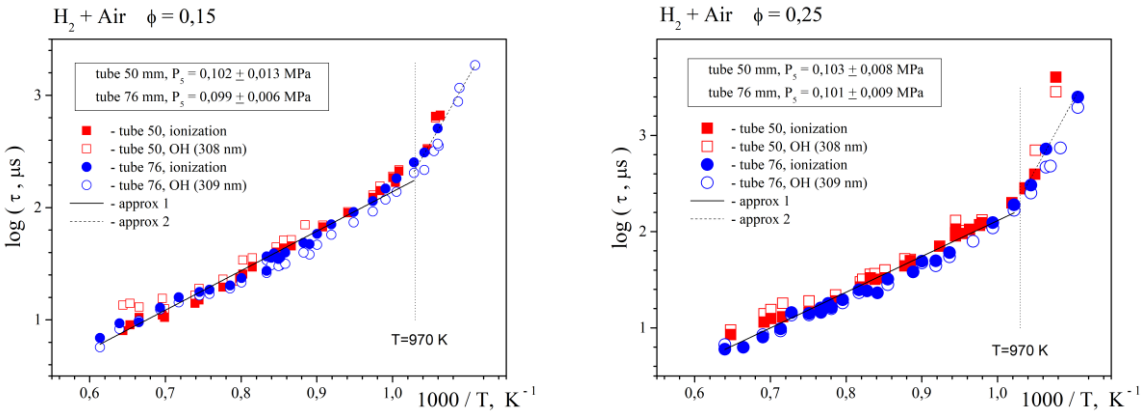

Figure 1: Ignition delay time vs. reciprocal temperature in ultra-lean φ=0.15 (left) and φ=0.25 (right) hydrogen-air mixtures. Measurements behind reflected shock waves.

The data presented can be roughly divided into two groups, each of which fits well on a straight line. Between the groups of data there is a kink in the temperature region of the order of 960-970 K. For φ=0.15 hydrogen-air mixture (Figure 1, left) following approximations (with corresponding activation energies) was found:

$$Log\ (\tau) = -1.373 + 3.515\left(\frac{1000}{T}\right)\ \ with\ E = 67.3\ \frac{KJ}{mole}\ ,\ \text{for T>970K} \qquad (1a)$$

$$Log\ (\tau) = -9.76 + 11.76\left(\frac{1000}{T}\right)\ \ with\ E = 224.9\ \frac{KJ}{mole}\ ,\ \text{for T<970K} \qquad (1b)$$

For φ=0.25 hydrogen-air mixture (Figure 1, right) such approximations are:

$$Log\ (\tau) = -1.6 + 3.717\left(\frac{1000}{T}\right)\ \ with\ E = 71.2\ \frac{KJ}{mole}\ ,\ \text{for T>970K} \qquad (2a)$$

$$Log\ (\tau) = -12.5 + 14.43\left(\frac{1000}{T}\right)\ \ with\ E = 276.2\ \frac{KJ}{mole}\ ,\ \text{for T<970K} \qquad (2b)$$

In (1-2) τ – ignition delay time (μs), T – post reflected shock temperature (K), E – activation energy.

Recently [1] the simulation results of ignition delays of lean and ultra-lean hydrogen-air mixtures were compared for 5 detailed kinetic mechanisms (DKMs) which are currently widely

discussed in the literature with regard to H_2–O_2 mixtures. It was shown that any DKM considered in this study can be applied with a satisfactory degree of accuracy to simulate autoignition and combustion of lean and ultra-lean hydrogen–air mixtures at a pressure below 6 bar. Unfortunately, comparison with experimental results was not provided.

A simulation of ignition delay times using two popular kinetic mechanisms [2, 3] discussed in [1] and Gri-mech 3.0 [4] was performed in this study. All calculations were completed using an academic version of ANSYS Chemkin-Pro [5] software. The initial pressure was set at 1 bar, and temperature is varied between 800 and 1700 K. NASA format thermo files were used with each DKM. Ignition delay τ was defined by the time corresponding to the 5% rate of pressure rise at constant volume. Results of simulations with comparison to experimental data are presented on figure 2. Both experimental and theoretical data (except calculation with gri-mech mechanism) demonstrate a kink in the temperature-delay curves approximately at 960-970 K.

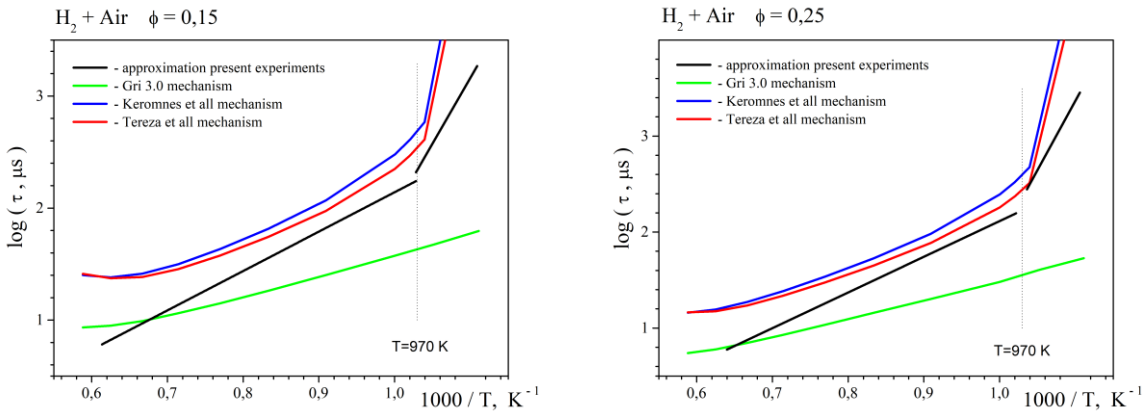

Figure 2: Ignition delay time vs. reciprocal temperature in ultra-lean φ=0.15 (left) and φ=0.25 (right) hydrogen-air mixtures. Comparison of approximation of experimental results and results of simulation using detailed kinetic mechanisms [2], [3] and [4].

4 Conclusions

Ignition delay times of ultra-lean (φ=0.15 and φ=0.25) hydrogen-air mixtures under normal shock wave reflection were measured experimentally using two shock tubes in temperature range 902-1630 K and pressure of 1 atm. The obtained results correlate well, it means the results are reliable.

A simulation of ignition delay times using several popular detailed kinetic mechanisms was performed in this study. Comparison of simulation result with experimental data indicates than the Gri-mech 3.0 mechanism is not suitable to simulate autoignition of ultra-lean hydrogen-air mixtures at atmospheric pressure. On the contrary, detailed kinetic mechanisms proposed by Keromnes et all. and Tereza et all. qualitatively and quantitatively correlate with experimental data well, results of simulation with Tereza's mechanisms are more closely.

Acknowledgements

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