Induction and reaction time measurements in hydrogen-air mixtures for a wide stoichiometry range at high temperatures and pressures

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1   Introduction

The critical conditions and mechanisms of hydrogen oxidation are explained in the theory of chain reactions by the competition of the reactions of branching and termination of chains [1–4]. One of the most important consequences of this theory is the existence of hydrogen-oxygen explosion limits in a temperature-pressure plane [2] and the complex functional dependence of the ignition delay time on the pressure and temperature of the reaction mixture [5].

The reaction rates of hydrogen oxidation ($T > 800$ K) at low post-shock pressures (> 0.2 MPa) has been thoroughly studied and validated with the use of a large amount of shock-tube experiments behind incident and reflected shock waves in mixtures highly diluted with argon. At these conditions the ignition delay usually is inversely proportional to the oxygen partial pressure and decreases with increasing the initial pressure. Therefore, for low-pressure range fast chain branching reactions with the participation of H, OH, and O radicals [1–4] are dominating in reaction mechanism of hydrogen oxidation.

The growing of initial pressures (> 0.2 MPa) increases the role of the chain branching reactions with the participation of HO_2 molecules formed due to trimolecular reaction $H + O_2 + M = HO_2 + M$ and favors the removal of active hydrogen atoms from the fast chain branching determining the ignition at low pressures. The branched cycle, in which HO_2 molecules are formed, consists of a number of slow reactions increasing the characteristic time of hydrogen oxidation and the ignition delay time. The functional behavior of induction time on temperature and pressure is extremely important of hydrogen oxidation at elevated pressures, and is usually established by using detailed numerical simulations [6, 7], or empirical temperature approximations for induction times on the basis of low-pressure measurements. Moreover, existing kinetic schemes of hydrogen oxidation are not validated extensively by experimental measurements at high pressures. Only few works [8–11] were devoted to studies of high-temperature hydrogen auto-ignitions at elevated pressures of 0.2 – 0.9 MPa.

Thus, the range of pressures 0.2 – 2 MPa and temperatures 1000 – 1600 K, characterized by a changing in the hydrogen-oxygen chain reaction mechanism was practically not investigated. The present work gives results of experimental studies of ignition and reaction times of hydrogen-air mixtures at pressures of 0.1 – 0.6 MPa, temperatures of 1000 – 1600 K and stoichiometries 0.5 – 2.

2   Experimental setup

The self-ignition measurements were carried out in shock tube with inner diameter of 50 mm and a length of 8.5 m behind a reflected shock wave. The test section of the shock tube (Figure 1) was manufactured of a single piece of transparent organic glass. Its inner diameter was round (the same as the shock tube – 50 mm). The cross-section of external wall was rectangular. The reflecting surface of the shock tube was manufactured of transparent organic glass too.

Two measuring cross-sections were located in the test section at the distance of 98 mm and 198 mm from the reflecting wall. Each measuring cross-section was consisted of one PCB 113B24 high-frequency piezoelectric pressure sensor and an ion current sensor (installed at an angle of 45° to the pressure sensor) there. In addition, one pressure sensor and ion current probe was mounted into transparent reflecting wall. All applied sensors were connected to high-frequency digital oscilloscopes. The registered signals were displayed on a personal computer.

The chemiluminescence from the shock tube volume was recorded through the transparent reflecting wall using photomultiplier with diaphragm and double narrowband filters. We registered the chemiluminescence of the OH radical transition ($A^2\Sigma - X^2\Pi$) at a wavelength of $\lambda = 308.9$ nm.
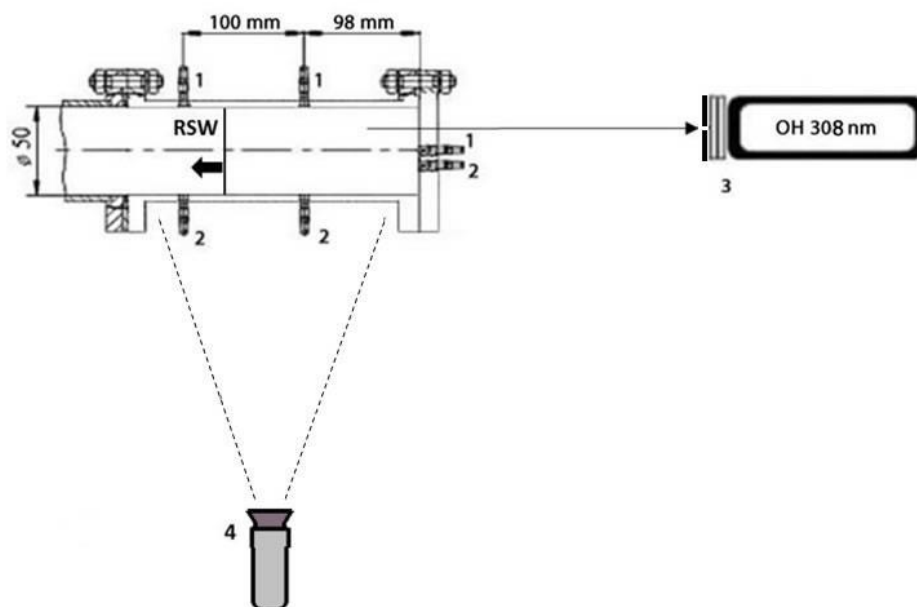

Figure 1: Schematic of the test section for induction time measurements in the shock tube. 1– high-frequency pressure sensors, 2 – ion-current sensors, 3 – photomultiplier with diaphragm and double narrowband filter, 4 – high-speed video camera.

The induction times of the studied mixture were determined from reflecting wall pressure records, the reflecting wall ion current measurements, and the chemiluminescence detections.

In the first case, the induction time (t_pressure) was the time interval between the arrival of the incident shock wave to the reflecting wall and the subsequent pressure increase associated with self-ignition of the mixture behind the reflected wave. In the second case, the induction time (t_ion) was the time interval between the arrival of the incident shock wave to the reflecting wall and the appearance of the ion current (increase by 5% of the its maximal level). In the third case, the induction time (t_OH) was the time interval between the arrival of the incident shock wave to the reflecting wall and the appearance of the photoluminescence of the OH radical (increase by 5% of its peak level).

The reaction times of the studied mixture (t_{reaction}) were determined by means of ion current measurements at the reflecting wall. It was the time interval between the appearance of the ion current (increase by 5% of its peak level) and reaching its maximum level.

The study was carried out for the following mixtures:

Mixture 1 – 29.580 % H_2 + 14.790 % O_2 + 55.630 % N_2 (stoichiometric hydrogen-air mixture with $\phi = 1$);

Mixture 2 – 45.652 % H_2 + 11,413 % O_2 + 42,935 % N_2 (rich hydrogen-air mixture with $\phi = 2$);

Mixture 3 – 14.790 % H_2 + 14.790 % O_2 + 70.420 % N_2 (lean hydrogen-air mixture with $\phi = 0.5$ diluted with 15 % N_2).

The test mixtures were prepared by the method of partial pressures. Gas parameters of the mixtures behind incident and reflected shock waves (Table 1) were computed by using the shock-adiabatic curve assuming frozen chemistry, known temperature dependence of heat capacity, and shock wave velocity measurements with accuracy ±0.5% at different locations along the tube. The Chapman–Jouguet detonation velocity V_{CJ} in preheated gas flow behind incident shock wave was calculated using a laboratory-developed thermochemical equilibrium computer code. To study the temperature-dependence of self-ignition delay and activation energy, all comparative shock-tube experimental runs in stoichiometric, lean, and rich shock-tube experimental runs were done at constant post-shock pressures of the gases (Table 1) behind reflected shock wave.

The main errors in our experimental measurements were caused by two main reasons. The first is the error in measuring the velocity of the incident shock wave ~ 0.5%, which led to an error in measuring temperature, pressure and density of ~ 0.75%; ~ 1.5%; ~ 0.7% respectively. The second is the error in measuring induction time, which was 10% – 15% for all studied parameter ranges.

3   Results and discussion

The induction and reaction times of the stoichiometric, rich and lean (with 15 % N_2 dilution) hydrogen-air mixtures at high temperatures (900 – 1600 K) and pressures (0.1 – 0.6 MPa) have been measured in the shock tube. Experimental results obtained by using different methods and performed evaluations presented in Figure 2 and Table 1.

Table 1: The post-shock conditions and measurement results for studied mixtures.

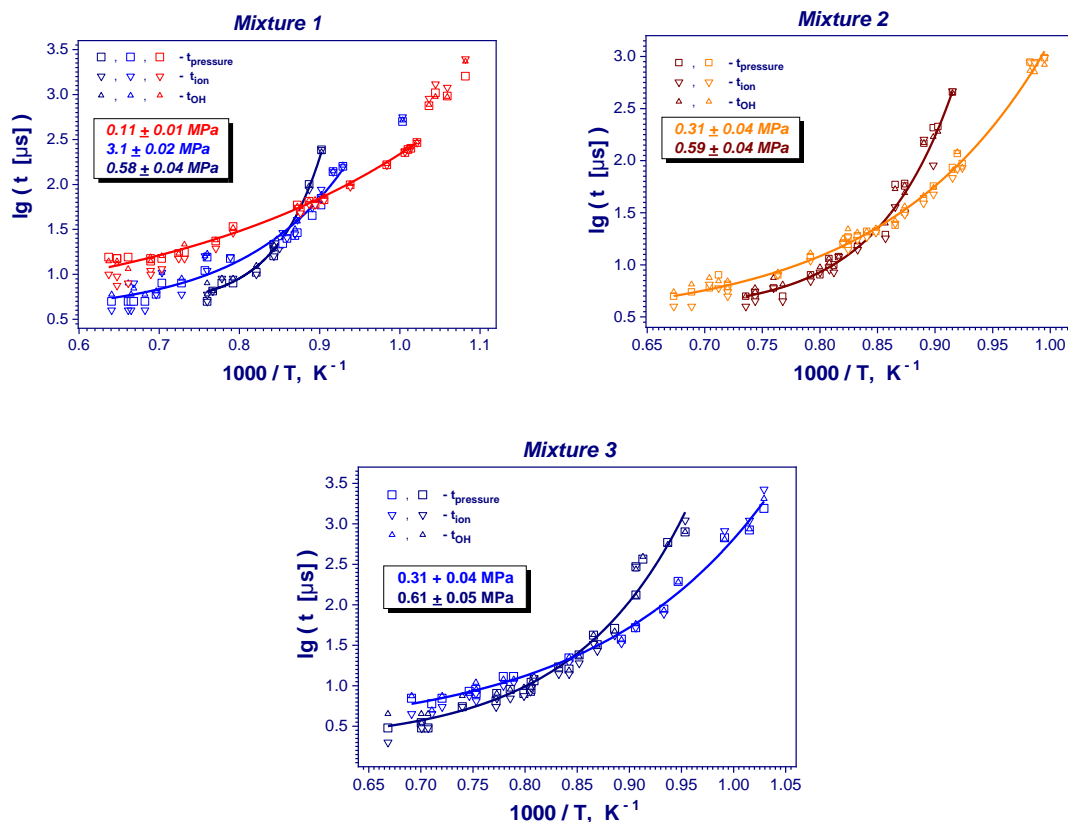| Mixture	Post-shock pressure, MPa	Post-shock temperature, K	Induction time, µs	Reaction time, µs	Critical temperature, K	Activation energy, kJ
1	0.11 ± 0.01	900 – 1600	16 – 2500	3 – 35	1020	64.6 (> 1050 K)
	0.31 ± 0.02	1000 – 1560	2 – 600	2 – 10	1070	69.3 (> 1050 K)
	0.58 ± 0.04	1100 – 1320	5 – 240	3 – 12	-	-
2	0.31 ± 0.04	1000 – 1500	4 – 975	2 – 47	-	76.8 (> 1050 K)
	0.59 ± 0.04	1100 – 1360	4 – 450	3 – 18	-	82.7 (> 1050 K)
3	0.31 ± 0.04	950 – 1350	8 – 2660	2 – 15	1060	81.7 (> 1200 K)
	0.61 ± 0.05	1150 – 1450	2 –2230	2 – 17	-	78.2 (> 1550 K)

Figure 2: Induction times vs. reciprocal temperature in studied hydrogen-air mixtures at different post-shock pressures.

With the temperature increasing the self-ignition delays decreasing dramatically from thousand to several µs. In the chosen coordinate system, the dependence is not linearly, but line segments can be identified.

The reaction times also decreasing to the value near 2 µs with the temperature increasing, but the dependence is not so intense.

To evaluate the activation energies (Table 1) in studied mixtures, the high-temperature range of obtained dependence between induction time and reciprocal temperature was linearly approximated. It can be seen that detected values are in the interval 64 – 83 kJ and vary < 6 kJ with pressure changing.

The critical temperature of the strong self-ignition mode (Table 1) was identified for some conditions based on the analysis of the absolute velocity of the reflected shock wave at different locations (98 and 198 mm) from the reflecting wall. This velocity is the sum of reflected shock wave velocity in the laboratory coordinate system and the gas flow velocity behind the incident shock. The evaluations of the critical temperature of the strong self-ignition mode detected, that it is in the interval 1000 – 1100 K. It can be seen that these values are quite close to the temperatures at which the activation energy of mixtures changes.

4   Conclusions

Induction and reaction times of hydrogen-air mixtures have been thoroughly studied behind reflected shock waves at extremely high temperatures and mean pressures 0.1, 0.3, 0.6 MPa. The measurements were performed in the shock tube with completely transparent test section of 0.5 m long. Experiments

were carried out at temperatures range of 1000 – 1600 K and equivalence ratios of $\phi = 0.5 – 2$. The focusing was made to produce the measurements at extremely high temperatures 1400 – 1600 K. Induction times were determined using OH emission profiles, pressure and ion current measurements. Reaction times of the mixtures were deduced by means designed reflecting wall ion current sensor with spatial resolution of 0.2 mm. The transparent test sections allowed performing the complete imaging of reaction volume over the length of 0.25 m upstream the reflecting wall by means a high-speed camera.

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