

Two-dimensional Modeling of the Ignition Length Decrease in Hydrogen Mixture with Oxygen Excited in Electric Discharge

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1 Introduction

There is great interest in application of non-equilibrium plasma for the plasma-assisted combustion [1]. It was demonstrated both experimentally and theoretically that plasma active particles, mostly radicals influence burning process leading to decrease of ignition temperature, reducing induction delay time or length of induction [2] and enhancing the flame velocity [3]. In addition to radicals vibrationally and electronically excited molecules can also enhance the chemical reaction rates at reduced temperatures [4].

There are very few data on the influence of non-equilibrium plasma with electron excited molecules (especially $O_2(^1\Delta_g)$) on initiation and branching reaction in fuel-contained mixtures in hydrogen (hydrocarbon)-contained mixtures [5]. The measurements of the rate constants of these reactions as a function of temperature are complicated both by the presence of active odd oxygen (radical O + ozone O_3) in plasma itself [6] and by the secondary reactions at elevated temperatures [7]. The role of $O_2(^1\Delta_g)$ generated in the discharge plasmas on the ignition of hydrogen-contained mixtures (H_2 , CH_4 , etc.) was demonstrated in recent experiments [2,3] where atomic oxygen was removed by adding small impurities of NO [3] or in heterogeneous reactions on the surface covered with HgO [2]. All the same, concentration of atoms $O(^3P)$ was not measured, while it was shown [6] that for similar conditions atomic oxygen may considerably decrease due to heterogeneous loss in reactions with HgO, but some residual concentrations of odd oxygen remained in the excited oxygen flow.

Results of the experiment [2] has been analyzed recently using the kinetic scheme [8] on zero- [9] and one-dimensional [10] models that do not take into account radial temperature and flow velocity inhomogeneities emerging in the reactor, which may affect the induction length. Besides, it was assumed that residual concentrations of odd oxygen in excited flow from discharge can be neglected. These factors may affect on the rate constants of reactions involving $O_2(^1\Delta_g)$.

The objective of the present study is to reveal the main processes with singlet oxygen which stimulate the of combustion in hydrogen-oxygen mixtures, as well as using measured data [2] on the ignition length to determine the rate of branching reaction $H+O_2(^1\Delta_g)\rightarrow O+OH$. For this purpose the

comprehensive numerical study of all stages of the experiment [2]: DC discharge in oxygen, transport in drift tube and flow reactor were carried out.

2 Describing the Experiment and Numerical Model

The experimental setup for the present simulations was described in [2]. Steady state combustion in an H_2-O_2 mixture was arranged in a continuously operating flow reactor (700 mm long quartz tube with an inner diameter of 18 mm) with the transparent side walls downstream the mixing zone of subsonic co-flows of cold reactants separately supplied to the reactor inlet. The reactor operating pressure was 10 Torr, and mass flows were set such that the fuel-oxidant ratio equaled to 2.5:1. To provide the ignition in the flow reactor, the walls of the chamber were heated up to 780K [2].

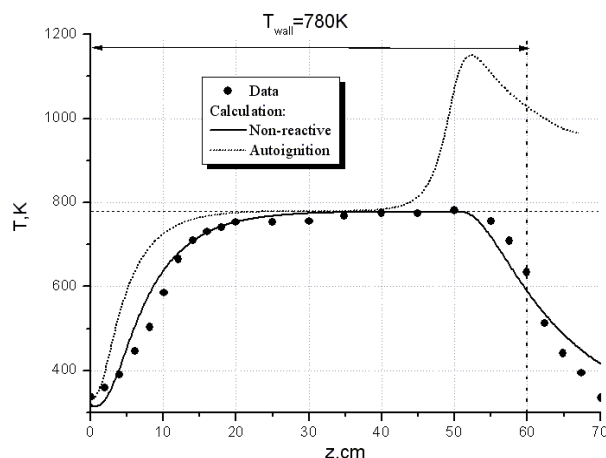


Figure 1. Temperature profiles at the axis of reactor: points - data from [2], lines (solid, dotted) - our simulations.

Longitudinal temperature profile at the axis of reactor chamber was measured with thermocouple, Fig.1 (dots), in the case of non-reactive gas - N_2 flow. The oxygen flow was excited in water cooled DC discharge tube and then transported to the flow reactor through the drift tube [2]. The tube walls in discharge cell and drift tube were covered with mercuric oxide HgO for heterogeneous removal of O atoms. It was observed changes in the ignition lengths by varying the discharge power (i.e. the yield of $O_2(^1\Delta_g)$ in the oxidizer-gas flow) [2].

The calculations in discharge cell were performed using one-dimensional (on the radius) self-consistent model of DC-discharge with constant gas flow through the tube at constant oxygen pressure. Numerical model of the DC-discharge includes continuity equations for all components in the diffusion-drift approximation and the Poisson equation for the radial component of the electric field E . Value of the axial electric field was obtained from the conservation equation of total current. Then at the outlet of the discharge model, we obtained the distributions of gas components and temperature at the tube radius, which were used for modeling the drift tube and flow reactor. The parameters of heterogeneous losses of O and $O_2(^1\Sigma)$ on the walls were set $\gamma=1$ and $\gamma=0.1$ [6] respectively because the walls in discharge cell and drift tube were covered with mercuric oxide HgO .

To simulate the flow reactor and the drift tube we used a self-consistent two-dimensional gas dynamic model of mixing reactor [11] that was modified to describe the combustion. Reactor model was assumed axial symmetry and can be used to calculate premixed, or mixing with co-flow injection. The simulations solved time-dependent Navier-Stokes equations including effects of compressibility, convection, diffusion, heat conduction, viscosity, and chemical reaction kinetics for the reactive species H_2 , O_2 , H, O, OH, H_2O , HO_2 and H_2O_2 taken from [12]. The problem was treated as two dimensional with cylindrical geometry (r, z) [11]. The reaction scheme was supplemented by reactions for active particles - $O_2(^1\Delta_g)$ and O_3 from [13,14], including 16 reversible reactions.

3 Modeling Results and Discussion

Fig.1 shows the gas temperature distribution along the heated chamber, calculated (curves) and experimentally measured using a thermocouple [2] (points) in non-reactive gas. As seen, the temperature profile is determined by the axial flow rate. Based on this calculation, the cooling of the tube wall downstream of the heated zone ($z \geq 55$ cm) was taken into account in the reactor model.

The modeling of autoignition obtained in mixture of $\text{H}_2:\text{O}_2 = 5:2$ for the experimental conditions was compared with that reported in photos [2]. Fig. 2 shows the resulting temperature and mixture components - H_2 and OH profiles, for the case of autoignition. Stable combustion in [2] was observed at the reactor length of about 50 cm and bright zone equaled approximately 10 cm.

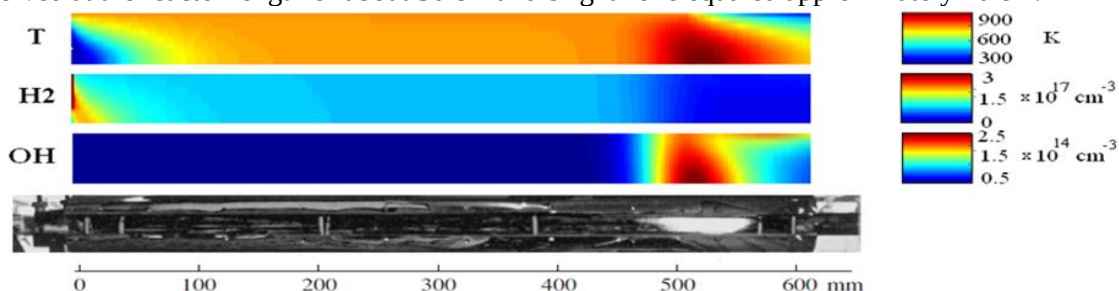


Figure 2. Temperature and H_2 , OH profiles in flow reactor for the case of autoignition; bottom photo from [2].

The induction length, calculated on our model for the autoignition, agrees well with the measured one, Fig.2. In the simulation the induction length was determined by the maximum of OH radical concentration. The maximum gas temperature is near 1150 K at the ignition point. Due to the rapid cooling at the end of the reactor (Fig.1) the zone of high energy release in the burned gas has a length about 10 cm after the ignition point, Fig.2. The radical OH rapidly increases before ignition and has inhomogeneous distribution along the tube radius, which is associated with inhomogeneity of gas temperature. The concentration of molecular hydrogen decreases rapidly after ignition.

Modeling was performed also for the experimental conditions [2] in case of autoignition when discharge was switched off, using kinetic processes in $\text{H}_2\text{-O}_2$ mixtures taken from [8]. It was obtained the ignition didn't occur on the length of the heated part of the reactor (Fig.1). According to our calculations, the received induction length is about 65-70 cm, subject to heating the reactor walls on the length of 70 cm to 780K. The sensitivity analysis under studied conditions [12] showed that the rate of classical branching reaction $\text{H}+\text{O}_2 \rightarrow \text{O}+\text{OH}$ is the critical issue for autoignition delay ($\sim 90\%$), but chain initiation $\text{H}_2+\text{O}_2 \rightarrow \text{OH}+\text{OH}$ and branching $\text{O}+\text{H}_2 \rightarrow \text{H}+\text{OH}$ reactions are much less sensitive - not exceeding 5% and 8% respectively. The rate constant of reaction $\text{H}+\text{O}_2 \rightarrow \text{O}+\text{OH}$ used here taken from [5] rises more rapidly with increasing temperature from 300 to 800, than the same from [8].

The simulations of ignition in flow reactor with switched on discharge were carried out. The modeling of the discharge was performed for the total discharge current - $I = 2, 4$ and 10 mA, that corresponds to experimental conditions [2], where current varied in the range 2 - 30 mA.

Table 1. Oxygen components at the outlet of the DC-discharge model.

$I = 10$ mA	$\text{O}_2(^3\Sigma_g^-)$	$\text{O}_2(^1\Delta_g)$	$\text{O}_2(^1\Sigma_g^-)$	$\text{O}(^3\text{P})$	O_3
$E/N = 80$ Td, $W = 106$ J/mmol	$9.28 \cdot 10^{-1}$	$5.02 \cdot 10^{-2}$	$7.37 \cdot 10^{-3}$	$1.47 \cdot 10^{-2}$	$1.74 \cdot 10^{-5}$

Operating pressure was 10 Torr, oxygen flow through the discharge tube of 2.6 mm radius equaled 9.6 mgs^{-1} . Discharge cell length was 30 cm. Table 1 shows an example of resulting oxygen components at the outlet of the DC-discharge model averaged over the radius of discharge tube. Calculated specific molar discharge input energy $W=106$ J/mmol is in good agreement with experiment [2] value - 107 J/mmol ($I=10\text{mA}$, $U=4200\text{V}$). In addition average gas temperature in the discharge is 650K, which corresponds to the measured in [2] - 640K. Calculated $\text{O}_2(^1\Delta_g)$ yield from discharge cell is about 5%, with walls covered by HgO, while atomic oxygen is about 1.5%. It is worth to note that resulting atomic oxygen concentration at the outlet of the discharge tube in this case is about 5 times lower than that under similar conditions (current density and gas pressure) without HgO [6]. Fig.3 shows profiles

of oxygen components computed in drift tube while excited flow transported to the reactor chamber for the output discharge parameters corresponding values from Table 1.

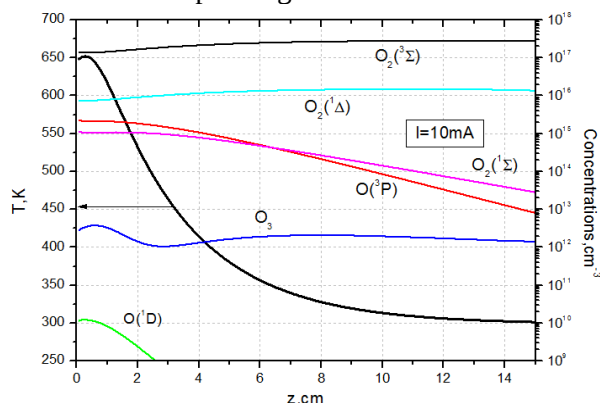


Figure 3. Temperature and oxygen components profiles along the length of the drift tube (at the axis).

O-atoms fraction at the exit of drift tube is reduced by almost 500 times and is about $3 \cdot 10^{-5}$ (Fig. 3), due to heterogeneous reactions on the wall surface with HgO. The concentration of ozone also decreases in 3.5 times. Thus at the reactor inlet the fraction of $O_2(^1\Delta_g)$ in excited oxygen flow equals 4.6% and the total fraction of odd oxygen - $\chi(O+O_3)=3.3 \cdot 10^{-5}$. Temperature of the flow entering the reactor from transport region is reduced to 300K, Fig.3.

Fig.4 shows ignition when the discharge is switched on with input parameters of Fig. 3. As seen from Fig.4 zone of hot burned gas is extended along the reactor tube, compared with the case of autoignition due to small heat losses to the hot walls.

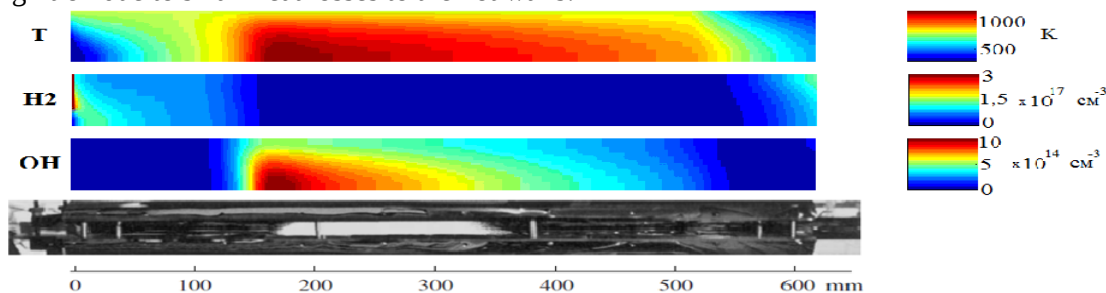


Figure 4. Temperature and H₂, OH profiles in flow reactor. Discharge current - I=10mA; bottom photo from [2].

The induction length equals to approximately 17cm which is about 3 times less compared with autoignition case (Fig.2.) and consists well with the experimentally observed one. As follows from the modeling of the discharge and drift tube, in spite of the walls covering by HgO, the excited oxygen flow, mixed in a reactor with hydrogen, contains residual fractions of odd oxygen, approximately $\chi(O+O_3)=3 \cdot 10^{-5}$ for discharge currents I=2-10mA, i.e. concentration is about 10^{13} cm^{-3} . Under studied conditions this value of odd oxygen is sufficient to start classic branching reaction $O+H_2 \rightarrow H+OH$ and rapid increase the concentration of radicals in "cold" region ($z \leq 10 \text{ cm}$), Fig.4., skipping the stage of direct initiation in the reaction $H_2+O_2 \rightarrow H+HO_2$ ($OH+OH$). At the second stage there is an acceleration of chain branching and the formation of active radicals OH and O via reaction (1a):



Existing models of hydrogen oxidation in the presence of excited oxygen species, for example [8], use the reaction (1a) with the total rate constant determined experimentally in temperature range 300-423K [15] and 523-933K [16]. Though the quenching of $O_2(^1\Delta_g)$ in reaction (1b) is also discussed [7]. Thus, in [7] the rate constant of branching channel (1a) was about 6% relative to the total (1a,b) one from [15] in the same temperature range 300-423K. In [13] it was proposed to reduce the probability of branching channel (1a) to 10-20%. But unfortunately there is no data on the relation of these two

channels at temperatures above 423K and that is especially important at combustion temperatures. So determination of channels ratio in (1) is vitally important for combustion with $O_2(^1\Delta_g)$.

For this reason calculations of ignition length under studied experimental conditions [2] were carried out at the different values of parameter α to reveal the best agreement with experimental data. An arrenius dependence $k_1=6.5 \cdot 10^{-11} \cdot \exp(-2530/T)$ [4] for total rate constant (1) was used in our simulations as a first starting approximation. The simulation results are shown in Fig.5. The best agreement with the experimental data [2] at different discharge currents were achieved for $\alpha=0.1$.

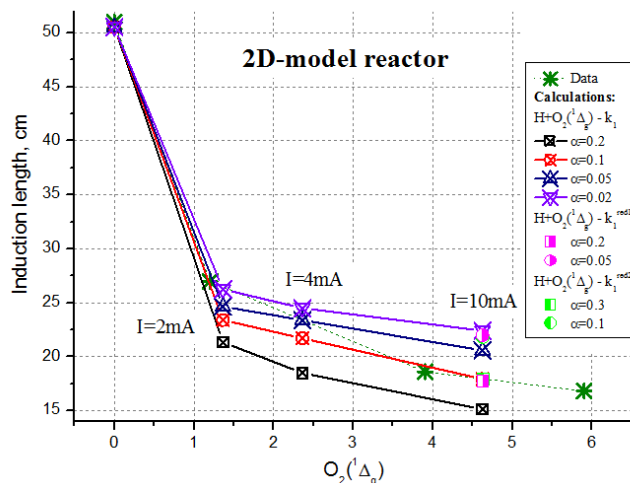


Figure 5. Induction length dependence of singlet oxygen mole fraction. Experimental data were taken from [2].

It was also shown that the induction length is most sensitive to reaction (1a) at $O_2(^1\Delta_g)$ fraction more than 4% ($I=10mA$) [12]. However, apart from the unknown relation between reaction channels (1a) and (1b), the data spread for the total rate constant (1) in [16] is within the order of magnitude. As shown in [13] the measured in [17] decay rate of $O_2(^1\Delta_g)$ behind the shock wave in $O_2:H_2$ mixture in the same temperature range 500-1000K corresponds to two processes involving $O_2(^1\Delta_g)$: up to 700K main contribution to the loss of $O_2(^1\Delta_g)$ gives the process $O_2(^1\Delta_g)+HO_2 \rightarrow O_2+HO_2^*$ [18] and above 700K - $O_2(^1\Delta_g)$ decreases due to reaction (1). The sensitivity analysis of data from [17] made in our simulations [12] shows that the rate of reaction (1) should be 2-4 times lower than in [16] at temperatures higher than 700K to satisfy the experimental data [17], but such values are within the error range from [16]. We calculated the induction length, reducing total reaction rate constant by 2 - k_{red1} and 4 - k_{red2} times at studied temperatures. Fig.5 shows the results of these calculations in case $I=10mA$. As seen, the best agreement in comparison with experimental data was obtained for the probabilities of the branching channel 0.2 and 0.3, respectively for k_{red1} and k_{red2} . Summarizing obtained results we can estimate the value of rate constant (1a) at 780K as follows: $0.1 \cdot k_1 \approx 0.2 \cdot k_{red1} \approx 0.3 \cdot k_{red2} \approx (2.4 \pm 0.2) \cdot 10^{-13}$. It means that probability of reaction channel (1a) may take up to 30%. Note that reaction (1b) leads to additional heating. A sensitivity of the induction length to total rate constant was also revealed. It was shown that the total rate constant (1) can not be lesser than about $(8.0 \pm 0.7) \cdot 10^{-13}$.

The operating pressure is low enough to manifest the influence of reaction $O_2(^1\Delta_g)+HO_2 \rightarrow O_2+HO_2^*$ on the induction length. This process is expected to be an important in $H_2-O_2-O_2(^1\Delta_g)$ kinetics at higher pressures, $P \geq 1Bar$, where three-body processes $H+O_2+M \rightarrow HO_2+M$ play a significant role. But this requires a further careful study.

3 Conclusions

A comprehensive numerical study of ignition in the H_2-O_2 mixture with DC-discharge activation for the experimental conditions [2] was carried out. The influence of singlet oxygen on the initiation and branching chain reactions of combustion in hydrogen-oxygen mixtures was analyzed. The

sensitivity of the induction length to the total rate constant was revealed. The probability of branching channel in the reaction $\text{H} + \text{O}_2(^1\Delta_g)$ was observed depending on the value of the total rate constant. The estimated value of the reaction rate $\text{H} + \text{O}_2(^1\Delta_g) \rightarrow \text{O} + \text{OH}$ equals $(2.4 \pm 0.2) \cdot 10^{-13}$ at 780K.

Acknowledgements

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