The kinetic characteristic features of the low-temperature hydrogen oxidation during the induction period behind reflected shock waves

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Abstract. The experiments on the ignition of H₂–O₂ mixtures behind reflected shock waves were carried out. In these experiments the chemiluminescence of electronically excited OH⁺ radicals (λ = 308 nm) at the early stage of the ignition induction period is studied over the temperature range of 800 < T < 1050 K at a pressure of 0.1 MPa. The OH⁺ emission signal is measured for a time less than 1 ms, when the influence of physicochemical factors capable to influencing the homogeneous autoignition process such as flow turbulence in a boundary layer, various heterogeneous processes, and residual active particles is negligibly small. Significant difference between the ignition delay times derived from the pressure rise and sharp increase of the emission of electronically excited OH⁺ radicals was experimentally observed. The experiments showed that the onset of OH⁺ emission is always ahead of the time of pressure rise. Any regular dependence between the onset of OH⁺ emission and the initial temperature behind the reflected shock wave T₅₀ is not observed. This is indicative of a stochastic character of this process or hotspot ignition of the reactive mixture.

1. Introduction

The low-temperature oxidation of hydrogen (at T < 1000 K) is of considerable interest for hydrogen energetics and nuclear power plant safety [1], as well as for better understanding of the fundamental aspects of hydrogen ignition [2]. Kinetic mechanisms are typically validated using the experimental data on ignition delay time τ. Although extensive studies have been performed, the disturbing problem of a large scatter in experimental data (more than 6 orders of magnitude for τ) and results of computations by various kinetic mechanisms [3] remains unresolved.

To interpret the discrepancies revealed in the shock tube experiments, the following possibilities are usually considered:

1. Catalytic reactions on the walls [4],
2. Variation of the gas parameters behind the shock front [5],

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(3) quantum corrections of the rate coefficients [6],
(4) non-equilibrium distribution of the longitudinal velocity of molecules behind the shock front [7],
(5) the impurities [8],
(6) residual radicals and atoms [9],
(7) gas heating caused by interaction of the reflected shock wave with the turbulent boundary layer [10],
(8) the incompleteness of the kinetic mechanism [11].

The interpretation of the experimental results is complicated by the fact that the self-ignition at the low temperatures is not homogeneous [12]. For example, based on the ideas formulated in [12], the authors of [2] presented quantitative estimates, according to which, at $T < 1100 \text{ K}$, the deflagration burnout of hydrogen-bearing reactive mixture at separate hotspots can influence the self-ignition process. At present, the reasons for the appearance of the self-ignition spots remain unclear. In this connection, the question arises as for the extent of influence of each of the above factors on the self-ignition of H$_2$–O$_2$ mixtures, in particular, what role they play in the formation of self-ignition hotspots. The problems related to chemical kinetics, primarily the nature of the initiation reactions in H$_2$–O$_2$ system, are of special interest.

The authors of [13] considered the following three initiation reactions:

$$\begin{align*}
\text{H}_2 + \text{O}_2 &= \text{H} + \text{HO}_2, & \Delta H_{298} &= 53.6 \text{ kcal/mole}, \\
\text{H}_2 + \text{O}_2 &= \text{OH} + \text{OH}, & \Delta H_{298} &= 17.8 \text{ kcal/mole}, \\
\text{H}_2 + \text{O}_2 &= \text{H}_2\text{O} + \text{O}, & \Delta H_{298} &= 117.3 \text{ kcal/mole}.
\end{align*}$$

Reaction (3) is hardly possible because of its high endothermicity. At the same time, reaction (2) although being energetically favorable has been rejected by most researchers based on the theoretical analysis [13]. Thus, reaction (1) is the only initiation channel of oxidation of hydrogen–oxygen mixtures. At the same time, with decreasing temperature, the influence of reaction (2) on the autoignition process increases considerably [6].

The aim of the present work is to carry out the new experiments on the self-ignition of H$_2$–O$_2$ mixtures to develop a new approach for studying the kinetics of the low-temperature hydrogen oxidation behind reflected shock waves based on the optical measurements of OH$^*$ emission.

2. Experimental results and discussion

The experiments were carried out in a stainless steel shock tube (75 mm inner diameter, 1.5 m driver section, 3.2 m driven section). The driver gas was helium diluted with air. The diaphragm was burst spontaneously. The pressure was recorded by the piezoceramic pressure gauges (lead zirconate titanate) with a diameter of the sensitive element of 1 mm. The gauges were mounted flush with the inner wall of the shock tube. The pressure gauge was mounted in the optical observation cross section, 11 mm from the endplate of the shock tube. The parameters of the gas behind the incident and reflected shock waves were calculated from the initial pressure, mixture composition, and incident shock wave velocity using the theory of ideal flow in a shock tube. The velocity of the incident shock wave was determined over two measuring distances between three pressure transducers. The parameters behind the reflected shock front are designated as $T_{50}$ and $P_{50}$.

The kinetics of a H$_2$–O$_2$ mixture self-ignition was studied by recording the chemiluminescence from electronically excited OH$^*$ radicals ($\lambda = 308 \text{ nm}$) over a temperature range of $800 < T_{50} < 1053 \text{ K}$ at a pressure of $P_{50} = 0.11 \pm 0.02 \text{ MPa}$. The OH$^*$ signal was recorded using
Figure 1. Typical time histories of the OH∗ emission and pressure profiles for the self-ignition of the 20% H2 + 10% O2 + 70% Ar mixture behind reflected shock waves: (a)—P50 = 0.095 MPa, T50 = 806 K; (b)—P50 = 0.107 MPa, T50 = 856 K; (c)—P50 = 0.132 MPa, T50 = 951 K.

The temperature dependence of the ignition delay time for the mixture being studied is displayed in figure 2. One can see that in some experiments the values of τp and τOH∗ differ

a FEU-51 photomultiplier in conjunction with an interference filter. The level of possible carbon-containing impurities, as determined from the emission signals of CH∗ (λ = 429 nm), C2∗ (λ = 516.5 nm), CO2∗ (λ = 360 nm) in auxiliary experiments, was found to be below 1 ppm. The 20% H2 + 10% O2 + 70% Ar mixture was tested.

Figure 1 shows typical time profiles of the OH∗ signals and pressure time histories for various temperatures behind reflected shock waves. Actually, we determined two different ignition delay times: from OH∗ emission (τOH∗) and from pressure rise (τp). The ignition delay times τOH∗ and τp were determined as the time interval between the arrival of the reflected shock wave in the observation cross-section and the onset of a sharp rise of OH∗ emission (τOH∗) or fast pressure growth (τp), respectively. As can be seen from figure 1, significant difference between the ignition delay times derived from the pressure rise and sharp increase of the emission of electronically excited OH∗ radicals is experimentally observed. The experiments showed that the onset of OH∗ emission is always ahead of the time of pressure rise. The direct dependence between the onset of OH∗ emission and the initial temperature behind the reflected shock wave is not observed. This is indicative of a stochastic character of this process or hotspot ignition of the reactive mixture. If the difference between the (τOH∗) and (τp) is minimal (figure 1a), an abrupt increase of the OH∗ emission signal without any preliminary growth is observed. At the same time, as can be seen from figures 1b and 1c, a particular preliminary rise of OH∗ emission signal is observed before the onset of OH∗ emission. In this case one can speak about two-stage emission process of OH∗, which are caused by different physical-chemical processes. One possible explanation of this experimental observation is the influence of optical emission caused by the heterogeneous and stochastic hotspots appeared in the reactive mixture long before the onset of the homogeneous pressure rise.

The temperature dependence of the ignition delay time for the mixture being studied is displayed in figure 2. One can see that in some experiments the values of τp and τOH∗ differ
Figure 2. Temperature dependence of the ignition delay time for the 20%H2 + 10%O2 + 70%Ar mixture at a pressure of \( \sim 0.11 \) MPa. Circles designate \( \tau_{\text{OH}^*} \), squares correspond to \( \tau_p \). The curve represents the results of calculations of \( \tau_{\text{OH}^*} \) and \( \tau_p \) by the reaction mechanism borrowed from [14] with reaction (2).

The results of calculation of \( \tau_p \) in the framework of the CHEMKIN III package [15] with the use of a set of reactions for the H2–O2 system from the kinetic mechanism [14] extended to include reaction (2) with a rate constant \( k_2 = 3 \times 10^{11} \exp[-40 \text{ kcal/mol}/(RT)] \) cm\(^3\)/mol/s are also shown in figure 2. For numerical analyses of the \( \tau_{\text{OH}^*} \) ignition delays we followed the assumptions formulated in [16].

According to [16], the only source of chemiluminescent emission of OH* in a H2–O2 mixture is the reaction

\[
O(^3\text{P}) + H(^2\text{S}) + M \rightarrow \text{OH}(A^2\Sigma^+) + M, \quad \Delta_H^0 = -8.4 \text{ kcal/mol}. \tag{4}
\]

Since the luminescence quenching of OH* proceeds very fast [16], a steady-state concentration of OH* sets in, and, therefore, the emission signal can be represented as

\[
I_e = R_C A_C \times [O][H], \tag{5}
\]

where \( I_e \) is the emission intensity, \( R_C \) is the radiation constant, and \( A_C \) is the instrumental constant. Given that the values \( R_C \) and \( A_C \) remain unchanged during the experiment, \( I_e \) is proportional to \([O][H]\).

The values of \( \tau_{\text{OH}^*} \) calculated according to 5 turned out to be in excellent agreement with the simulated \( \tau_p \) values. Therefore, in figure 2 the results of both calculations (\( \tau_{\text{OH}^*} \) and \( \tau_p \)) are designated by the common line. At the same time, it is interesting to note that the experimental values of \( \tau_{\text{OH}^*} \) and \( \tau_p \) differ from each other in the majority of our experiments. This difference does not demonstrate any temperature dependence.

As can be seen from figure 2, in the temperature range \( T > 900 \) K, the results of kinetic simulations and experimental measurements are in satisfactory agreement. At the same time,
at $T < 900$ K, a considerable deviation between the calculated and measured values of $\tau$ is observed. Similar results were obtained in [10] for a stoichiometric $\text{H}_2$–$\text{O}_2$ mixture. As far as the numerical modeling within the framework of a particular kinetic mechanism cannot provide explanation of the experimentally observed difference between $\tau_{\text{OH}^*}$ and $\tau_p$, one can conclude that the source of the early emission of $\text{OH}^*$ is determined not by chemical kinetics but by the other physical-chemical reasons.

3. Conclusions
It is shown that within the low-temperature range studied ($800 < T < 1050$ K) a pronounced difference is observed between the ignition delays for a $\text{H}_2$–$\text{O}_2$–Ar mixture determined from different parameters. The experimentally measured values of $\tau_{\text{OH}^*}$ are either equal or shorter than $\tau_p$ and the difference between them does not demonstrate any regular temperature dependence. In the case of considerable difference between $\tau_{\text{OH}^*}$ and $\tau_p$, the two-stage emission of $\text{OH}^*$ can be observed, which can be explained by the appearance of emission from the stochastic nascent hotspot in advance of homogeneous self-ignition of the reactive mixture. The numerical modeling demonstrates that a pronounced difference between $\tau_{\text{OH}^*}$ and $\tau_p$ cannot be explained only within the framework of the existing chemical kinetics and the other physical-chemical reasons, which are capable to provide the appearance of hotspot ignition of $\text{H}_2$–$\text{O}_2$ mixtures within the temperature range studied, should be taken into account.

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