Numerical simulation of the autoignition of hydrogen–air mixtures behind shock waves

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Abstract. Problems related to the autoignition of hydrogen-air mixtures are highly important for the operation safety of nuclear reactors and for hydrogen power engineering. In spite of extensive studies in this area, there are still many problems directly concerned with the ignition delay times of H₂/O₂ mixtures and with the conditions under which these processes occur. This paper deals with the numerical analysis of the data available in the literature on O, H, and OH yields in order to determine the influence of the primary channels of the initiation of H₂/Air mixtures. The numerical modeling of the available literature data on the ignition delays of hydrogen-air mixtures made it possible to describe the shock tube measurements of ignition delays within the framework of a unified kinetic mechanism over a temperature range of 930–2500 K at pressures from 0.1 to 8.7 MPa.

1. Introduction

The autoignition of hydrogen-air mixtures is of considerable scientific and practical importance directly related to the problems of hydrogen electric power generation [1, 2] and operation safety of nuclear power stations [3]. In spite of extensive studies carried out in this field by different research groups, it is still impossible to describe all available experimental data within the framework of a single kinetic model [4].

A comprehensive review of the ignition delay time τ for hydrogen-air mixtures measured on various experimental installations is presented in [5]. As can be seen from the temperature dependence of the ignition delay time τ presented in [5], the scatter in τ values in the temperature range of 800 to 1200 K is about six orders of magnitude.

To explain this scatter, a variety of factors have been considered in the literature, such as the incompleteness and imperfection of the kinetic mechanisms [6, 7], occurrence of catalytic reactions on the reactor walls [4], fluctuations of the parameters of the gas behind the shock wave [8], quantum corrections to the rate coefficients [9], nonequilibrium distributions of the longitudinal velocity of molecules behind a shock front [10, 11], the presence of active sites on the impurity particles [12], the presence of radicals and atoms formed from gaseous organic impurities [13, 14], and gas heating in the turbulent boundary layer [15–17].
In addition, it was supposed that the process of autoignition at low temperatures differs from the homogeneous autoignition. According to the hypothesis put forward in [2], at $T < 1000$ K, hot spots emerge, giving rise to deflagration flame propagation. As a result, the mixture begins to burn out long before the homogeneous autoignition. Such hot spots were observed experimentally [18]. However, the reason for their formation remains unclear, so many researchers do not support this hypothesis.

In addition to practical relevance, the autoignition of $\text{H}_2/\text{O}_2$ mixtures has fundamental kinetic aspects. In particular, the problem of the initiation reaction for the $\text{H}_2/\text{O}_2$ system has not been resolved completely. The literature considers three main initiation reactions [19]:

\[
\begin{align*}
(R1) \quad & \text{H}_2 + \text{O}_2 = \text{H} + \text{HO}_2, \quad \Delta H_{298} = 53.6 \text{ kcal/mole}, \\
(R2) \quad & \text{H}_2 + \text{O}_2 = \text{OH} + \text{OH}, \quad \Delta H_{298} = 17.8 \text{ kcal/mole}, \\
(R3) \quad & \text{H}_2 + \text{O}_2 = \text{H}_2\text{O} + \text{O}, \quad \Delta H_{298} = 117.3 \text{ kcal/mole}.
\end{align*}
\]

Reaction (R3) appears to be uncompetitive because of its extremely high endothermicity. At the same time, reaction (R2), although energetically favorable, has ignored by the majority of researchers in view of the results of quantum-chemical calculations [19]. Therefore, reaction (R1) has been considered as the only initiation step in the hydrogen/air system.

In the present work, we tested the validity of the assumption that reaction (R1) is the only initiation step in this system by trying to describe various experimental data on the ignition delay time behind reflected shock waves over a wide range of temperatures, pressures, and fuel and oxidizer concentrations within the framework of a unified reaction mechanism.

2. Numerical modeling and discussion
All the calculations were carried out using the CHEMKIN III software. The rate constants of the reverse reactions and the thermal effects of the elementary reactions were calculated using the standard of NASA polynomials [20]. The GAS-PHASE KINETICS package in CHEMKIN III is designed by default to work with thermodynamic data in the form used in the NASA chemical equilibrium code. In this case, seven coefficients are needed for each of two temperature ranges. CHEMKIN-PRO can use the NASA database directly without any modification.

As we compared the results obtained with the use of different kinetic mechanisms, to provide consistency of calculations, for each of the kinetic mechanism under consideration those thermodynamic polynomials were utilized, which were presented in the corresponding papers. If calculations were carried out with the use of our own kinetic scheme, the data for thermodynamic polynomials were borrowed from [21].

Our kinetic scheme was based on the kinetic mechanism of reactions for $\text{H}_2/\text{O}_2/\text{N}_2$ mixtures borrowed from [22]. This mechanism was supplemented by initiation channel (R2). Finally, we obtained the kinetic scheme comprised of 21 reactions. As far as our numerical modeling covered the pressure range from the atmospheric pressure up to the pressure of several MPa, the rate coefficients of the reactions of monomolecular decomposition were supplemented by the enhanced third-body efficiencies borrowed from [14] in the form suitable for CHEMKIN III software.

The thermodynamic data in the form of NASA polynomials were used to calculate the equilibrium constants and from them the reverse-rate coefficients were calculated for a particular reaction. The only parameter, which was varied in our kinetic mechanism, was the rate coefficient of reaction (R2). According to [23–27], the observable value of activation energy $E_a$ of the rate coefficient of reaction (R2) falls in the range of 39–48 kcal/mole. In this case, the majority of researchers accept the value of 39 kcal/mole.

Therefore, we accepted the value of 40 kcal/mole for the activation energy in the rate coefficient of reaction (R2) and the value of pre-exponential factor of this rate coefficient $k_2$ was determined form the best fit of the results of our calculations with the whole collection
of experimental data considered in the present paper. We also compared the results of our calculations with the results of numerical simulations with the use of the widely known kinetic mechanisms presented in [28–31], in which the initiation channel (R2) was absent.

Comparison of the results of our calculations and calculations with the use of kinetic mechanisms presented in [28–31] with the experimental data on the time histories of H atoms [32], O atoms [33] and OH radicals [32–34] is presented in figures 1 and 2. As can be seen from these figures, for all presented experimental conditions, we succeeded in good quantitative description of the time profiles of H, O, and OH. In [33], the authors, based on their own numerical simulations with the use of a shorter kinetic mechanism, comprised of 15 reactions, determined the rate coefficient $k_1$ from the time profile of O atoms with reaction (R2) excluded from their kinetic mechanism.

![Figure 1. Comparison of the (a) H-atom [32] and (b) O-atom [33] time profiles experimentally measured (symbols) and calculated (lines) by the kinetic mechanisms from the indicated works at the following conditions behind reflected shock waves: (a) 0.99%H$_2$ + 0.1%O$_2$ in Ar, $T_{50} = 1700$ K, $P_{50} = 0.079$ MPa, (b) 25 ppm H$_2$ + 6.124%O$_2$ in Kr, $T_{50} = 1981$ K, $P_{50} = 0.0688$ MPa.](image)

![Figure 2. Comparison of the OH time profiles measured (symbols) and calculated (lines) by the kinetic mechanisms from the indicated works at various conditions behind reflected shock waves: (a) a mixture 5%H$_2$ + 0.493%O$_2$ in Ar, $T_{50} = 1980$ K, $P_{50} = 0.0675$ MPa [32], (b) a mixture 0.4%H$_2$ + 0.4%O$_2$ in Ar, $T_{50} = 2590$ K, $P_{50} = 0.1075$ MPa [34].](image)

It should be emphasized that O atoms are produced directly neither in reaction (R1) nor in reaction (R2) but they appear only in the secondary reactions. Taking the value of $k_1$ from [29], which is approximately half as much as those obtained in [33], and adding reaction (R2) into the kinetic mechanism, we succeeded in quite good description of the presented time profile of
O atoms. From the best fit of the results of calculations with the experimentally measured time histories of O, H, and OH (see figures 1 and 2), we determined the rate coefficient of reaction (R2) as $k_2 = 3 \cdot 10^{11} \exp(-40000 \text{ cal/mole}/RT) \text{ cm}^3/\text{mole/s}$.

From the comparison of the results of all calculations presented in figures 1 and 2 one can conclude that the results of numerical modeling with the use of our own kinetic mechanism are similar to the results obtained with the use of the kinetic mechanism presented in [31]. One can see that in figure 1(a) they are in general agreement in spite of the fact that reaction (R2) in the kinetic mechanism from [31] is absent.

From this fact one can conclude that the ratio of the rate coefficients $k_1/k_2$ cannot be unequivocally determined from the high-temperature measurements of O, H, and OH time histories, presented in [32–34]. This conclusion was also supported by the sensitivity analysis carried out by us within the framework of CHEMKIN III software with the account of reaction (R2). For this reason, the value of $k_2$ presented by us should be considered only as an estimate within the framework of the whole kinetic mechanism.

At the same time, since the activation energy of reaction (R2) is considerably lower than the activation energy of reaction (R1), then it is quite probable that, with the temperature decrease, the influence of reaction (R2) should increase. Unfortunately, the experimental measurements of the time profiles of O, H, and OH radicals in the H$_2$/O$_2$ mixtures for the temperatures below 1600 K are not available in the literature.

On the other hand, the experimental data on the ignition delay times of the H$_2$/O$_2$ mixtures obtained in shock tubes up to the temperature of 930 K are available. We tried to describe these data taking into account that according to the concept proposed in [9] the influence of reaction (R2) manifests itself exactly for the temperatures $T < 1100$ K and at the high pressures.

The experimental measurements of the ignition delay times $\tau$ carried out for various H$_2$/O$_2$ mixtures and for different pressures were selected for numerical simulations. The comparison of the results of our numerical simulations with the experimentally observed values of $\tau$ presented in [35–37] are shown in figures 3, 4, 5. It should be emphasized that the values of $\tau$ presented in figure 3 were determined from the pressure increase in the H$_2$/Air mixture and the values of $\tau$ presented in figures 4 and 5 were determined from the maximum of emission signal of electronically excited OH$^*$ in the H$_2$/O$_2$ mixtures diluted with argon.

![Figure 3](image_url)

**Figure 3.** Comparison of the temperature dependences of the ignition delay times calculated in the present work and measured in [35] from pressure rise for a mixture of 29.59%H$_2$+14.79%O$_2$+N$_2$ for $P_{50} = 0.25$ MPa.

To describe the maximum of OH$^*$ emission we supposed that the only reaction, which can provide sufficient amount of energy in H$_2$/Air mixtures to excite OH radical at a wavelength


Figure 4. Comparison of the temperature dependences of the ignition delay times experimentally measured from excited hydroxyl peak [36] (symbols) and calculated in the present work (curves) for various mixtures and pressures: (circles) 2%H$_2$+1%O$_2$+Ar mixture, $P_{50} = 3.3$ MPa; (squares) 0.5%H$_2$ + 0.25%O$_2$+Ar, $P_{50} = 6.4 - 8.7$ MPa; (triangles) 0.1%H$_2$ + 0.05%O$_2$+Ar, $P_{50} = 6.4$ MPa.

of $\lambda = 306.7$ nm, $A^2 \Sigma^+ - \chi^2 \Pi (0,0)$ ($\Delta H_{298} = -93.2$ kcal/mole), which was used to record the chemiluminescence signal of OH$^*$ in [36, 37], is the reaction

(R4) $O + H \rightarrow OH^*$ $\Delta H_{298} = -101.2$ kcal/mole.

Taking into account that the extinction of the excited state of OH$^*$ proceeds very rapidly [38], under assumption of quasistationary distribution of the excited states of OH$^*$, with a high probability one can determine the emission signal as a product

$I_e = K_R A [O][H]$

where $I_e$ is the emission intensity, $K_R$ is the emission constant, $A$ is the apparatus function. The last two values do not depend on temperature and pressure and, thus, the value of $I_e(t)$ can be considered to be proportional to the product of the instant concentrations of H and O atoms multiplied by a constant factor $K_R A$. For this reason, when our data were compared with the results obtained in [36,37], the maximum of the product $[O][H]$ was accepted as the maximum of OH$^*$.

One can see from figures 4 and 5 that our kinetic mechanism, which includes reaction (R2), provides good agreement of the calculated values of $\tau$ with the experimentally observed ignition delay times within a wide range of pressure from 0.1 up to 8.7 MPa. It is evident from figure 3 that, at high temperatures ($T > 1100$ K) the mechanisms under consideration give similar values of $\tau$, but at the same time, with the temperature drop to 900 K, the calculated values of the ignition delay times demonstrate disagreement, which is as high as an order of magnitude in $\tau$ values. The mechanism of ignition of a H$_2$/O$_2$ mixture presented in the current work, which includes reaction (R2), gives $\tau$ values closest to the experimentally observed in [35].

3. Conclusion

Based on the results of numerical simulations, one can conclude that the mechanism of ignition of hydrogen-air mixtures supplemented by initiation channel (R2) quite well describes both the time profiles of the primary products and the ignition delays at temperatures of $930 < T < 2500$ K and pressures of $0.1 < P < 8.7$ MPa and various initial concentrations of reagent for mixtures diluted with an inert gas and for H$_2$/Air mixtures. The value of the rate coefficient of reaction (R2) was evaluated from the best fit of the calculation results to the experimental data.
Figure 5. Comparison of the temperature dependences of the ignition delay times experimentally measured from excited hydroxyl peak [37] (symbols) and calculated in the present work (lines) for various mixtures and pressures: (circles) 1%H$_2$+0.53% O$_2$+Ar, $P_{50}$ = 0.1 MPa; (triangles) 0.095%H$_2$+0.048%O$_2$+Ar, $P_{50}$ = 6.5 MPa.

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