

Low-temperature ignition delay for hydrogen–air mixtures in light of a reaction mechanism with quantum correction

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ABSTRACT

A reaction mechanism with quantum correction is used to model low-temperature/high-pressure autoignition of lean hydrogen–air mixtures. This approach provides a good approximation for experimental data on autoignition delay and the low activation energy observed in experiments. Calculated results demonstrate that ignition delay time is inversely proportional to pressure, squared. The proposed scaling reduces spread in experimental data. The application of a quantum correction to hydrogen oxidation provides a basis for developing a general reaction mechanism that can be used to predict the autoignition behavior of hydrogen over an entire temperature/pressure range relevant to rocket engine conditions.

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1. Introduction

Improving rocket engine efficiency became an acute problem in recent years [1–4]. The use of hydrogen as a fuel in prospective propulsion systems is attractive due to an anticipated high energy efficiency. Moreover, water as the main product of hydrogen combustion fully meets environmental standards. Design of new hydrogen combustion systems is impossible without comprehensive knowledge of hydrogen oxidation kinetics [1,5]. In many cases, experimental data on autoignition dynamics are required to validate mechanisms for exothermic reactions in gases. Autoignition is quantitatively described in terms of ignition delay τ . However, even after more than 100 years of research in hydrogen oxidation chemistry, the rate constants for the reactions that constitute a chain mechanism remain a matter of dispute. One reason for the lack of consistency between the reaction mechanisms proposed in different studies is wide scatter in the experimental data used for validation. A comprehensive survey presented in a recent paper [6] demonstrates that a spread in measured ignition delay values can exceed five orders of magnitude in the low-temperature range of $T < 900$ K. Another important and still unresolved issue is that conventional reaction mechanisms of hydrogen oxidation substantially over predict ignition delays. Values of τ determined experimentally at $T < 900$ K can be several orders of magnitude lower than the corresponding calculated ones [7]. Possible explanations of

the discrepancy were discussed recently, but no ultimate conclusion has been reached (see [6–9] and references therein). In this context, new approaches may help elucidate the behavior of reactive hydrogen-containing mixtures at relatively low temperature and high pressure. The modified reaction mechanism suggested in [10], where quantum corrections were introduced, is particularly promising as demonstrated in [11,12]. The present study focuses on the application of the theory developed in [10] to low-temperature autoignition of lean hydrogen–air mixtures. The analysis is restricted to mixtures with equivalence ratios of $\varphi < 0.5$ at relatively high pressures ($P > 0.5$ MPa) and $T < 900$ K, which are important for propulsion applications but remain a challenge for modeling based on conventional mechanisms.

2. Calculated results

According to [10,12], the rate of reaction can be expressed by the Arrhenius equation

$$k(T) = \delta A \exp(-E_a/T),$$

with the quantum correction factor

$$\delta = 1 + \frac{0.61 \cdot P}{(E_r + T)\sqrt{T}} e^{\frac{E_r}{T}} \sum_l C_l \left(\sigma_{0al} \frac{1}{\sqrt{m_a}} \left(\frac{m_b}{m_a + m_b} \right)^{2/3} \left(\frac{m_a + m_l}{m_l} \right)^{1/6} + \sigma_{0bl} \frac{1}{\sqrt{m_b}} \left(\frac{m_a}{m_a + m_b} \right)^{2/3} \left(\frac{m_b + m_l}{m_l} \right)^{1/6} \right), \quad (1)$$

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where $E_r = E_a - Q$ (E_a is the activation energy in K, Q is the heat of reaction in K), C_l and m_l are the relative molar concentration and molecular weight of the l th species, and σ_{obl} and σ_{oal} are the total scattering cross sections for molecules a and b (in units of 10^{-15} cm^2) at an energy of E_r .

With decreasing pressure and increasing temperature, the value of δ approaches unity (i.e., the quantum correction to reaction rate becomes negligible). An increase in pressure or decrease in temperature leads to a significant increase in δ and a corresponding steep increase in reaction rate. Note that the correction factor is significant when the reaction involves a barrier ($E_a > Q$). This is the case for the chain initiation reaction $\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{OH}$, as pointed out in [12]. However, the inclusion of this reaction in hydrogen oxidation kinetics is questionable because there exist alternative reaction paths and widely disparate parameter values have been suggested in the literature for the rate constant of this reaction. The detailed analysis below is restricted to three widely used chain-initiation reactions, with parameter values listed in Table 1.

Reaction R1 is the main chain-initiation step in various current mechanisms of hydrogen oxidation. The parameter values for R1 in Table 1 are taken from a recently validated mechanism [16]. Note the wide disparity of the parameter values for reaction $\text{H}_2 + \text{O}_2 = \text{OH} + \text{OH}$ between R2 and R3: the ratio k_{R3}/k_{R2} varies between $5.6 \cdot 10^4$ and $1.8 \cdot 10^6$ over the temperature range from 900 to 700 K. The extremely low value of k_{R2} inferred from computations [14] was the main reason for removing reaction R3 from most hydrogen oxidation mechanisms in the last decade. Nevertheless, a more careful analysis is required to evaluate the contribution of $\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{OH}$ to the dynamics of low-temperature/high-pressure autoignition of lean hydrogen–air mixtures. Fig. 1 presents the ignition delay calculated for the 15% H_2 +85%Air mixture with $\varphi=0.42$ at $P=0.6$ and 5 MPa (solid curves) by using the mechanism proposed in [16]. Open circles represent the results of calculations with reaction R2 included. It is clear that the inclusion of R2 does not affect the calculated values of τ ; i.e., reaction R2 cannot compete with R1, as emphasized in [17]. The delay times calculated with R3 included (open triangles in Fig. 1) are only slightly lower (by less than 20%). Thus, regardless of the parameter values used, the inclusion of $\text{H}_2 + \text{O}_2 \rightleftharpoons 2\text{OH}$ does not lead to any significant change in the calculated ignition delay.

Next, we analyze the behavior of τ as a function of temperature when the quantum correction is employed. Fig. 2 presents the results of calculations using the mechanism of [16] with reaction R2 included. The corrected ignition delay values are up to several orders of magnitude lower than those calculated without the correction. This is due to a significantly higher rate constant for reaction R2 calculated by using Eq. (1). Note also a marked decrease in effective activation energy. It can be explained by examining asymptotic behavior of the reaction rate. According to Eq. (1), the corrected value of $k(T) \sim \delta \exp(-E_a/T)$ tends to behave as $k(T) \sim \exp(-Q/T)$ with decreasing temperature. Finally, the behavior of $\tau(P)$ and $\tau(\varphi)$ exhibits features characteristic of low-temperature ignition. Dashed and dot-and-dash curves in Fig. 2 represent the results for 5 MPa and 0.6 MPa adjusted to a pressure of 2 MPa. The low-temperature ignition delay calculated without quantum correction is roughly proportional to $P^{-0.7}$. When the

Table 1

Rate constant $k(T) = A(T/298.15)^n \exp(-E_a/T)$ for chain initiation reactions.

Reaction	$A, \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	n	E_a, K	Source
R1 $\text{H}_2 + \text{O}_2 = \text{HO}_2 + \text{H}$	5.176E+05	2.43	2.70E+04	[13] $\times 0.7$
R2 $\text{H}_2 + \text{O}_2 = \text{OH} + \text{OH}$	1.65E+13	0.47	3.51E+04	[14]
R3 $\text{H}_2 + \text{O}_2 = \text{OH} + \text{OH}$	1.738E+13	0.00	2.43E+04	[15]

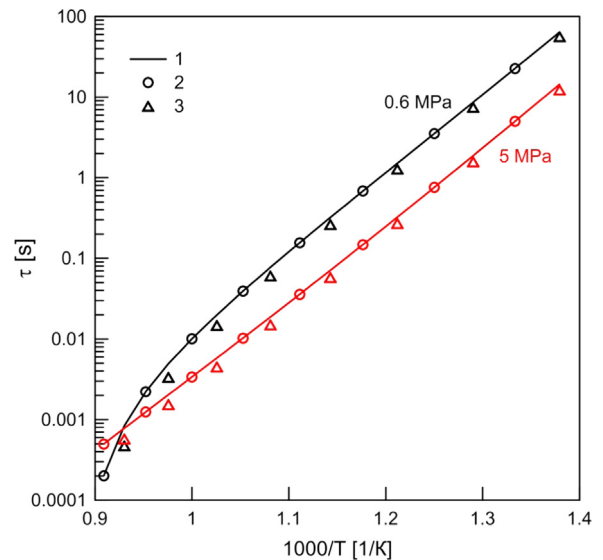


Fig. 1. Temperature dependence of self-ignition delay calculated for 15% H_2 +85%Air at $P=0.6$ and 5.0 MPa: 1 – original mechanism of [16]; 2 – mechanism of [16] + R2; 3 – mechanism of [16]+R3.

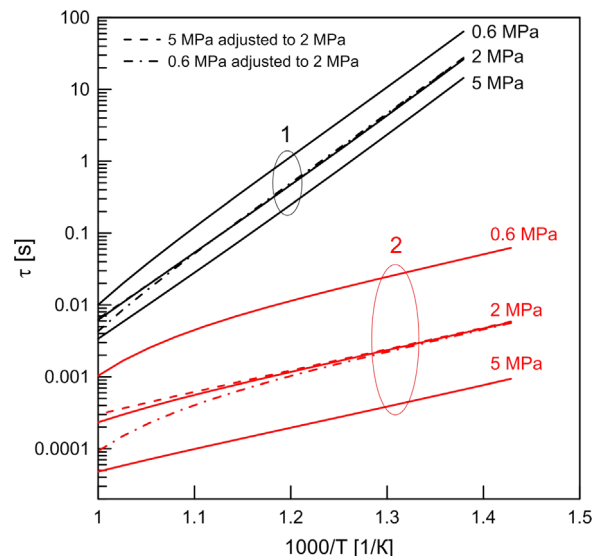


Fig. 2. Calculated and adjusted temperature dependence of ignition delay for 15% H_2 +85%Air at several pressures: 1 – mechanism of [16] without correction; 2 – mechanism of [16]+R2 with quantum correction.

quantum correction is used, the effect of pressure is more pronounced: $\tau \sim P^{-2}$. This scaling relation can be used to approximate experimental results instead of the commonly adopted $\tau \sim P^{-1}$. Additional calculations performed for lean hydrogen–air mixtures with various equivalence ratios indicate that $\tau \sim \varphi^{-0.7}$ regardless of the quantum correction.

3. Comparison with experiment

Fig. 3 compares experimental data with kinetic modeling results. Experimental data for $\varphi < 0.5$, $P > 0.5$ MPa, and $T < 900$ K reported in [6,18–23] were adjusted to a pressure of 2 MPa and equivalence ratio of 0.42 by using the scaling relation $\tau \sim P^{-2}\varphi^{-0.7}$. The data of [20] are represented in the form of an experimentally-based correlation for a hydrogen–air mixture:

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