



# Inhibition of plasma-assisted ignition in hydrogen–oxygen mixtures by hydrocarbons



Ilya N. Kosarev<sup>a</sup>, Sergey O. Belov<sup>a</sup>, Svetlana V. Kindysheva<sup>a</sup>, Andrey Yu. Starikovskiy<sup>b</sup>,  
Nickolay L. Aleksandrov<sup>a,\*</sup>

<sup>a</sup> *Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region 141700, Russia*

<sup>b</sup> *Princeton University, Princeton, NJ 08544, USA*

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## ABSTRACT

The effect of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> addition on the ignition of a stoichiometric hydrogen:oxygen mixture was experimentally analyzed using a shock tube with a discharge cell. Ignition delay time was measured behind a reflected shock wave after a high-voltage nanosecond discharge and in its absence using mixtures with small percentages of hydrocarbons. The obtained results were compared with ignition delay times in a mixture without hydrocarbon addition. It was shown that C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> inhibit the hydrogen–oxygen reaction and that the inhibition effect is much more profound when the mixtures are ignited after a high-voltage nanosecond discharge. A numerical simulation of the discharge and ignition phases was used to show the main mechanisms that control the inhibition of hydrogen:oxygen ignition by hydrocarbons. The densities of atoms, radicals, excited particles and charged particles produced in the discharge plasma were calculated and used as input parameters for ignition modeling. Reasonable agreement was obtained between the calculated and measured plasma-assisted ignition delay times in the mixtures under consideration. The analysis of primary reaction pathways for hydrocarbon species was used to demonstrate the inhibition mechanisms of ignition in hydrogen:oxygen mixtures excited by non-equilibrium discharge plasma.

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## 1. Introduction

Understanding the ignition properties of hydrogen in oxygen and air is important for its safe use as an energy carrier. A wide range of ambient conditions are expected for the employment of hydrogen as a fuel in commercial and residential fuel cells. Therefore it is necessary to understand the ignition behavior of hydrogen in the presence of trace contaminants that could be inhibitors or promoters.

Previous studies showed that a number of additives including hydrocarbons [1–6], halogen-substituted hydrocarbons [3,4,7], and iron- [3,8] and phosphorus-containing [9] compounds inhibit hydrogen ignition. Inhibiting additives affect the second limit of the hydrogen–air reaction [1,2], reduce flame speeds [3,5,8,9], lengthen ignition induction times [4], increase ignition temperature [6], lengthen the deflagration-to-detonation transition delay [6], and shorten flammability limits [7].

Inhibition mechanisms are usually associated with inhibitor-assisted recombination of key flame radicals, especially H, O and OH. Hydrogen atoms are particularly important in ignition and flame propagation since the chain branching reaction  $H + O_2 \rightarrow OH + O$  plays a crucial role in hydrogen flames. Recombination of these radicals with inhibiting additives leads to fewer other radicals. As a result, the hydrogen–oxygen reaction is inhibited due to reduced chain branching.

The inhibition of the hydrogen–oxygen reaction by hydrocarbons is most effective when there are catalytic atom scavenging cycles. For hydrogen atom removal, the reactions that comprise the catalytic cycle are [4,10]



and



Reaction (1) leads to the replacement of H atoms capable of branching by less active hydrocarbon radicals. They recombine with other H atoms to form hydrocarbon molecules. As a result,

\* Corresponding author.

E-mail addresses: [nick\\_aleksandrov@mail.ru](mailto:nick_aleksandrov@mail.ru), [aleksandrov.nl@mipt.ru](mailto:aleksandrov.nl@mipt.ru) (N.L. Aleksandrov).

one RH molecule causes the recombination of many H atoms to form H<sub>2</sub> molecules.

Previous studies of the inhibition of the hydrogen–oxygen reaction have dealt with self-ignition or ignition by a spark in which a thermally equilibrium plasma was generated. In this work, we studied the inhibition of non-equilibrium plasma-activated ignition. A non-equilibrium plasma with a large amount of chemically active species was generated by a high-voltage nanosecond discharge. Plasma-assisted ignition (PAI) and plasma-assisted combustion (PAC) in fuel-oxidizer mixtures have attracted considerable interest in recent decades due to the possible applications (see Ref. [11] and reviews [12–18]). It was shown experimentally and numerically that with the use of non-equilibrium discharge plasmas it is possible to reduce ignition delays, to decrease ignition temperatures and to increase flame stabilization limits and flammability limits in fuel-oxidizer mixtures. As a result, the use of non-equilibrium discharge plasmas seems to be promising for high speed flames and for automotive engines [15,17]. To quantitatively analyze the mechanisms of PAI and PAC, experiments must be conducted under well-controlled conditions. In this case, numerical approaches allow the simulation of production of chemically active species in the discharge phase, as well as the simulation of rapid gas heating due to reactions in the discharge and its afterglow.

The use of a shock tube equipped with a discharge cell permitted the study of PAI under well-controlled uniform conditions [13,15–17]. It also permitted the simulation of plasma and ignition processes after a high-voltage nanosecond discharge [13,15–17]. This method has been applied previously to the study of PAI of hydrogen [19], saturated hydrocarbons [19–22], acetylene [23], ethylene [24] and ethanol [25]. The purpose of this work is to study the inhibition effect of hydrocarbon addition on the ignition in a stoichiometric hydrogen:oxygen mixture excited by a nanosecond discharge plasma using the same shock tube technique. Understanding the inhibition mechanisms in this case could provide insight into the dominant processes that control ignition initiated by non-equilibrium plasmas.

## 2. Experiment and measured results

Shock tubes are widely used to measure autoignition delay times in combustible mixtures. In this work, ignition delay times were measured with the shock tube technique to study the inhibition of plasma-assisted ignition in a stoichiometric hydrogen:oxygen mixture by hydrocarbons. The non-equilibrium plasma was generated by a high-voltage nanosecond discharge that was initiated in a heated gas mixture behind the reflected shock wave.

The experimental setup used in this study is essentially the same as the one used in our previous work [19,21,26]. In short, the experiments were conducted in the shock tube of a 25 × 25 mm<sup>2</sup> square cross section, a 1.6 m long low-pressure channel and a 60 cm long high-pressure chamber (see Fig. 1). The stainless-steel channel and the Plexiglas discharge section were equipped with windows for optical diagnostics. The high-voltage electrode and the grounded electrode were the metal end plate of the tube and the opposite grounded steel section of the tube, respectively. A nanosecond discharge was initiated by high-voltage pulses produced with a Marx-type high-voltage generator. A starting voltage was between 100 and 160 kV. A forming ferrite line was used to sharpen the high-voltage pulse. The rate of voltage rise was several kilovolts per nanosecond at the output of the forming line.

Ignition was studied in a stoichiometric H<sub>2</sub>:O<sub>2</sub> mixture diluted with He (30%) and Ar (60%) and in the same mixture but with 0.1% of either C<sub>2</sub>H<sub>4</sub> or C<sub>2</sub>H<sub>6</sub>. The effect of inhibition is more profound at lower gas temperatures. In shock-tube experiments, the temperature behind a shock wave is lower when a fuel:oxygen mixture is

diluted with a low atomic mass gas. To reduce the temperature behind a shock wave, we diluted the combustible mixtures with 30% He and 60% Ar rather than with 90% Ar.

Ignition delay time was measured behind a reflected shock wave. The temperature of the gas in this region was between 840 and 960 K for PAI and between 1060 and 1660 K for autoignition, respectively. The corresponding pressure was between 0.1 and 0.5 atm for autoignition and between 0.6 and 0.85 atm for PAI. The values of gas temperature and pressure were obtained from the measured velocity of the incident and reflected shock waves on the basis of the 1D shock tube model. In our shock-tube experiments, the range of measured ignition delay times was about two orders of magnitude (from 10 to 1500 μs). In this case, it was impossible to take a series of measurements with and without plasma at the same initial temperatures for the parameters of the high-voltage generator used. Therefore, the temperature ranges are different for PAI and autoignition. Here, it is possible to characterize the effect of discharge plasma on fuel ignition by comparing gas temperatures at which the same values of ignition delay time are reached after the discharge and without it.

Three laser Schlieren systems installed along the shock tube were used to measure shock wave velocity. We defined ignition delay time as the time interval between the Schlieren signal indicating arrival of the reflected shock wave at the diagnostic cross section and the onset of the leading front of CH emissions at 431 nm. The emission onset was determined by extrapolating the tangent line to zero emission intensity. A high-voltage nanosecond discharge was initiated at the instant the reflected shock wave attained the diagnostic cross section.

Two capacitive gauges and a magnetic current gauge (Rogowski coil) were used to measure the electric field in the discharge and the discharge current, respectively (see the insert in Fig. 1). The gauges were calibrated with a high-voltage signal of known amplitude and duration. From the measured data, the energy deposited in the discharge phase and the reduced electric field  $E/N$  ( $N$  is the gas number density) were obtained. The parameter  $E/N$  governs all electron characteristics including the rates of electron-impact production of chemically active species during the discharge.

We also calculated the values of  $E/N$  using the measured values of the discharge current  $I = enwS$ , where  $e$  is the elementary charge,  $n$  is the electron density,  $w = w(E/N)$  is the electron drift velocity and  $S$  is the cross-section of the discharge cell. The electron density and the drift velocity were obtained from a numerical solution of the electron balance equation and the Boltzmann equation, respectively (see Section 3). Figure 2 shows the calculated values of  $E/N$  at the instant of highest discharge current in the mixtures under consideration. Most of the discharge energy was deposited when  $E/N$  was between 50 and 64 Td (1 Td = 10<sup>-17</sup> V cm<sup>2</sup>). These values are several times higher than the breakdown threshold for the mixtures studied.

We validated the values of  $E/N$  determined from the discharge current by comparing the deposited energy values calculated using two different approaches. This parameter controls the amount of chemically active species produced in the discharge. Figure 3 compares the discharge energy calculated on the basis of  $E/N$  values estimated from discharge current dynamics and the discharge energy calculated using the electric fields directly measured in the experiment. There is reasonable agreement between the two sets of data. This comparison shows that the method used to obtain  $E/N$  values from the measured discharge current is adequate.

Figure 4 compares the measured data on delay times for autoignition and plasma-assisted ignition in a stoichiometric H<sub>2</sub>:O<sub>2</sub>:He:Ar mixture with and without a 0.1% addition of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. The inhibition of H<sub>2</sub> ignition by the additives under study is observed in all cases. It follows from the data presented in this figure that the inhibition effect for autoignition is small and is more

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