KINETICS OF PLASMA ASSISTED COMBUSTION AT LOW REDUCED ELECTRIC FIELDS

Liang Wu, Alexander A. Fridman and Andrey Yu. Starikovskiy*

Drexel University, Philadelphia, PA, USA
astar@drexel.edu

The paper presents the results of numerical analysis of the role of singlet oxygen in plasma assisted ignition in hydrogen-oxygen and hydrogen-air mixtures. A kinetic mechanism of the effect of singlet delta oxygen (SDO) molecules was determined by calculating numerically the ignition characteristics.

Several possible approaches have been proposed for plasma enhancement of ignition of hydrogen-oxygen and hydrocarbon-oxygen mixtures [1]. Among them, the electronically excited molecules may be of great importance because of its high efficiency. Thus, a numerical study of kinetic mechanism of singlet oxygen in hydrogen-oxygen mixture is presented here. Recent experimental results have shown that with existence of singlet oxygen molecules, the ignition delay time could be greatly reduced in hydrogen-oxygen mixture [2].

The ignition process was numerically simulated using the kinetic scheme given by [3], which include 12 particle species (H_2, H, O_2, O, O_3, $O(^1D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma^+_g)$, OH, HO_2, H_2O_2, H_2O) and 80 reactions. Calculations were carried out in the zero-dimensional approximation at a fixed gas pressure. In calculations, we determined the ignition delay time as the interval between the instant at which singlet delta oxygen molecules were injected and the onset of abrupt increase of gas temperature. To validate the calculated results, the comparison has been made between the experiment from [3] and our simulations:

Mole fraction of SDO (%)	0	1.2	4	6
Induction Zone Length, Lin (cm)	51	27	18.6	16.8
Ignition delay time from [3], τ_e (ms) =L_{in}/v_0	13	6.8	4.7	4.2
Calculated ignition delay time τ_c (ms)	14	7	5	4

To show the mechanism of the singlet delta oxygen influence on the ignition process, Fig. 1a and 1b compare the evolution in time the calculated rates of the dominant chemical reactions for autoignition and plasma-assisted ignition. It follows from the calculation that an injection of sufficient concentration of singlet delta oxygen molecules leads to an increase of ignition initiation. Indeed, in the induction phase of autoignition, the rates of the reactions are low during the initial phase and jump by several orders of magnitude immediately before ignition. In the case of plasma-assisted ignition, the active singlet delta oxygen produces significant concentration of OH radicals from the very beginning. Due to the high density of OH radicals, the rate of the reaction $H_2+OH=H_2O+H$ is high. Consequently, the rates of chain branching reactions have been increased dramatically. As a rule, in the induction period of SDO assisted ignition, the role of the radical reactions becomes more profound than that of the reactions with the main components.
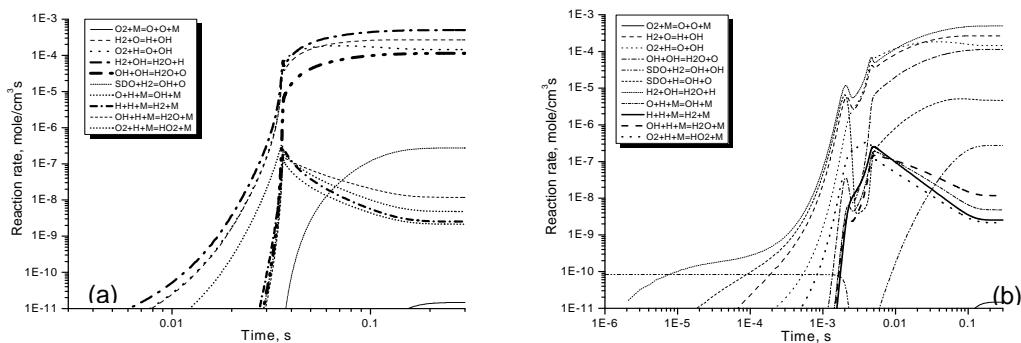

Figure. 1: The evolution in time of the calculated rates of the main chemical reactions for autoignition (a) and ignition with 6% singlet delta oxygen (b).

To compare the efficiency of SDO initiation in fuel-air and fuel-oxygen mixtures the energy distribution was calculated in air and pure oxygen plasma. The energy distribution calculations were done by varying the concentration of nitrogen in the mixtures. As from Figure 2, without nitrogen the discharge optimization (E/n~6 Td) allows of the most energy to go into the excitation of singlet oxygen including delta and sigma states. However, by raising the amount of nitrogen in the mixture, the energy distribution is changed significantly. Starting with 20% of nitrogen in the mixture, triplet nitrogen has more energy deposited than singlet oxygen. When the nitrogen concentration reaches the air level (~80%) more than 50% of the discharge energy goes into nitrogen to create vibrationally excited nitrogen (discharge is optimized for maximum SDO production). Meanwhile, the energy to excite oxygen is about one order of magnitude lower, which is less than 2%.
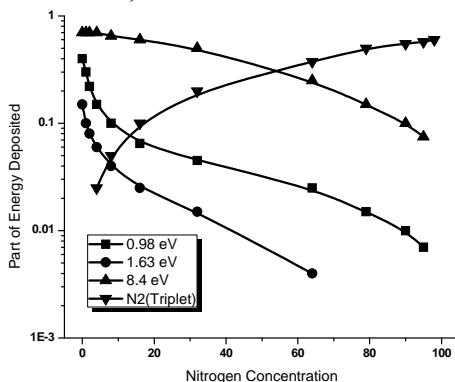

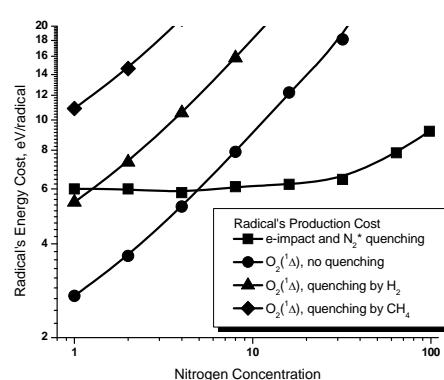Figure 2. Energy distribution with different nitrogen concentration

Figure 3. Energy cost of radicals production at different nitrogen concentrations

In Figure 3 the energy costs for two different channels of radicals production (singlet oxygen excitation and oxygen atoms produced by quenching of nitrogen triples states and direct dissociation by e-impact) were calculated with different concentration of nitrogen. Similar to Figure 2, with low concentration of nitrogen, the cost to generate the radicals through singlet oxygen excitation is lower than the cost of oxygen dissociation by electron impact and quenching of excited nitrogen (~3 eV and ~6 eV). However, taking into account SDO quenching by H_2, one can estimate that even for low nitrogen concentration the energy price of the radical is almost the same for both channels (5 eV vs. 6 eV). Moreover, with slightly more nitrogen, for example in 10% nitrogen containing mixture, the energy required to dissociate the oxygen molecules is much less than the energy to form electronically excited oxygen molecules. In air, this difference between the two channels becomes enormous. This further proves that in air, dissociation of oxygen molecules is much energy efficient rather than radicals formation through excitation of singlet oxygen molecules.

We have made a numerical study of the ignition of hydrogen-oxygen mixtures with the participation of singlet oxygen molecules and showed that it agrees well with the measurements from the experiment [2]. It follows from the analysis of the calculated results that, with singlet delta oxygen molecules, the high concentration of active species leads to the decrease of ignition delay time. In order to obtain most efficient ignition stimulation under various conditions, relatively low electric field E/n (~6 Td, singlet delta oxygen excitation) could be applied in pure oxygen electric discharge. Larger value of E/n (~300 Td, molecular oxygen dissociation) is recommended for high efficiency of plasma assisted ignition in air plasma.

References
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