Ignition of hydrocarbons by nonequilibrium plasma: experiment and modelling

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Introduction

There are different opinions concerning the interaction between nonequilibrium plasma and combustion. For discharges at low reduced electric fields, low–energy excitation, such as vibrational excitation or excitation of lower electronic states [1] is important. At higher electric fields, role of dissociation by an electron impact becomes dominant. At the same values of the electric field, active production of radicals [2] takes place. Some authors claim [3] that ions are important for ignition kinetics.

It is quite typical to numerically analyze the discharge effect on a combustible mixture by artificially injecting different radicals at the initial moment of calculations. Paper [4] investigated numerically the kinetic paths to radical–induced ignition of a methane–air mixture. Paper [5] gave the calculations of the impact of radicals addition on the extinction limits of H_2 and CH_4 flames in a perfectly stirred reactor. They investigated the comparative effect of O, H, N, and NO_x additions.

The experimental data testifying the increased efficiency of ignition/combustion under non-equilibrium plasma may rarely be considered as unambiguous. In this sense the experiments where, at least, some uncertainties are artificially excluded or where the authors compare their experiments with kinetic calculations may help in understanding the mechanism of combustion by nonequilibrium gas discharge plasma.

Experimental approach.

In this paper we consider the continuation of our previous work at the conditions where the impact of nanosecond pulsed discharge and ignition are separated in time [6, 7]. Shock tube technique is used to obtain fixed pressure and temperature behind the reflected shock wave below the threshold of autoignition. High–voltage nanosecond discharge in the form of the fast ionization wave (FIW) [8] is organized in the last section of the shock tube at the moment when the reflected shock wave comes to the cross–section of measurements. Typical gas temperatures T_5 are within the range of 900–2000 K, and pressures P_5 are in the range of 0.2–1.0 atm. Here, the nanosecond discharge is spatially uniform up to the gas densities about 10^{19} cm^{-3} at high voltage amplitudes as high as tens and hundreds of kV. This means that the plasma is non–thermal in quite a large volume.

A typical experimental setup is described elsewhere [6]. In each experiment the delay time for autoignition was compared with the ignition delay time for ignition by a nanosecond discharge developed in the end–plate section of the shock tube. The section was made of dielectric material and the discharge developed between the end plate of the shock tube and stainless steel part 20 cm apart. The shock tube had

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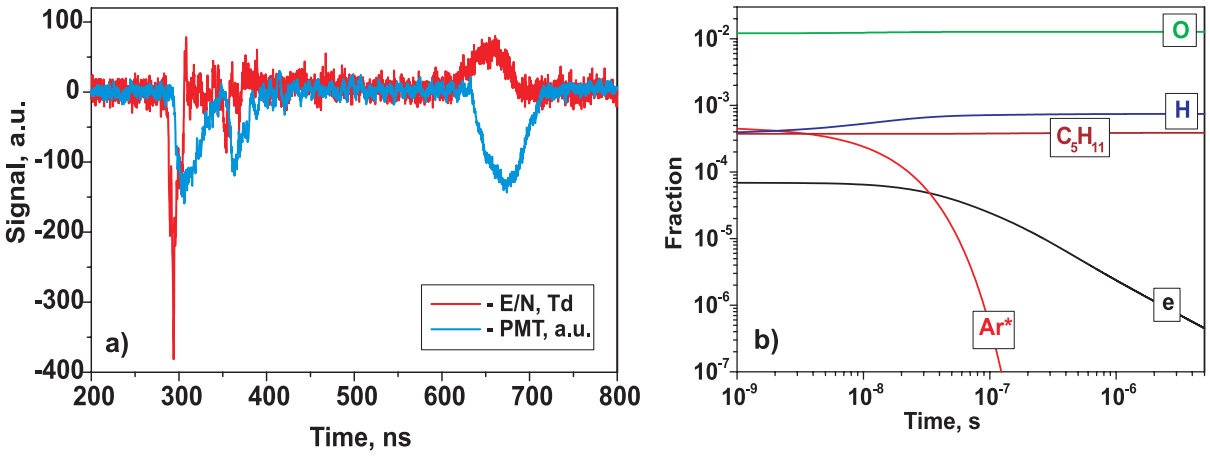

Figure 1: a) – typical temporal behavior of electric field and signal from the photomultiplier. CH_4:O_2:N_2:Ar = 1:4:15:80 mixture, T_5 = 1180 K, P_5 = 0.4 atm, U=-150 kV; b) – typical calculated densities of active species. C_5H_{12}:O_2:Ar = 1.1:8.9:90, T_5 = 1390 K, P_5 = 0.5 atm, U=-110 kV.

rectangular cross-section of 25x25 mm. Eight optical windows were used to provide optical diagnostics. The ignition delay time was determined from a sharp increase of OH (306 nm) or CH (431 nm)emission. It is worth to mention here that CH emission and OH emission give similar ignition delay time. The system for monitoring the shock wave parameters included a system for measuring the velocities of the incident and reflected shock waves by means of the laser schlieren technique and a system for controlling initial pressure. The gas density (ρ_5), pressure (P_5), and temperature (T_5) behind the reflected shock wave were determined from the known initial gas mixture composition, the initial pressure, and the velocity of the incident shock wave. Correction of such approach and of the calculation of T_5 has been checked by controlling IR emission of CO_2 additives (1 %) in specially prepared controlled mixtures.

High voltage pulses with the amplitude in the range 100–160 kV at the high–voltage electrode were used to initiate the discharge. The duration of the pulse was about 40 ns, and 1–2 re–reflections were observed during 0.2 μs depending upon the parameters of the experiment.

The experiments were carried out with a set of stoichiometric mixtures C_nH_{2n+2} : O_2 (10%) diluted by Ar (90%) for hydrocarbons from C_2H_6 to C_5H_{12}. In each experiment, we kept parameters T_5 and P_5 the same for autoignition and ignition by the discharge. The main aim of the present paper was to calculate numerically the shift of the ignition delay time for hydrocarbon–oxygen mixtures numerically in the assumption that the main process which causes the ignition is productions of radicals in nanosecond discharge and in early afterglow, and to compare the results with experimental data.

Numerical modelling and comparison with the experiments

Numerical simulation of production of active particles by the high–voltage nanosecond discharge was reduced (i) to the simulation of production of active particles (electrons, ions, excited particles, atoms and radicals) in a high electric field in the discharge and (ii) to the simulation of conversion of the active particles during plasma decay after the active phase of the discharge. Active particles under consideration were excited Ar atoms, O atoms, H atoms, radicals of hydrocarbon molecules, electrons and positive ions. Production of negative ions and complex positive ions (Ar_2^+, O_4^+, etc.) was neglected because of high (> 1000 K) gas temperatures in the discharge gap. At the end of plasma decay, only atoms and radicals were assumed to dominate the composition of active particles, whereas the existence of long–lived excited states was neglected.

Simulation of the processes during the discharge was carried out using electric fields measured in the

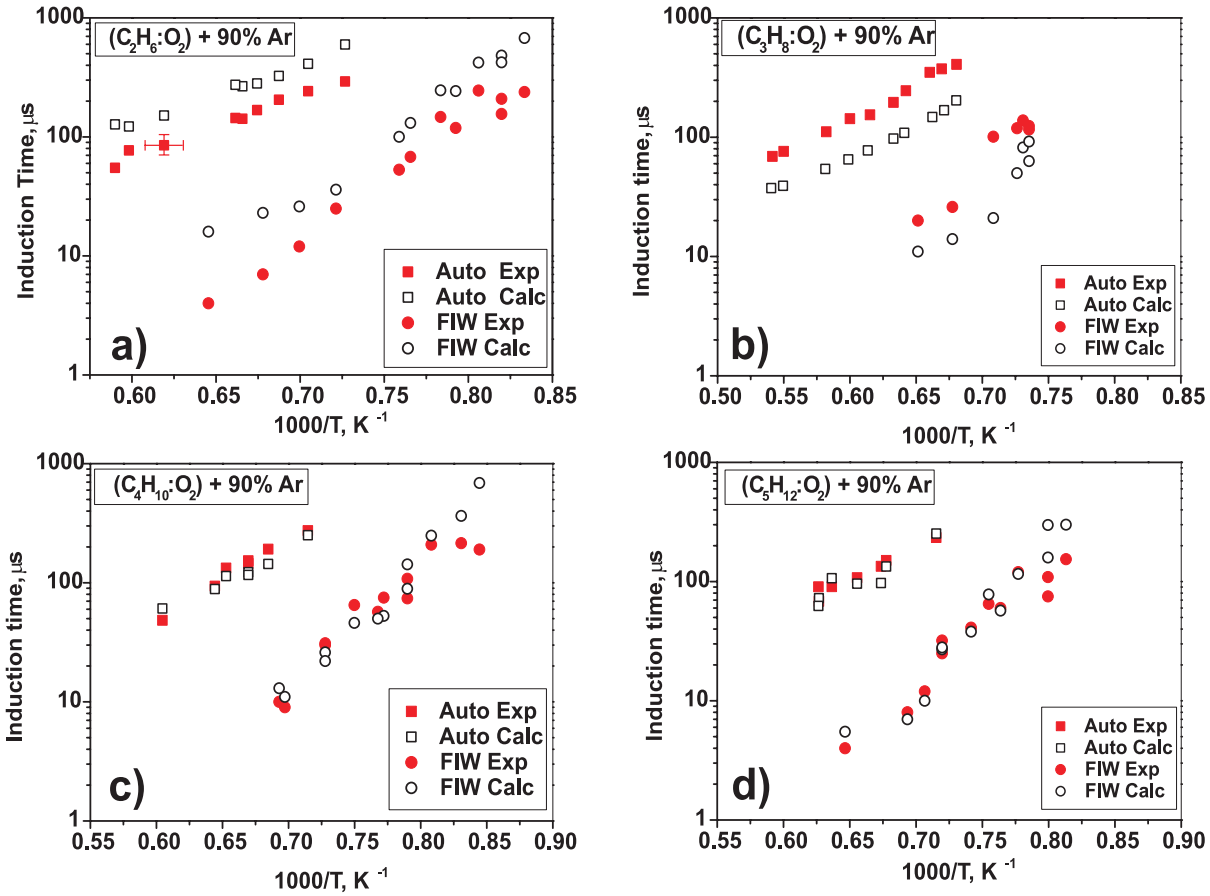

Figure 2: Autoignition (designated as "auto") and ignition by nanosecond discharge in the form of fast ionization wave (designated as "FIW") for a) C_2H_6; b) C_3H_8; c)C_4H_{10}, and d) C_5H_{12} – containing mixtures. Comparison of experiments and calculations.

discharge gap at every instant. Electron drift velocity and rate coefficients were calculated by solving the electron Boltzmann equation in the classical two–term approximation. The rate coefficients and transport coefficients calculated from the Boltzmann equation were used to simulate the evolution in time of the densities of active particles in a high electric field during the discharge. In this discharge phase, because of its short duration, the loss of active particles can be neglected. As a result, the evolution in time of the densities of these particles in this phase was analytically determined from the corresponding balance equations. In the experiments under consideration, the main pulse of applied voltage was generally followed by several smaller pulses. Production of active particles was simulated also in these additional discharge phases. As a rule, in this case production of atoms, radicals and excited neutral particles was noticeable, whereas production of electrons and ions was not important.

The evolution of the densities of active particles between and behind voltage pulses was simulated using a numerical solution of the balance equations. In this phase, in a zero electric field charged particles were removed due to dissociative electron-ion recombination producing an additional number of atoms and radicals. The last particles were also produced due to charge exchange of positive ions on hydrocarbon molecules and due to quenching of excited Ar atoms by oxygen and hydrocarbon molecules. In our kinetic model, in the end charged and excited particles were excluded from the consideration and the gas mixture consisted of initial neutral species and atoms and radicals produced during the discharge

and in its afterglow. The densities of atoms and radicals were used further as input parameters for a computer program to simulate ignition in the mixtures under consideration.

Fig. 1, a gives typical behavior of the electric field and signal from the photomultiplier for methane–air stoichimetric mixture diluted with Ar. Under our experimental conditions, signal from the photomultiplier corresponds to the emission of short–lived (radiative lifetime is 40 ns) second positive system of molecular nitrogen. This emission reflects adequately a stage of the discharge development. Fig. 1, b shows an example of the evolution in time of the densities of dominant active species in the afterglow of the discharge in the $Ar{:}O_2{:}C_5H_{12}$ mixture.

A zero–dimensional simulation of autoignition and artificial ignition by the discharge was performed at constant pressure using CHEMKIN code [9]. Autoignition was modelled using mechanism proposed by Tan [10] for C_2H_6–C_3H_8 containing mixtures, and mechanism used by Zhukov and Starikovskii [11] (based on Westbrook mechanism [12]) for C_4H_{10} and C_5H_{12} containing mixtures. These mechanisms were supplemented with the reactions of formation and quenching of OH radical in $A^2\Sigma$ state to compare the numerical and experimental results. The results of the calculations are given in Fig. 2. Let us note that here we have quite reasonable agreement both for autoignition and for the ignition by nanosecond discharge. This means that under our experimental conditions we can describe the plasma assisted ignition assuming that the main governing factor accelerating the ignition is production of radicals, dissociated and electronically excited species by the discharge.

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