Ignition and Oxidation of Hydrocarbons by Pulsed Nanosecond Discharge

Ilya N. Kosarev[1], Nickolay L. Aleksandrov, Nikolay B. Anikin[2], Andrey A. Nikipelov[1], Svetlana V.Kindusheva, Svetlana M. Starikovskaia[3] and Andrey Yu. Starikovskiy[4]

[1]Moscow Institute of Physics and Technology, Russia
[2]University of Groningen, the Netherlands
[3]Ecole Politechnique, France
[4]Drexel University, United States

The use of nonequilibrium plasma at temperatures close to autoignition temperature may give significant benefit in comparison with equilibrium heating. There are experimental papers where researchers report that they observe an ignition treating a gas with nonequilibrium plasma at ambient temperature. To prove possibility of nonequilibrium plasma to ignite gas mixtures at conditions where the autoignition is impossible and to analyze efficiency of nonequilibrium plasma in total, it is necessary to study detailed kinetics in combustible mixtures under the action of a discharge. In this paper we give an example of experimental analysis of different combustible mixtures, based on saturated hydrocarbons, staring from CH_4 up to $C_{10}H_{22}$, under the short pulsed volume discharge at ambient and elevated temperatures.

1 Low-temperature oxidation

In this part, we describe results of the experiments concerning oxidation of different combustible mixtures at ambient temperature under the action of periodical nanosecond discharge and preliminary analysis of kinetics in such a system. A discharge was excited in a 20 cm in length discharge tube with an inside diameter of 47 mm and outside diameter of 50 mm by negative-polarity pulses with an amplitude of 11 kV, duration at half-height of 25 ns, rise time of 5 ns, and repetition rate of 40 Hz. The experimental setup and measurements procedures are described in detail in [1].

The investigation revealed that the oxidation times determined by the radiation of different bands do not differ significantly (15 % or less), for this reason to analyze discharge kinetics we used full oxidation time defined by $CO(B^1\Sigma–A^1\Pi)$ emission. Figure 1 gives the times of complete oxidation of hydrocarbons in all investigated mixtures [1] and in stoichiometric $C_2H_5OH+O_2$ mixture at the same energy input. One can well see that the time of oxidation of methane is systematically approximately twice those of other hydrocarbons in mixtures with both oxygen and air. For the remaining

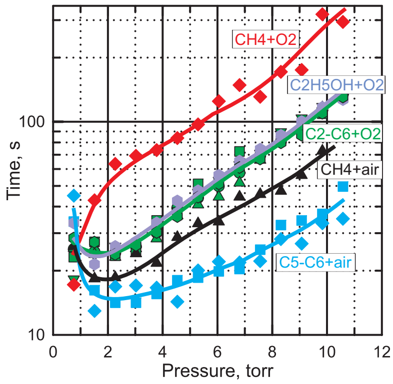

Figure 1. Oxidation time for different mixtures.

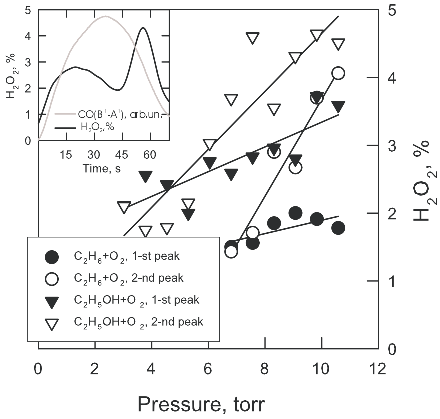

Figure 2. Peak concentrations of H_2O_2 for stoichio- metric mixtures of C_2H_6 and C_2H_5OH with O_2.

Correspondence to: astar@drexel.edu

hydrocarbons, the oxidation times do not differ within the experimental error. In mixtures with air, the characteristic times of oxidation of hydrocarbons including methane are two or three times lower than that in similar mixtures with oxygen. In view of the smaller total amount of hydrocarbon in mixtures with air at the same initial pressures, the rate of oxidation in mixtures with air is approximately twice slower than in mixtures with oxygen. Therefore, beginning with ethane, the time of oxidation in stoichiometric mixtures with oxygen or air is the same for any hydrocarbons. Methane oxidizes approximately twice slower than any other investigated hydrocarbons.

The absence of the dependence of the time of oxidation on the type of hydrocarbon beginning with ethane may be explained most realistically by the weak effect of excited and charged particles produced in the discharge from fuel molecules, in compare with the particles produced from intermediate substances, and oxidation products.

The chemical activity of investigated hydrocarbons is varied essentially, but oxidation times are the same for almost any hydrocarbon under the same experimental conditions. It means that there is very strong feed-back: an intermediate produced from any hydrocarbon is very active in reactions with radicals and consumes radicals better than the main hydrocarbon. A good choice for the role of the intermediate is H_2O_2. We controlled the H_2O_2 density in stoichiometric mixtures of C_2H_5OH, C_2H_6, CH_4 with O_2 (Figure 2). The measurements were performed using UV-absorption at 200-215 nm. As we expected the concentration increased with the hydrocarbon chemical activity. For the methane mixture we did not observe H_2O_2 but for C_2H_5OH the intermediate density was twice as one for C_2H_6. Second absorption peak appeared with the CO density drop on a low main hydrocarbon density background and is probably related to CO oxidation only. Thus, competition of main hydrocarbon and H_2O_2 governs the oxidation process at low temperature. At elevated temperature H_2O_2 can produce OH radicals efficiently, and the influence on an oxidation process needs to be investigated in detail.

2 Ignition at high temperatures

The influence of nonequilibrium plasma of pulsed discharge as an igniter of combustible mixtures at elevated temperatures was investigated via shock tube technique. The main aim of this part of work was to answer the question how the discharge changes the ignition delay time for different hydrocarbons in a homological series. Experiments were carried out behind a reflected shock wave, as in classic experiments on the autoignition of combustible mixtures. The shock tube (25x25-mm square cross section) had a 1.6 m long working channel. The last section of the shock tube was made from plexiglas and had eight optical windows (quartz and MgF_2). The end plate (EP) of the tube was made of dielectric with metal central part, which served as a high-voltage electrode. Another electrode was the grounded steel section of the shock tube. The nanosecond discharge was initiated at the instant at which the reflected shock wave arrived to the observation point. To achieve uniform ignition at the observation cross-section, we had to perform experiments 55 mm apart from the end plate. At the same time, classical autoignition experiments are carried out a few millimeters from the and plate of a shock tube to avoid gasdynamics effects. So, we made a series of additional experiments 5 mm apart from the end plate and determined ignition delay time to calibrate the system.

Velocity of a shock wave was measured by Schlieren system consisted of three HeNe lasers and a set of photodiodes (PD). 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. Ignition delay time was controlled using emission of different transitions: OH emission (λ=306.4 nm, $A^2\Sigma – X^2\Pi$ transition) and CH emission (λ=431.3 nm, $A^2\Delta – X^2\Pi$ transition). It has to be mentioned that the operating time of this shock tube is about 500 μs, and all data outside this range are rather indicative. In the paper we present all the data obtained to provide the reference points for a comparison with the case of ignition by a nanosecond discharge. For each experiment with the discharge we controlled current through the discharge cell and voltage drop between high-voltage electrode and cross-section of measurement with nanosecond time resolution.

As a result, we determined the energy input from the discharge into a gas. The experiments were carried out with a set of stoichiometric mixtures C_xH_{2x+2}:O_2 (20 %) diluted by Ar (80 %) for hydrocarbons from CH_4 to C_4H_{10} and for stoichiometric mixtures C_xH_{2x+2}:O_2 (20 %) diluted by Ar (90 %) for hydrocarbons from CH_4 to C_5H_{12}. The temperature behind the reflected shock wave (T_5) varied from 950 to 2000 K, and the pressure (P_5) was between 0.2 and 1.0 atm. In each experiment, we kept parameters T_5 and P_5 the same for autoignition and ignition by the discharge.

Figure 3 demonstrates an example of dependence of the ignition delay time *vs* temperature for autoignition and ignition by nanosecond discharge for butane-containing mixture. Permanent control of the electrical parameters, such as electrical current and voltage, proves that all experiments were carried out for the conditions which correspond to uniform spatial development of the discharge (for details see, for example, [2]). Energy measurements have been performed for all the experiments with discharge. We controlled total energy density assuming that the energy input is uniform in space. The main part of experimental points is within interval 5-15 mJ/cm^3. Estimations show that direct input of this energy into heat leads to an increase of temperature of about 50K.

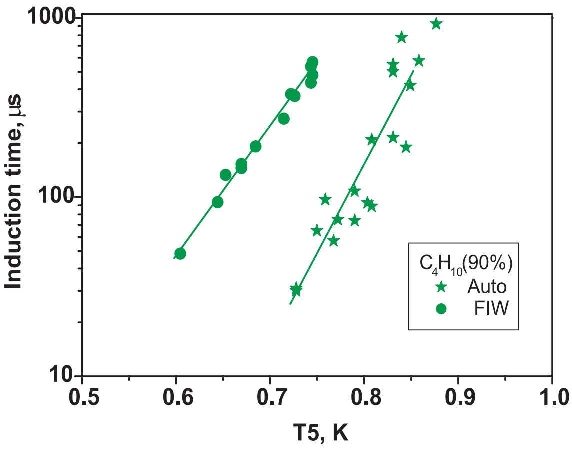

Figure 3. Ignition delay time for butane - containing stoi- chiometric mixture with 90 % Ar.

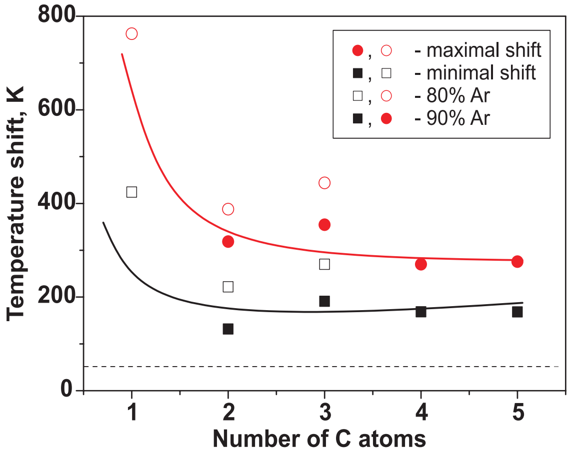

Figure 4. Temperature shift at fixed ignition delay time for different hydrocarbon--oxygen mixtures.

To analyze gas discharge influence on different hydrocarbons, we estimated a shift of ignition temperature (in K) for fixed ignition delay times. We have taken 500 µs as a reference point for minimal temperature shift and have restricted ourselves by 100 µs when determining maximal temperature shift. For methane, the autoignition curve was extrapolated to 100 µs. The result is represented in Figure 4. It is seen that for a series of hydrocarbon containing mixtures, starting from ethane containing and up to pentane containing one the difference comprises 170-300 K for mixtures diluted by 90 % of Ar, and 250-400 K for mixtures diluted by 80 % of Ar. For methane-oxygen stoichiometric mixture, diluted by 80 % of Ar, the shift is 420-760 K. The results for low and elevated temperature seems to be mutually contradictory, but it is not so. Really, oxidation of methane at ambient temperature takes place slowly because it is not easy to dissociate CH_4 molecule even by an electron impact. At elevated temperatures, an additional dissociation of methane in the discharge, let it is not ultra-efficient, and dissociation of oxygen by electron impact, lead to significant acceleration of ignition of mixture with a long ignition delay time. As for methane-air stoichiometric mixture with 90 % dilution, we are not able to obtain the autoignition there, but under the action of discharge we certainly ignite the mixture. It has to be noted that the shift in ignition delay time at fixed temperature comprises, at least, an order of magnitude.

For active radicals dynamics investigation in the discharge afterglow we used a set-up designed for investigations of pulsed nanosecond barrier discharge plasma influence on a flame. The set-up consisted of quartz burner, electrode system, nanosecond high voltage generator and gas (methane and air) supply system. Quartz nozzle in use had rectangular cross-section (2 x 30 mm^2). The investigations were made for pulses of positive polarity (it provides significantly greater effect), 12 ns FWHM, pulse amplitude range was 7-12 kV, pulse repetition rate varied from 1 kHz up to 10 kHz.

The energy input into the flow was approximately 0.5 mJ per pulse. Methane-air mixture with equivalence ratios 0.6-1.4 was supplied, the flow velocity reaching 5 m/s. Kinetic model for low-temperature oxidation of different hydrocarbon fuels was analyzed. The results were compared with the experimental data. Important role of O atoms production in the discharge has been shown as well as ratio between O(^{3}P) and O(^{1}D), O(^{1}S) atoms initial concentration. Data obtained for flow of room temperature are presented in Fig. 5. Such a constancy of OH in the first microsecond agrees with modeling of O atom throw in the mixture with GRI 3.0 provided O(^{1}D) relates to O(^{1}S) as 40 % vs 60 % with experimental uncertainty of about 10%. Analysis of OH decay time over mixture temperature in Arrhenius coordinates reveals OH starts to participate in chain reactions in the vicinity of mixture temperature as low as 600 K, this might be explained with the assumption of some additional heating from nitrogen vibrational relaxation for example. Lean mixtures were in use in high temperature experiments since mixtures with $\phi = 1$ were ignited with several or even one voltage pulse. This could occur from heating the needle tip by discharge or by radical volume ignition since reduced fields and currents near the tip were higher because of geometry factor. The cause of such ignition is of our interest and will be studied further. Concentrations of OH, produced by discharge in both cases of flame present and preheated mixture are encouragingly in good agreement reaching some 300ppm for the latter and 200 ppm for the former.

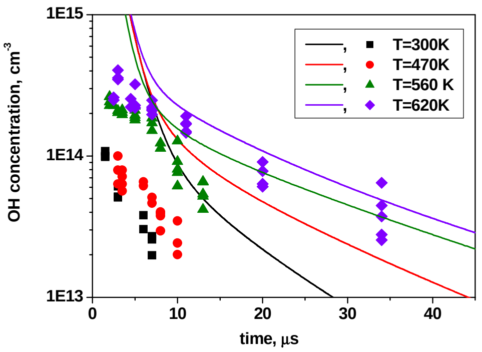

Figure 5. OH concentration dynamics in discharge afterglow. Propane-Air. P = 1 atm.

3 Conclusions

So, for a set of combustible mixtures with hydrocarbons, we investigated oxidation at ambient temperature and ignition at elevated temperature under the action of nanosecond pulsed discharge. It was demonstrated for ambient temperature, that saturated hydrocarbons beginning with ethane up to decane under the same experimental conditions (initial pressure, energy input, and equivalence ratio) are oxidized for one and the same time. The time of oxidation of saturated hydrocarbons in lean and stoichiometric mixtures is approximately directly proportional to the equivalence ratio of the mixture. Fuel dissociation, ionization and excitation of internal degrees of freedom paly an unessential role in the oxidation process. Otherwise, the electron--fuel collisions processes are important for the methane oxidation. The shift of ignition delay time and of the temperature of ignition under the action of nanosecond discharge at controlled parameters of the discharge and a gas have been obtained experimentally for homological family of hydrocarbons. Stoichiometric mixtures of methane, propane, butane and pentane with oxygen diluted by argon has been tested under the same experimental conditions. It has been shown that the shift of the ignition delay time is maximal for methane, and practically the same for all other investigated hydrocarbons.

References

[1] N.B. Anikin, S.M. Starikovskaia and A.Yu. Starikovskii *Plasma Physics Reports* **30(12)** (2004) 1028-1042.

[2] S.M. Starikovskaia, N.B. Anikin, S.V. Pancheshnyi, D.V. Zatsepin and A.Yu. Starikovskii *Plasma Sources Sci. Technol.* **10** (2001) 344-355.