

IGNITION OF HOMOLOGICAL SERIES OF HYDROCARBONS BY VOLUME NANOSECOND DISCHARGE

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Abstract

Ignition of homological series of hydrocarbons from CH_4 to C_4H_{10} under the action of nanosecond discharge was investigated. Significant shift of ignition delay time in comparison with autoignition was obtained for all mixtures. Experiments with ignition by excimer laser flash-photolysis were carried out to study the role of excited atomic species in the ignition of combustible mixtures.

Introduction

Experimental setup to investigate ignition of hydrocarbon-oxygen mixtures includes shock tube combined with a nanosecond high voltage generator. The tube allows to get temperatures in the range of 700-2500 K. Gas parameters behind the reflected shock wave are calculated from velocity of the shock wave, which is measured by Schlieren system. Dielectric end-section of the shock tube with $2.5 \times 2.5 \text{ cm}^2$ rectangular channel 20 cm long is used as a discharge cell. The end plate of the shock tube serves as a high-voltage electrode, and the discharge closes on the stainless steel part of the shock tube. Ignition delay of the combustible mixture is determined as a sharp increase of an OH emission at 306 nm and/or CH emission at 431 nm. In order to measure energy input electrical parameters (voltage and current) of the discharge are monitored with nanosecond resolution by means of magnetic current gauge and capacitance gauges. To study the spatial structure of the discharge and the uniformity of ignition and combustion, we carried out an additional series of experiments in which the emission intensity (integrated over the wavelength range 300-800 nm) was measured with a PicoStar HR12 ICCD camera. The discharge produces a lot of species: electronically excited atoms and molecules, ionized particles, vibrationally excited components.

To elucidate the role of atoms and electronically excited species we have performed experiments with ignition initiation by ArF laser at the same experimental conditions as the ignition by the discharge. Laser flash was organized with a controlled delay behind the reflected shock wave at controlled shock wave velocity and initial gas pressure. These parameters allowed us to calculate gas temperature (T_5) and pressure (P_5) behind the reflected shock wave. Time delay of the ignition was determined from OH emission, like in a case with autoignition and ignition by the discharge. We used PEM21 calibrated piezoelectric detector to measure energy input from laser radiation into the gas.

To investigate slow alkanes oxidation under nanosecond pulse-periodic discharge in stoichiometric and lean mixtures with air and O_2 the discharge was initiated in the tube by negative polarity pulses with amplitude 11 kV, 25 ns duration and 5 ns rise time and 40 Hz repetition rate. Discharge cell was made of screened quartz tube with inner diameter 47 mm and outer — 50 mm. The low-voltage electrode was connected to the screen. Distance from the edge of high voltage electrode to low-voltage electrode was 200 mm. System of electrical parameters diagnostics consisted of back current shunt mounted in the screen of the cable and the mobile capacitive gauge under the screen of the cell. Emission intensity of set of molecular transitions was measured in time-resolved and integral regimes. Time-resolved measurements were used to obtain lifetime and quenching constants for the emission states and to separate crossed bands. Measurements of integral emission allowed to obtain full oxidation time. Emission passed through the 30 mm diameter CaF_2 window in the ring low-voltage electrode. In the methane containing mixtures absorption of He-Ne laser emission on the $\lambda = 3.3922 \mu\text{m}$ was measured. All time-resolved (nanosecond) measurements were executed at the beginning of discharge and after oxidation process finished in the regime of 128 pulses averaging. Density of H_2O_2 was controlled using absorption in UV region of spectrum (at 210 nm). Kinetic scheme was proposed to describe kinetic peculiarities of oxidation in low-temperature region.

Stoichiometric gas mixtures of methane, propane, butane and pentane diluted with Ar (10% of mixture : 90% of Ar) have been investigated under the same experimental conditions. To initiate the ignition nanosecond discharge of 110 kV (negative polarity) and 40 ns duration has been used. It is demonstrated that high-voltage nanosecond discharge is an efficient tool of ignition of different hydrocarbons. Results

for the ignition delay and shift of a temperature threshold under the action of nanosecond discharge have been obtained experimentally and compared with maximal possible temperature shift for a case when all the energy from discharge goes to gas heating. It allows to demonstrate efficiency of nonequilibrium plasma in a problem of ignition. Calculation of delay time for autoignition were performed and compared with experimental data.

Role of different species in the ignition process has been analyzed. To do that, we carried out experiments, in which nanosecond gas discharge was replaced by flash-photolysis from excimer ArF laser at a wavelength of 193 nm. Mixtures of special composition ($N_2O:H_2:O_2$ in different proportions diluted with Ar) were used to elucidate the role of atomic oxygen in $O(^1D)$ state.

Ignition Experiment

The influence of nonequilibrium plasma pulsed discharge as an ignitor of combustible mixtures at various pressures and temperatures were investigated via shock tube technique. Experiments were carried out behind a reflected shock wave, as in classic experiments on the autoignition of combustible mixtures.^{9,10} The experimental setup (see Fig. 1) consisted of a shock tube (ShT) with a discharge cell (DC), a gas evacuation and supply system, a system for ignition with discharge, and a diagnostic system. The shock tube (25×25-mm square cross section) had a 1.6 m long working channel. The length of the high-pressure cell (HPC) was 60 cm. There were two pairs of windows for optical diagnostics along the stainless-steel working channel. The last section of the shock tube with a 25×25-mm square cross section was made from 40 mm thick plexiglas and had eight optical windows (quartz and MgF_2). The metal end plate (EP) of the tube served as a high-voltage electrode. Another electrode was the grounded steel section of the shock tube.

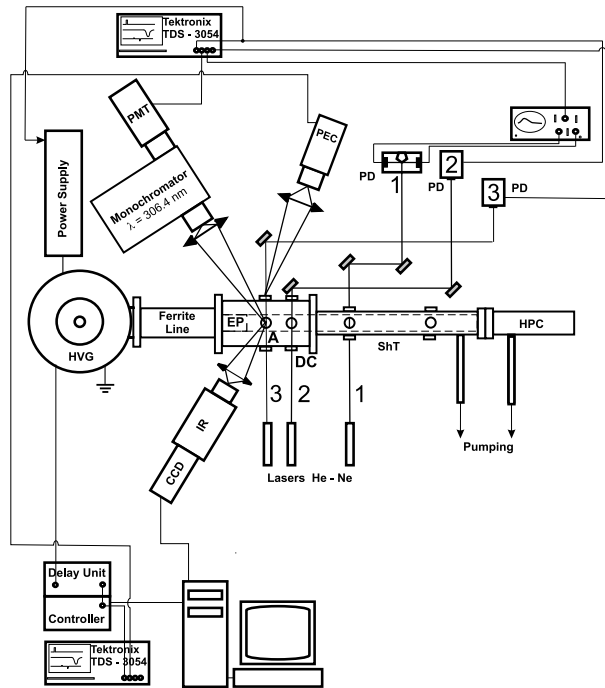


Figure 1: Scheme of the experimental setup. CCD — A — cross-section of measurement, CCD-camera, DC — discharge cell, EP — end plate, HPC — high pressure cell, HVG — high voltage generator, ShT — shock tube, PD — photodiode, PEC — photoelectric cell, PMT — photomultiplier.

The nanosecond discharge was initiated at the instant at which the reflected shock wave arrived to the observation point (point A in Fig. 1). High-voltage pulses were produced with a Marks type high-voltage generator (HVG). At the output of the forming line, the voltage growth rate was about 8 kV/ns, which enabled the operation of the gas discharge in the form of a fast ionization wave (FIW) in the dielectric section of the shock tube. The velocity of the ionization wave front was 10^9 – 10^{10} cm/s, depending on the experimental parameters.

The diagnostic system consisted of a system for monitoring the shock wave parameters, a system for detecting ignition, a system for studying the spatial structure of the discharge and combustion, and a

system for monitoring the electric parameters of the nanosecond discharge. 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 OH emission ($\lambda = 306.4$ nm, $A^2\Sigma(v' = 0) \rightarrow X^2\Pi(v'' = 0)$ transition) in microsecond time scale. Simultaneously we controlled emission from the discharge with nanosecond time resolution, current through the discharge cell and voltage drop between high-voltage electrode and cross-section of measurement.

Ignition. Results and Discussion

As a reference result, we considered data obtained for the methane – synthetic air stoichiometric mixture, diluted by argon.¹¹ What is important that we came back to this mixture during 1.5 years with a gap of a half of a year, and a summary of all these data, published, for example, in,¹² confirms an excellent reproducibility of the results.

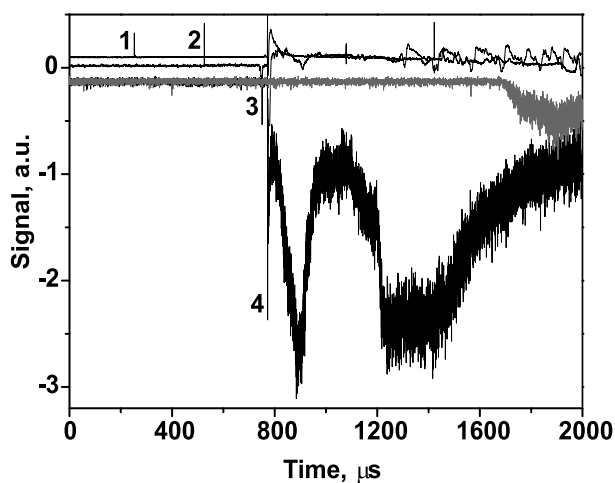


Figure 2: Typical oscillograms from Schlieren detectors (upper curves) and from photomultiplier (two lower curves). Methane-containing mixture. 1, 2 – direct shock wave, 3 – reflected shock wave, 4 – discharge. Gray curve from photomultiplier corresponds to autoignition, black one – to ignition by FIW.

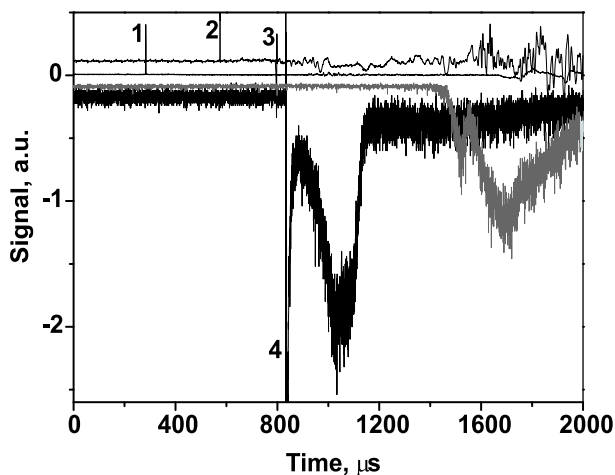


Figure 3: Typical oscillograms from Schlieren detectors (upper curves) and from photomultiplier (two lower curves). Butane-containing mixture. 1, 2 – direct shock wave, 3 – reflected shock wave, 4 – discharge. Gray curve from photomultiplier corresponds to autoignition, black one – to ignition by FIW.

The question about efficiency of ignition of different hydrocarbons in homological series by the nanosec-

ond discharge is still remains open. This part of the paper is devoted to results of experimental investigation of ignition delay under the action of a nanosecond discharge. 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} . The temperature behind the reflected shock wave (T_5) varied from 980 to 1630 K, and the pressure (P_5) was 0.17 to 1.0 atm. Composition of investigated mixtures is represented in Table 1.

Table 1: Investigated mixtures

Alkane	CH_4	C_2H_6	C_3H_8	C_4H_{10}
	6.7%	4.4%	3.3%	2.7%
O_2	13.3%	15.6%	16.7%	17.3%
Ar	80%	80%	80%	80%

The strongest change in OH emission intensity had been observed for methane – oxygen mixture, diluted by argon. This is shown in Fig. 2. For the conditions of this pair of experiments, Schlieren signals are practically the same, but discharge (it is indicated by a vertical line in the Figure) shifts the ignition delay by hundreds of microseconds. The same effect, but less pronounced, is observed for all series of hydrocarbons. As an example, difference in emission with and without discharge is represented for butane – oxygen mixture, too (see Fig. 3).

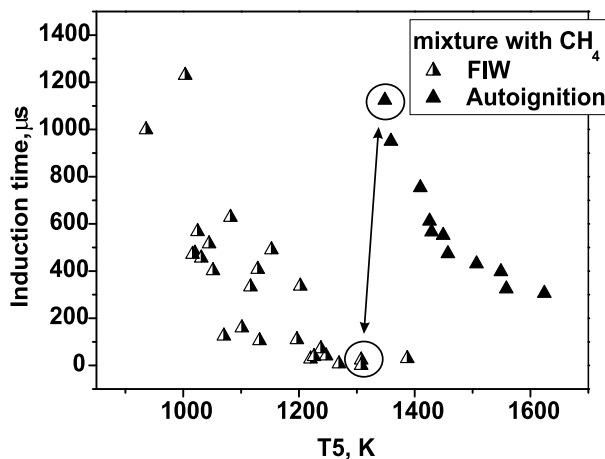


Figure 4: Ignition delay time *vs* temperature for methane – containing mixture.

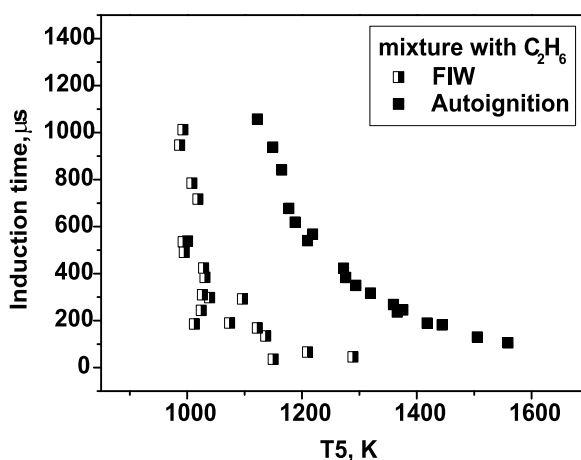


Figure 5: Ignition delay time *vs* temperature for ethane – containing mixture.

Figures 4–7 demonstrate dependence of ignition delay time for autoignition and ignition by nanosecond discharge for all investigated mixtures. It is clearly seen that ignition delay is well-pronounced in all the

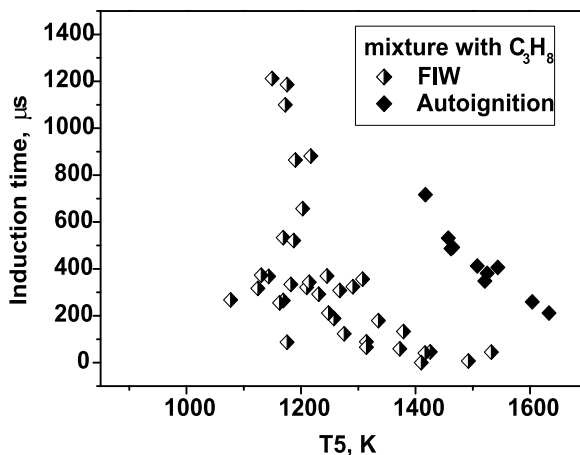


Figure 6: Ignition delay time *vs* temperature for propane – containing mixture.

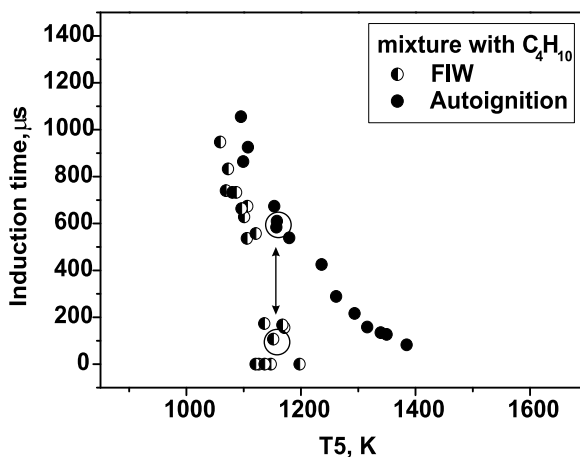


Figure 7: Ignition delay time *vs* temperature for butane – containing mixture.

cases. Difference for C_4H_{10} is the strongest in a region of 1100–1200 K, while for C_3H_8 the difference is practically constant within a range of 1400–1600 K and comprises about 200 K.

Energy measurement have been performed for different mixtures. The results are demonstrated in the Fig. 8. It is obvious that the energy values are of the same order of magnitude as in methane-containing mixture. This is quite clear, because for mixture with 80% of Ar dilution and 13 – 17% of O_2 , energy input into discharge will be determined preferably by Ar– O_2 mixture. It is seen from the Figure, that the main part of experimental point is within interval 7–13 mJ/cm³ (this region is separated with two horizontal lines).

Laser Ignition. Experiment

The diagnostic system used for ignition by the discharge was modified to control ignition by laser flash-photolysis. A flash of UV-radiation of ArF excimer laser (“Center of Physical Devices” production, Troitsk, $\lambda = 193$ nm) was organized behind the reflected shock wave instead of the nanosecond discharge. Laser output reached 0.2 J. The laser radiation was supplied to the dielectric section of the shock tube through the optical window perpendicularly to the shock tube axis in the same cross-section where we performed measurements in a case of the ignition by nanosecond discharge. Laser spot had approximately rectangular shape with 5×21 mm dimensions and was controlled by special sensible paper.

A piezoelectric detector (PEM21) with 21 mm diameter of receiving site was used to determine energy input from laser radiation into the gas. Signal from PEM21 was controlled every time before the experiment, when the system was pumped up to 10^{-2} Torr and then during the experiment. Knowing spectral transmission of MgF_2 windows in this spectral range (were controlled by Varian Cary50 Spec-

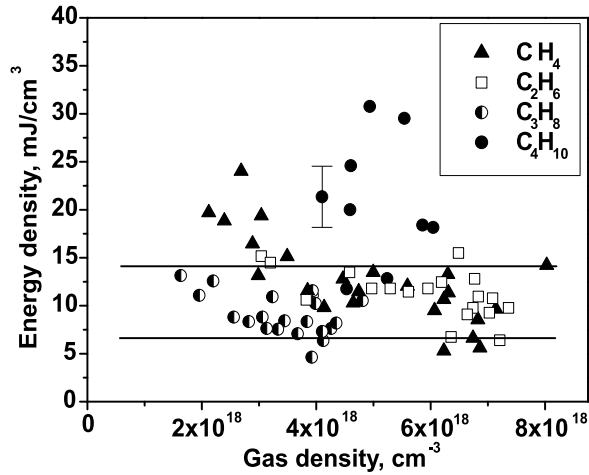


Figure 8: Energy input into a gas for different gases.

trophotometer) we calculated energy input into a gas. We organized experiment so, that energy input in the discharge and energy input from a laser were within one order of magnitude. We controlled initial gas pressure and shock wave velocity, and parameters behind the reflected shock wave were calculated as in the previous case. Ignition delay time was calculated from the OH emission at 306 nm.

The experiments were repeated with the same mixture for autoignition, discharge initiation of ignition and ArF flash-photolysis. Ignition delay times were compared for all cases. To make these experiments, we chosen N_2O as a main absorbing component. Really, N_2O is known to be very efficient as an oxidant. On the other hand, it absorbs radiation at 193 nm better than molecular oxygen. To demonstrate this, cross-sections of molecular oxygen and N_2O molecule are represented in the Fig. 9. So, experiments were performed in gas mixture $N_2O:H_2:Ar = 1:1:8$. In our earlier experiments 1% of CO_2 was added to a gas mixture for control of a gas temperature using emission in IR range of spectrum.

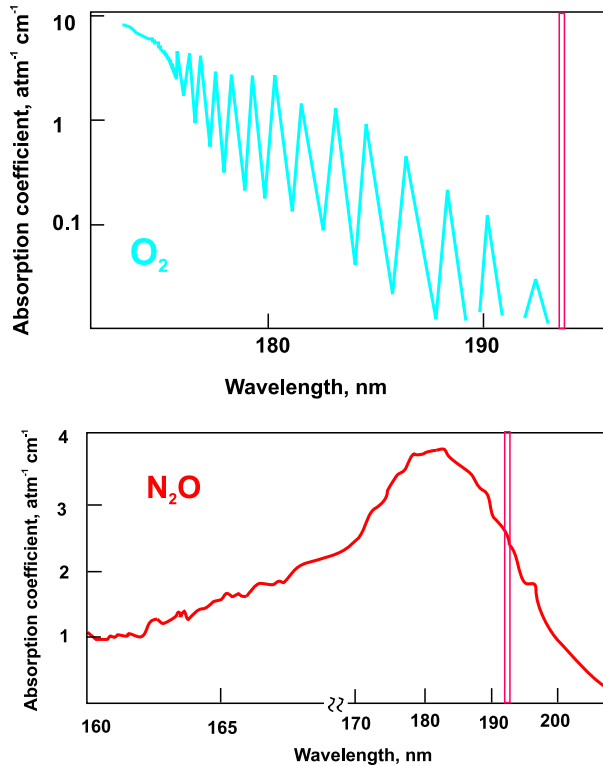


Figure 9: Cross-section of absorption: **a** — for molecular oxygen, **b** — for nitrous oxide. Region of ArF laser generation is marked with vertical lines.

Laser Ignition. Results and Discussion

Typical energy input in a gas in experiments with flash-photolysis is demonstrated by Fig. 10. The shape of a laser beam is quite uniform. It is represented in a right hand side of the figure. Energy value obtained by piezoelectric gauge was divided by volume $5 \times 20 \times 25$ mm, where 25 mm is a transverse size of a shock tube channel.

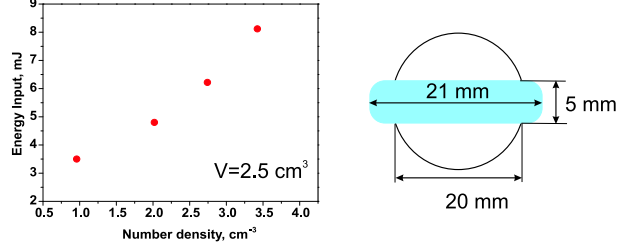


Figure 10: Typical energy input in experiments with laser flash-photolysis. A shape of a laser beam is on the right part of a figure.

It is known that N_2O photolysis takes place via the reactions:



at this weight of reaction (1) is 99%. $O(^1D)$ is a metastable atom, its life time is 150 s, and usually it loses excitation in collisions with other species. It may destruct N_2O via the reactions



On the other hand, $O(^1D)$ has to be active in ignition. The results of our preliminary experiments (with 1% CO_2 in gas mixture) demonstrated no effect on ignition delay, in spite of a fact that nanosecond discharge shifts the threshold by hundreds of K, which is typical for this discharge in different gas mixtures. Behavior of mixture with 1% CO_2 additive is illustrated by Fig. 11.

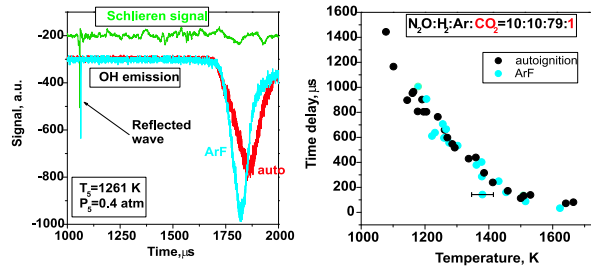


Figure 11: Typical oscillograms and time delay dependence upon gas temperature for gas mixture with additive of carbon dioxide.

We tried to use mixture $N_2O:H_2:Ar = 1:4:5$ (also with 1% CO_2) and to focus laser radiation, but we were not able to shift the ignition delay. At the same time, in gas mixture $N_2O:H_2:Ar = 1:1:8$ without CO_2 additives we have obtained some systematic result, which is represented in the Fig. 12. We obtained at least four points, where ignition by laser differed significantly from autoignition.

Previous analysis demonstrate the following: on one hand, CO_2 is rather strong quencher¹³ of $O(^1D)$ radicals:



Constant rate for the reaction (5) is $2 \cdot 10^{-11}$ cm³/s, and typical estimated time of $O(^1D)$ destruction in our system due to the presence of CO_2 may be as short as 2 μs. On the other hand, there is a lot of

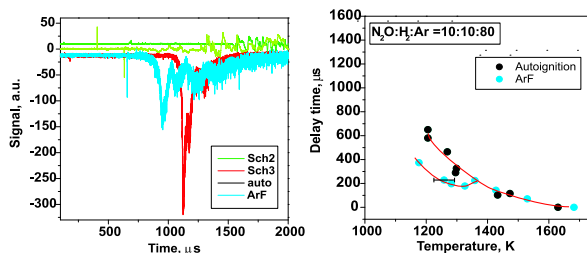


Figure 12: Typical oscillograms and time delay dependence upon gas temperature for gas mixture without additive of carbon dioxide.

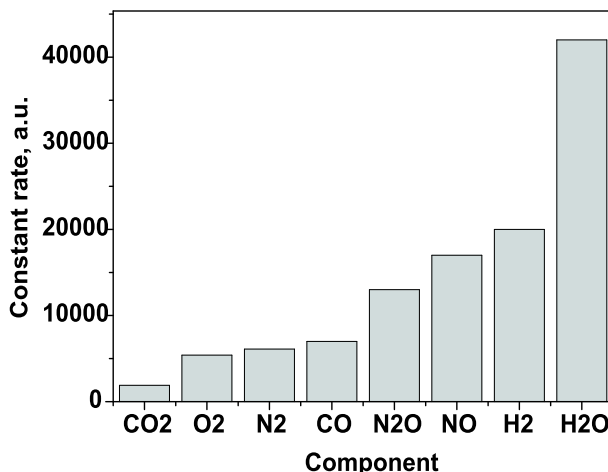


Figure 13: Comparison of constant rates for quenching of excited oxygen atom.

species, even in our system, which are much more active as excited oxygen atoms quenchers. They are, first of all, water and molecular hydrogen. In principle, water is a final product of combustion process and its amount may not be enough on the initial stage to prevent CO₂ to quench atomic oxygen. As for hydrogen, it do quenches O(¹D), but this is one of main helpful reaction in our system. We believe, that this point need to be investigated more carefully. It is necessary to obtain results for the shift of ignition delay by flash-photolysis again, just to be sure that they are reproducible and to analyze them.

Slow Oxidation by Pulsed Discharge

Slow oxidation of C₂H₂, CH₃COCH₃ and C₂H₅OH in stoichiometric and some lean mixtures with oxygen under the action of the nanosecond pulsed-periodic discharge has been investigated experimentally. CO oxidation under the action of the discharge in the stoichiometric mixture with O₂ in the presence of small additions of H₂ has been investigated experimentally.

The kinetics of slow oxidation of H₂, CH₄, C₂H₆, C₂H₅OH, C₂H₂, CH₃COCH₃ under the action of the nanosecond pulsed-periodic discharge in mixtures with oxygen at room temperature under nanosecond uniform discharge have been considered. Important role of O(¹D) and OH-radical has been determined in the kinetics. Main paths of radicals and atoms creation in the discharge has been shown. The kinetic scheme for the H₂, CH₄, C₂H₆ and C₂H₅OH oxidation at room temperature under the nanosecond discharge action has been developed. Measurements of H₂O₂ behavior at different regimes have been performed to validate proposed scheme. The results of calculation using this scheme are in the good agreement with experimental results.

Conclusion

The investigation of efficiency of the nanosecond discharge to ignite homological family of hydrocarbons has been started. Gas mixtures of methane, propane and butane has been investigated under the same experimental conditions. It is demonstrated that high-voltage nanosecond discharge is an effi-

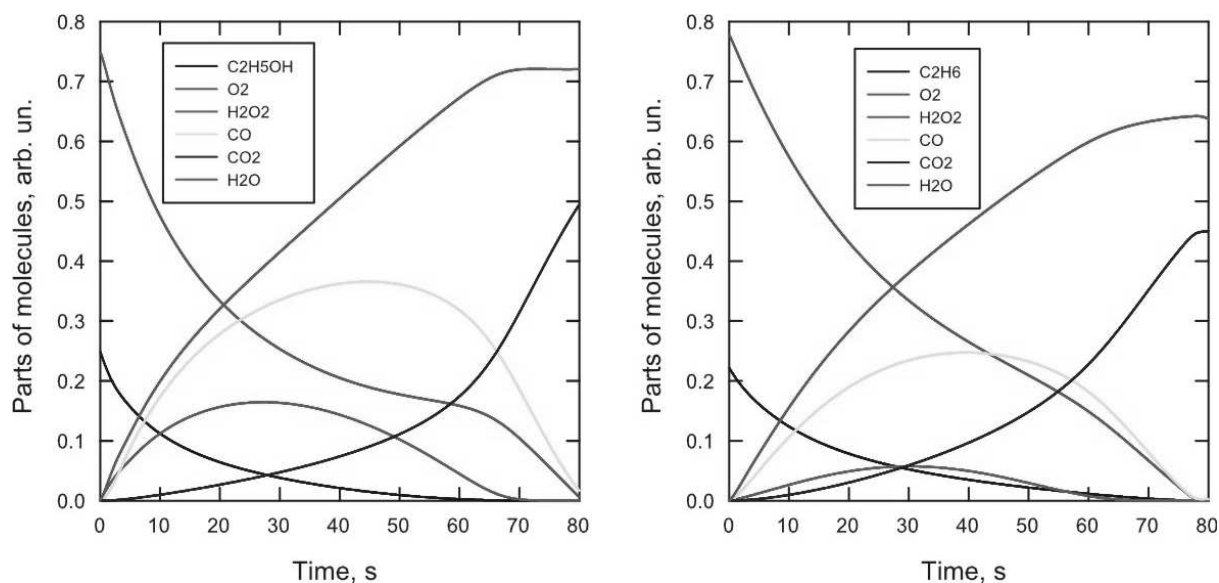


Figure 14: An example of the calculated parts of the molecules during oxidation process of C_2H_5OH and C_2H_6 in stoichiometric mixtures with oxygen. The initial pressure of the mixture is 6.8 torr. Dissociation degrees are corresponded to the 70% of the measured experimentally energy input in the discharge.

cient tool of ignition of different hydrocarbons. Results for the ignition delay and shift of a temperature threshold under the action of nanosecond discharge have been obtained experimentally.

Experiments to investigate ignition delay shift under the action of excimer laser flash-photolysis have been organized. It was found that small additives of CO_2 may influence significantly on the results. Preliminary analysis of possible mechanisms of $O(^1D)$ de-excitation has been performed. Ignition delay shift under the action of flash-photolysis has been obtained systematically in four points. Additional experiments are planned to prove or refute these preliminary results. In a case we will obtain the ignition delay shift it will be possible to estimate efficiency of excited atoms in the process of ignition. In a case the experiments will not demonstrate the difference between autoignition and ignition by flash-photolysis, we will have a ponderable reason to organize investigation of influence of charged particles (ions) on the ignition delay.

Acknowledgments

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