

Hydrogen oxidation and Ignition Development by Nanosecond High-Current Discharge

D.V. Zatsepin, S.M. Starikovskaia, A.Yu. Starikovskii

Moscow Institute of Physics and Technology, Moscow, Russia

E-mail: astar@neq.mipt.ru

Influence of the electric discharge on the reaction dynamics and ignition delay time were investigated experimentally and numerically for different hydrocarbon-air mixtures.

The discharge cell consists of quartz tube of length $l = 200$ mm and diameter of 47 mm with plate high-voltage electrode and ringed low-voltage electrode at faces made of aluminum. Impulses of negative polarity voltage of amplitude $|U_{gen}| = 13$ kV, 25 ns duration at half maximum of the amplitude and 2 ns rise time were fed with repetition frequency of $f = 40$ Hz from pulse voltage generator to the high-voltage electrode of the discharge tube.

Transition $H_2(a^3\Sigma_g^+ \rightarrow b^3\Sigma_u^+)$ results in the continuum in the discharge radiation spectrum which extends from 167 nm to the lowest infrared region of the spectrum. Temporal evolution of absolute concentration of the molecular hydrogen in the mixture was reconstructed on the basis of records of absolute radiation intensity for this transition at wave length $\lambda = 239$ nm with spectral resolution of $\Delta\lambda = 0.24$ nm. Population of the upper level of transition ($H_2(a^3\Sigma_g^+)$) is generated by the electron impact directly from the ground electron state of the molecule:



The discharge gap current amplitude varies from $I = 300$ A at $p = 3$ Torr to $I = 155$ A at $p = 7$ Torr. The current impulse duration at half maximum in this range was constant with a good accuracy and made up $\tau_{pul} \simeq 16$ ns.

The kinetic scheme that describes processes at the stage of electric current flow consists of ~ 750 chemical and ~ 8700 vibrational exchange processes with participation of 83 particles including electron-excited and charged atoms and molecules, electrons, radicals, non-excited components.

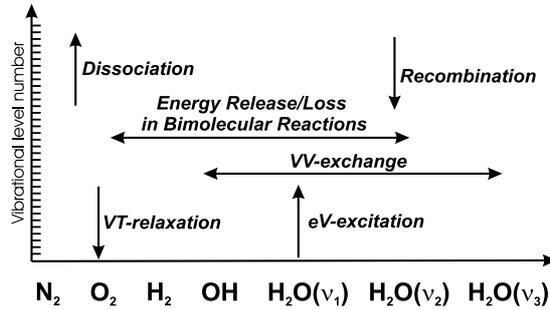


Figure 1: Vibrational energy exchange diagram. H₂-air mixture. Calculation of the VT and VV-processes rate constants was made within the frames of SSH-theory.

The following processes were taken into account: associative and Penning ionization, recombination of positive ions and electrons, attachment of electrons to atoms, detachment of electrons, interaction between neutral non-excited components, interaction between neutral excited and neutral non-excited components, conversion and recombination of ions.

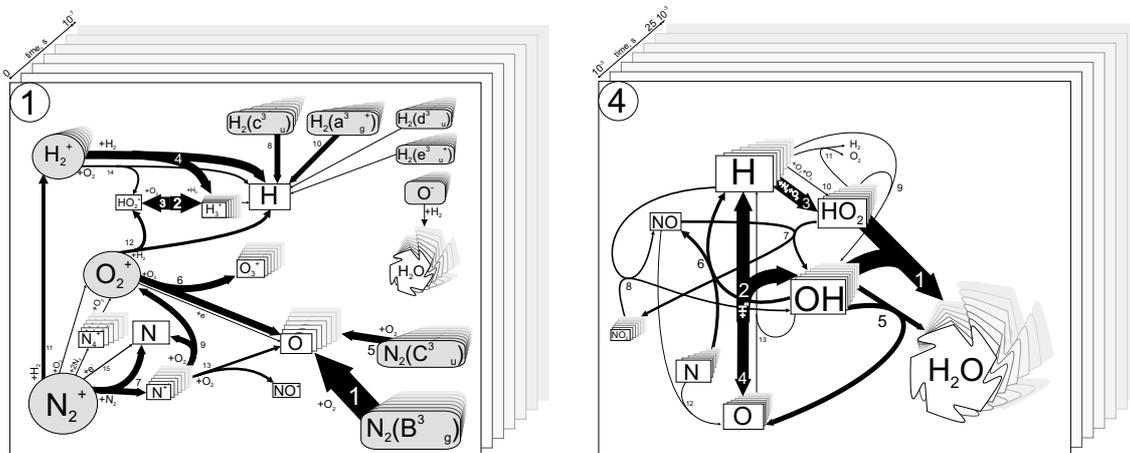


Figure 2: Diagram of active particle flows within time interval 1) – $\tau = 0 - 1 \times 10^{-7}$ s, 4) – $\tau = 1 \times 10^{-3} - 25 \times 10^{-3}$ s. Flow of active particles are shown for the most rapid channels of chemical conversions. The line thickness corresponds to this process rate, and number near it - its position in the hierarchy in the rate analysis of the kinetic scheme.

To calculate reaction rates with a participation of vibrationally-excited reagents we use an α -model modification.

Computation was performed in the mode of "direct modeling" i.e. the discharge gap current impulses that follow each by other were directly calculated with consideration of the variation of the mixture composition between and during the impulses.

Influence of the reduced electric field value in the discharge on the ignition delay time was estimated for H_2 -Air mixture at temperature $T = 1000$ K, pressure $P = 1$ atm, total energy release in the discharge $E = 4 \times 10^{-3}$ J/cm³. Results of these calculations are shown on the Figure 4.

Region of the most effective gas excitation, from the point of view of ignition initiation in the gas system, is in the range of reduced electric fields from 250 to 350 Td. This estimation coincides with the reduced electric field values in the region of the maximum energy release in the fast ionization wave. Thus, we confirm the high efficiency of the fast ionization wave as a pulse ignition initiator for gas-phase mixtures.

For the CH_4 -Air mixtures excitation under the affect of the pulse discharge is substantially more weak than for H_2 -Air mixtures. Molecule CH_4 has a relatively small cross-section of dissociation by electron impact. Besides, CH_4 molecules concentration in the stoichiometric mixture with air is considerably lower, than H_2 concentration. Therefore, ignition threshold shift for CH_4 -air mixtures is relatively small at low values of discharge energies. On the other hand, at high energy of the discharge ($E = 0.4$ J/cm³), ignition threshold shift exceeds 400 K in the all temperature range investigated.

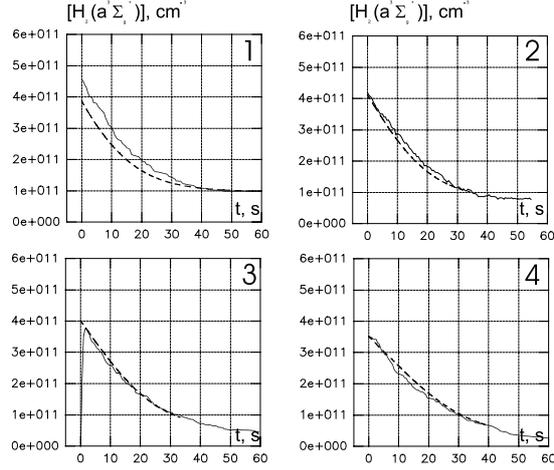


Figure 3: Profiles of absolute number density of the molecular hydrogen in $a^3\Sigma_g^+$ electron excited state in dependence on the pressure. Subfigures from 1 to 4 corresponds to initial mixture pressure $p = 4, 5, 6$ and 7 Torr respectively. The solid lines - experiment, dashed lines - calculation.

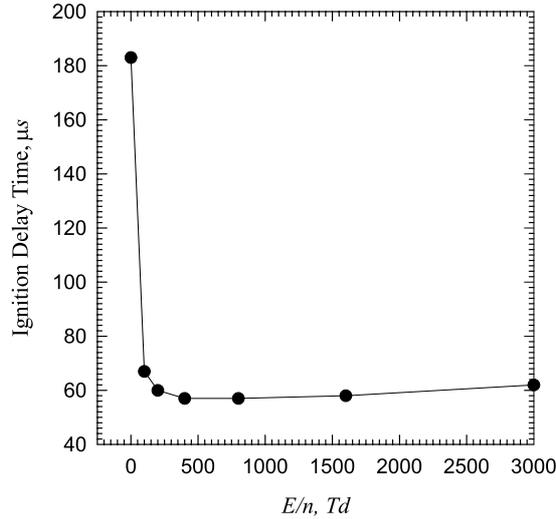


Figure 4: Ignition delay time *vs* Reduced Electric Field Value. H_2 -Air Stoichiometric Mixture. $P = 1$ atm. $T = 1000$ K. Total Energy Release $E = 4 \times 10^{-3}$ J/cm³.

Ignition threshold shift in the C_4H_{10} -Air system under the affect of the pulsed discharge is somewhat smaller than for the CH_4 -Air and C_2H_6 -Air mixtures (Figure 7). The value of the threshold shift is less than 300 K at the energy release $E = 0.4$ J/cm³. For the energy release $E = 0.1$ J/cm³ this shift becomes a negligible value under all investigated conditions. This behavior of the system perhaps is due to the characteristic features of the kinetics in C_4H_{10} -Air mixture. It is still a possibility of some defects in kinetic scheme. The additional investigations of this mixture are needed. From the other hand, influence of the pulsed electric discharge on the ignition is clearly seen in the wide range of initial

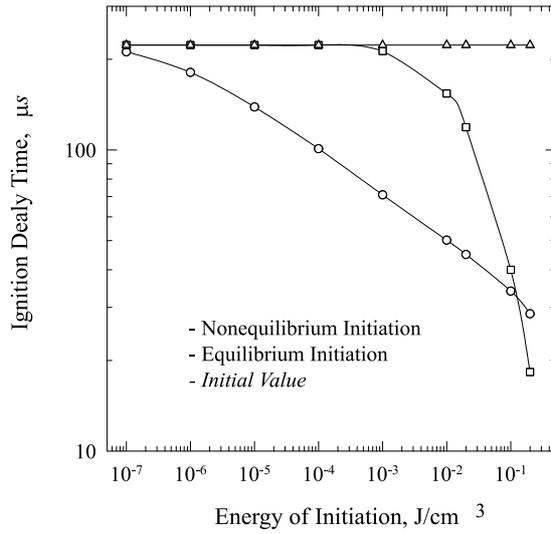


Figure 5: Ignition delay time *vs* energy consumption. H_2 -Air stoichiometric mixture. $P = 1 \text{ atm}$. $T = 1000 \text{ K}$. $E/n = 300 \text{ Td}$.

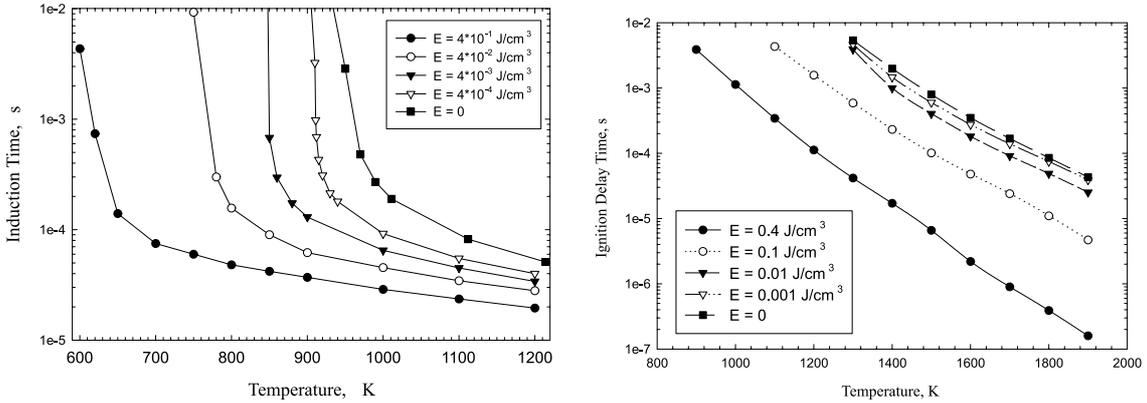


Figure 6: Ignition delay time *vs* Initial Gas Temperature. a) – H_2 -Air Stoichiometric Mixture. b) – CH_4 -Air Stoichiometric Mixture. $P = 1 \text{ atm}$. Non-equilibrium excitation. $E/n = 300 \text{ Td}$.

parameters.

The system sensitivity on the non-equilibrium excitation increases with pressure increasing and decreasing of the equivalence ratio. Absolute value of the ignition threshold shift remains sufficiently high and exceeds 300 K for the discharge energy $E = 0.4 \text{ J/cm}^3$ and 200 K for $E = 0.1 \text{ J/cm}^3$.

The proposed mechanism of chemical kinetics description in essentially nonequilibrium conditions gives a possibility of the quantitative analysis of vibrationally nonequilibrium processes and their influence of a whole chemical kinetics in the system. It was shown that in the conditions of a pulsed high-current nanosecond discharge the role of the processes with participation of vibrationally excited components is principal and significantly

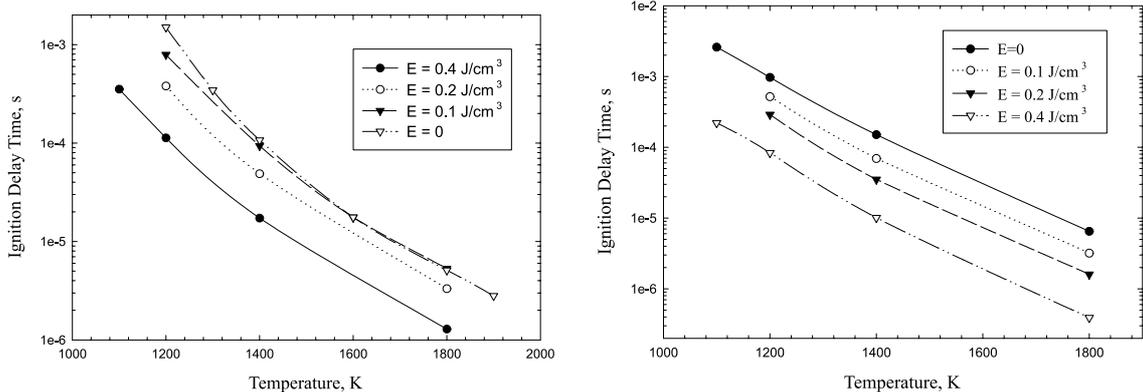


Figure 7: Ignition delay time vs Initial Gas Temperature. a) – C₄H₁₀-Air Stoichiometric Mixture. b) – C₈H₁₈-Air Stoichiometric Mixture. $P = 1$ atm. Non-equilibrium excitation. $E/n = 300$ Td.

influences the kinetics in the system.

The results obtained in the present work show us a possibility of utilizing the non-equilibrium gas discharge for wide control of hydrocarbon-air mixtures ignition and combustion. This control may be effective in the wide range of gas parameters: pressures, temperatures and equivalence ratios. It was shown that sensitivity of the ignition delay time with respect to the non-equilibrium excitation increases with pressure. The more important conclusion is that the induction time sensitivity increases for lean fuel-air mixtures with compare to the stoichiometric ones.

The kinetics scheme that describes ignition of chemically active hydrocarbon-air mixtures under action of ionization wave was constructed. Basic factors that determine the combustion process in such systems were revealed. A possibility of utilizing the non-equilibrium gas discharge for wide control of the hydrocarbon-air mixtures ignition and combustion was shown. This control may be effective in the wide range of gas parameters: pressures, temperatures and equivalence ratios. It was shown that sensitivity of the ignition delay time with respect to the non-equilibrium excitation increases with pressure. The more important conclusion is that the induction time sensitivity increases for lean fuel-air mixtures with compare to the stoichiometric ones. It was shown that for H₂-Air mixtures ignition threshold shift reaches the value of 400 K. This value decreases slightly for hydrocarbon-air mixtures. The absolute value of the ignition threshold shift remains sufficiently high and exceeds 300 K for C₈H₁₈-air mixtures.

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