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Features of Haloalkane Effect on the Concentration Limits and Induction Time for the Ignition of Methane−Oxygen Mixtures

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Abstract—A strong difference in the character of admixture effect on ignition by shock wave and spark initiation has been revealed using the haloalkane effect on the ignition of methane−oxygen mixtures as an example. It has been shown that the difference is determined by the presence of considerable concentrations of reactive intermediate species in an initial mixture, the qualitative difference in gas heating modes, and the strong difference between the temperature ranges of the processfor two these methods.

At present, in contrast to the known concepts, the chain mechanism of reaction is a necessary condition for gas combustion not only under extremely low pressures but also under atmospheric and elevated pressures [1]. A manifestation of the chain character of combustion consists in the fact that admixtures, in particular haloalkanes, decrease the ignition concentration limits for methane−air mixtures much stronger than inert gas admixtures (for example [1, 2]). The initial event of methane ignition prevention by, for example, a CF_3H admixture [1, 2] is the following reaction of atomic hydrogen detected by its mass spectrum in the methane flame [3]:

$$H + CF_3H = H_2 + CF_3. \qquad (1)$$

CF_3 radicals are considerably less reactive than H atoms. Therefore, the reaction chain terminates by reaction (1), and ignition becomes impossible.

However, experiments in [4, 5] show that the shock-wave ignition of a stoichiometric methane−oxygen mixture diluted with argon to 20% and containing 1−3% of studied haloalkanes is not prevented, but, on the contrary, occurs with a decreased induction time in the temperature range 1100−1800 K.

To elucidate the reasons for the different character of the dopant effect on the combustion of the same inflammable mixture depending on conditions and experiment procedure is of large interest for both combustion theory and methods to control combustion process using inhibitors and promoters.

The aim of this work is to elucidate the reasons of the above difference in the effect of haloalkanes on the ignition concentration limits and induction time. We focused our attention on the fact that this difference can result not only from the difference in experiment temperature ranges but also from the fact that the compositions of initial mixtures at the moment of ignition are essentially different. This explanation is confirmed by experimental data considered below.

Induction times were determined on a shock tube of a standard construction. A stoichiometric methane−oxygen mixture diluted with argon to 20% and containing 1−3% of studied haloalkanes (CF_3I, C_3F_7I, CCl_4, CF_3H, $C_2F_4Br_2$) was composed using partial pressures of the components. The tube was equipped with several PCB113B piezoelectric pressure transducers that allowed one to measure the speed of the incident shock wave by the basic method with an accuracy of up to 0.5%. The temperature and pressure of shock-heated gas "plug" behind reflected shock wave were calculated by common iteration methods in the approximation of one-dimensional theory of shock tube.

The induction time was determined from the emission signal of excited OH radical typical for the ignition of hydrocarbon−oxygen mixtures. For this purpose, we used a Hamamatsu H9307-03 photomultiplier equipped with an interference filter with the transmission range 310 ± 5 nm. The sharp buildup of the OH* chemiluminescence signal upon ignition was considered as the end of the induction time measured from the passage of the reflected shock wave through the studied section. The intersection of the tangent line at the point of the maximal slope of the OH*

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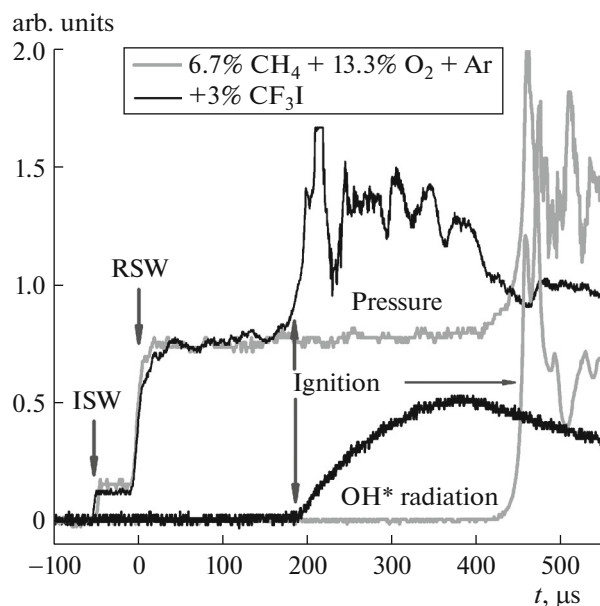*e-mail: eremin@ihed.ras.ru

Fig. 1. Typical oscillograms for pressure and OH radical chemiluminescence upon ignition of a methane−oxygen mixture without additives and in the presence of trifluoro-iodomethane at close shock wave parameters: $T_{RSW} = 1495 \pm 10$ K, $P_{RSW} = 4.8 \pm 0.2$ bar.

Fig. 2. Temperature dependences of the ignition delay time for a 6.7%CH_4 + 13.3%O_2 + Ar mixture containing additives of different haloalkanes.

emission profile with the time axis was considered to be the ignition moment. A sharp increase in pressure was almost simultaneously detected by the piezoelectric pressure transducer in the studied section. Examples of typical oscillograms are given in Fig. 1. It is clearly seen that the presence of the CF_3I dopant leads to considerable reduction of the ignition delay.

Figure 2 exhibits the measured induction times for the ignition of mixtures containing CF_3I and C_3F_7I additives [4, 5] and other halogen-containing compounds, as well as the results of numerical modeling with the use of the proposed kinetic mechanism for the pyrolysis of CCl_4 and CF_3H. Black circles correspond to the results of measurements in a control mixture 6.7%CH_4 + 13.3%O_2 + Ar at pressures behind of reflected shock wave in the range 4.0−6.5 bar. The solid black line is the result of simulation by the GRI-Mech 3.0 mechanism at the pressure $P = 5.0$ atm. It is seen that CF_3I and C_3F_7I admixtures decrease induction time like CCl_4, CF_3H, and $C_2F_4Br_2$ [4].

Shock wave is known to increase gas temperature to the specified high temperature jumpwise, in a fraction of a second, and ignition proceeds in this heated mixture. A partial degradation of chemical bonds of gas molecules, including haloalkane molecules, takes place at such high temperatures in the entire volume of the heated gas. Therefore, if the ignition induction time is close or longer than the characteristic dissociation time of these molecules, ignition begins in the presence of free atoms and radicals. Obviously, the emergence of these highly reactive species indicates
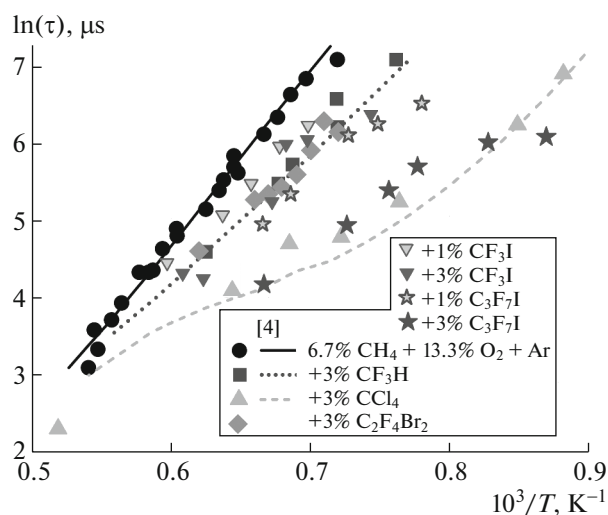
not only supplementary initiation of reaction chains but also their participation in the reaction chains at high temperatures produced by shock wave. Both these factors shorten the induction time of ignition of the entire mixture.

To elucidate the effect of the initiating shock wave on the initial mixture composition, we studied the characteristic time of haloalkane decomposition at temperatures of this experiment. The data of work [6] show that the characteristic times of decomposition for all haloalkanes, except for CH_3Cl, are considerably shorter than the ignition delay of a methane−oxygen mixture. Therefore, ignition actually proceeds in a mixture that initially contains relatively high concentrations of free atoms and radicals produced by the shock wave. Obviously, their reactions decrease the induction time as compared with a mixture not subjected to shock wave even at the same high temperatures.

In contrast to the procedure of shock wave initiation of ignition, to determine the effect of inhibitors on the concentration limits of ignition initiation by a spark of capacitor discharge is usually used. The high-speed synchronous recording of pressure and chemiluminescence in a closed reactor is performed with a piezoceramic pressure transducer and a photomultiplier [1].

No ignition takes place at inhibitor concentrations higher than the critical value. Only a discharge spark was detected by an oscillograph after starting the spark. No chemiluminescence inherent in ignition was observed. No short-term pressure growth was registered, which would be observed upon ignition and temperature growth. After the completion of experiment, the pressure of the mixture is equal to the initial

pressure accurate to a fraction of percent, which also shows the absence of reaction. At the same time, at the same amounts of nitrogen or another inert gas, the spark causes ignition and complete consumption of the deficient component in a fraction of a second. Dissociation of molecules and subsequent reactions of resulting molecule fragments proceed only in the capacitor discharge (energy of 3.2−3.6 J in different experiments) and in close proximity to the discharge. It follows from the discharge energy and the heat capacity of the gas mixture that the temperature in close proximity to the discharge when spark terminates is close to 3000−3200 K. The distance between the electrodes was 0.7−0.8 cm. The discharge zone volume is smaller than 0.5 cm^3. The calculation by the Einstein−Smoluchowski equation using the known thermal diffusivity of a methane−air mixture shows that the heat of discharge dissipates to a distance of ≈1 cm, i.e. in the volume 5−8 times larger than the discharge volume, even after tenths of a second after spark. Therefore, even at this distance from the discharge zone, the temperature drops by the same factor to reach a value below 450 K. Numerical modeling provides the same result because the degradation rate of active species is much higher than the formation rate. Therefore, the concentrations of active species become extremely low and close to equilibrium values at this temperature. Correspondingly, the rate of consumption reactions for initial molecules becomes insignificant because the molecules could not react with each other directly due to very large activation energies [1]. The reactor volume even in experiments described, for example, in [1] is at least 3.2×10^3 cm^3. The volume of the discharge zone is not larger than 1 cm^3. Therefore, it is obvious that the fraction of consumed oxygen could not be larger than 0.3%, which is shown by the measurements of initial and final pressures and chromatographic analysis.

In the absence of an inhibitor, the O and H atoms and free radicals formed in discharge in a moderately hot mixture react with the initial reagents to produce a chain reaction. The reaction proceeds with self-heating. The transfer of heat and active species due to thermal conduction and diffusion into adjacent layers of a fresh still unheated mixture initiates the chain reaction in this layer, thus producing chain sequential ignition. This provides continuous layer-by-layer ignition, i.e., flame propagation.

Thus, we have shown in this work that the revealed difference in the features of the haloalkane effect on methane ignition by spark and shock wave initiation of combustion is caused by the strong difference in the following factors: concentrations of intermediate reactive species in the initial mixture, gas heating modes, and the temperature ranges of the process.

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