On losing of ignition inhibiting properties of haloalkanes at elevated temperatures

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Abstract

An influence of haloalkanes CF_3H and CCl_4 (known as inflammation and explosion suppressors) on ignition of hydrogen-, acetylene- and methane-oxygen mixtures behind shock waves was experimentally studied. Modern kinetic mechanisms were used for numerical simulation. Expected inhibiting activity was observed in hydrogen and acetylene mixtures; contrary, methane ignition was significantly accelerated in presence of 0.5-10% haloalkane admixture. A simplified kinetic mechanism of this promoting effect was suggested.

Introduction

Various haloalkanes have a long history of their practical use in firefighting. It's commonly supposed that their efficiency of combustion suppression originates not only from oxygen replacement and the significant endothermicity of their vaporization and pyrolysis, which rapidly drops the temperature of the heat source, but also from the chemical inhibition of the chain reactions of combustion. The basic of chemical inhibition mechanism was presented in [1]. Nevertheless, in that classic work a counter promoting influence of chlorinated species on ignition at particular conditions was already mentioned. In a number of recent works it was shown that fluorinated hydrocarbons considered as flame inhibitors may as well accelerate ignition [2, 3, 4] and even be combustible themselves [5]. Thus, experimental studies of ignition of haloalkane-containing mixtures in a wide range of parameters which can support the development of a comprehensive model of pyrolysis and oxidation of haloalkanes and their influence of combustion development is still an actual scientific task of a great importance for modern fire extinguishing systems development and industrial risks analysis.

Specific objectives

This work is devoted to thorough investigation of previously reported promotion of methane ignition by fluoroform CF_3H (Freon-23) and carbon tetrachloride CCl_4 (Halon-104) admixtures [6] and to study of influence of that haloalkanes on hydrogen and acetylene combustion.

Experimental setup

Experiments were performed behind the reflected shock waves in a shock tube of a standard design with inner diameter of 50 mm. Lengths of high- and low-pressure section were 1.5 and 3.0 m correspondingly. Tube was equipped with several piezoelectric gauges which allow to measure incident shock wave velocity with an accuracy ~0.5% and calculate parameters of shock-heated media behind the reflected wave using common iteration method [7]. Investigated cross-section where the optical diagnostics were places was located at the distance 13 mm from the end plate of the tube.

During the pilot experiments a spectral properties of a reaction zone in various combustible mixtures were investigated using high-speed ICCD-camera *LaVision*. Being coupled with external spectrograph and operating in so-called StreakStar mode, it allowed to register time-resolved spectrum with a time resolution about 10 µs and spectral resolution ~5 nm. The sample of raw camera frame obtained in experiment in methane-oxygen mixture and the spectrum extracted during the analysis are presented in Fig. 1.
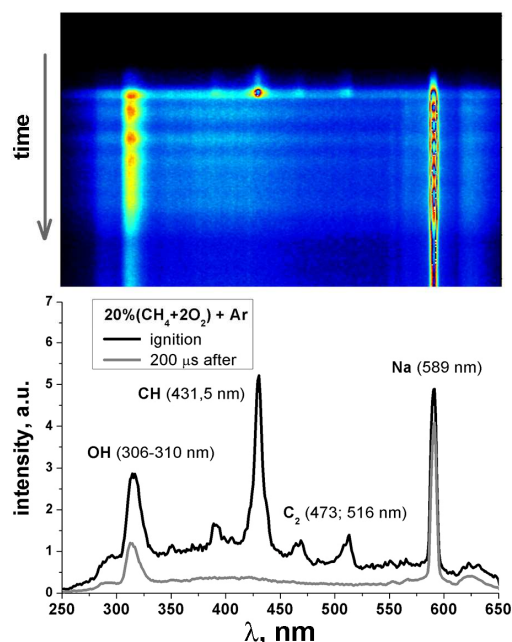

Fig.1. Raw frame and extracted spectra of combustion zone in mixture 20%(CH₄+2O₂)+Ar

Temperature during the induction time was too low for noticeable emission intensity, so camera had registered just black background there. During the initial phase of combustion strong lines of CH radical (435 nm) and Swan bands (473, 516 nm) were registered. OH radical emission (306-310 nm) and strong line of sodium (589 nm) was observed during the whole after-ignition time.

Comparison of the spectra obtained in pure methane-oxygen mixtures and the mixtures containing haloalkanes admixtures has shown that presence of both CF_3H and CCl_4 causes disappearance of Swan bands and dramatically reduces CH peak intensity. Possible explanation of this effect assumes that haloalkanes due to high pyrolysis endothermicity decelerate temperature increasing and, thus, reduce the amount of methane undergoing full decomposition up to atomic carbon subsequently forming C_2 dimers.

Radical OH is the characteristic species for hydrogen and hydrocarbons combustion. During the following experiments an OH signal registered by the photomultiplier equipped with interference filter 310+-5 nm was used for the determination of delay times in all investigated mixtures. Moment of the rapid rise of OH emission was considered as ignition. Simultaneously an increase of pressure was registered by pressure gauge in the investigated section of shock tube. Typical experimental signals of pressure and OH emission are presented in Fig 2.
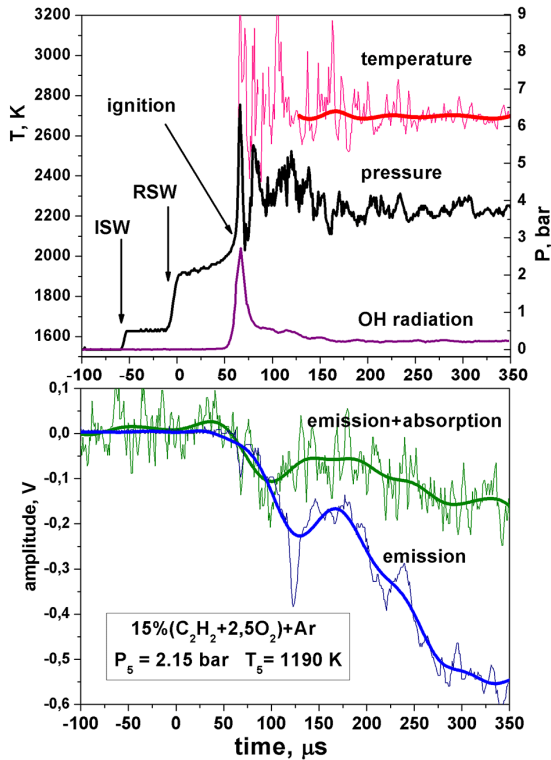

Fig.2. Typical signals obtained in mixture $15\%(C_2H_2+2.5O_2)+Ar$.

The sodium atoms are the inherent natural impurity in argon and in general they should be in the thermal equilibrium with the integral temperature of the mixture. In present work the pilot temperature measurements during the reaction time were performed by the generalized line reversal method on the sodium D-line at 589 nm. This method is based on simultaneous detection of emission and absorption of reactive mixture at the same wavelength. The main advantage of this method is that it requires only a calibrated light source; no knowledge of either optical properties of observable

reaction mixture or the spectral sensitivity of the detection system is needed.

The measurements were carried out by two identical optical channels that focus the light from the probe region via the pair of the calcium fluoride windows installed in a horizontal plane of the shock tube and further via lenses onto two photomultipliers (Fig. 3). The first channel registered an emission only. The second channel was exposed to radiation from reference source of known brightness temperature. Thus the second channel detected the combination of absorption and emission of reaction mixture. A calibrated etalon tungsten ribbon lamp was used as a reference light source. The light from the tungsten lamp was collimated with a lens and forwarded through the probe volume. The time resolution of the detection system was about 10 μs, the space resolution was 3 mm.

Taking into account Lambert-Beer's and Kirchhoff's laws one can get the expression for the temperature determination [8]:

$$T(t) = \frac{hc}{\lambda k_B} \left\{ \ln\left[1 + \left(\exp\left(\frac{hc}{\lambda k T_0}\right) - 1 \right)\left(1 - \frac{I_a(t) - I_0}{I_e(t)} \right) \right] \right\}^{-1} \quad (1)$$

Here h is the Plank constant; c – the speed of light; λ – the diagnostic wavelength; k_B–the Boltzmann constant; T_0 –the brightness temperature of reference source; I_a, I_e, I_0 – the intensities of emission+absorption signal, emission signal and the incoming intensity of radiation of the reference source correspondingly. Typical emission and emission+absorption signals and the temperature profile obtained during their analysis are presented in Fig 2.

Temperature measurements provide an additional integral parameters and are valuable for kinetic mechanism development and verification of numerical models.

Hydrogen

Haloalkane-containing mixtures $2\%CF_3H/CCl_4 + 10\%(2H_2+O_2)+Ar$ and $3\%CF_3H/CCl_4+20\%(2H_2+O_2)+Ar$, as well as reference mixtures $10/20\%(2H_2+O_2)+Ar$, were investigated. Obtained ignition time values are presented in Fig. 3 as dots. Minor inhibiting influence of CF_3H was observed; CCl_4 presence significantly increases ignition delay times and shifts the temperature dependence to higher temperature region.

Kinetic modeling was performed using ChemKin software package in an approximation of constant pressure reactor which should fit shock tube conditions well enough during the induction time. The results of calculations were the time profiles of considered species. Similarly to experimental approach, the modeled induction time was determined as the moment of rapid increase of OH radical concentration. Thermodynamical properties of the species considered were obtained from the database [9].

Modern kinetic scheme of hydrogen combustion presented in recent work [10], consisting of 20

reactions, was used for the modeling. As one can see in Fig. 3, where calculated ignition delay times shown as lines, this mechanism provide much better fit for obtained data than common GRI-Mech 3.0 scheme [11].
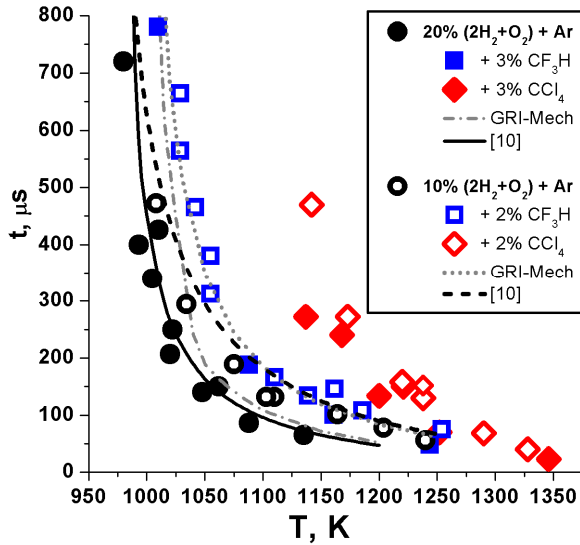

Fig. 3. Experimental (dots) and modeled (lines) temperature dependencies of ignition delay times in hydrogen-oxygen mixtures doped with haloalkanes at pressures 2.0-2.6 bar

Obviously, the observed inhibition effects are the case of general combustion suppression mechanism [1] suggesting that generalized halogenated species X participates in the following reactions:

$$O + X + M \rightarrow OX + M \quad (2)$$
$$O + X_2 \rightarrow OX + X \quad (3)$$
$$RX + H \rightarrow HX + R \quad (4)$$
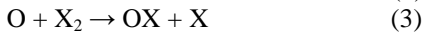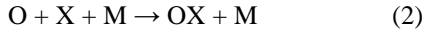
where R is a radical, less active than H and/or O. These reactions are in concurrence with the chain reactions that determine combustion progress:

$$H + O_2 \rightarrow OH + O \quad (5)$$
$$O + H_2 \rightarrow OH + H \quad (6)$$
$$OH + H_2 \rightarrow H_2O + H \quad (7)$$
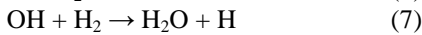
Detail description of the inhibition kinetic, though, is quite difficult due to high complexity of haloalkanes pyrolysis and oxidation mechanisms involving numerous active species. Thus, the kinetics of radicals consumption barely can be reduced to several key reactions and thorough design of corresponding mechanism was out of frame of this work.

Acetylene

An influence of investigated haloalkanes on ignition of acetylene-oxygen mixtures was studied in mixtures 0.5%CF$_3$H/CCl$_4$+3.5%(C$_2$H$_2$+2.5O$_2$)+Ar, 2% CF$_3$H//CCl$_4$+10%(C$_2$H$_2$+2.5O$_2$)+Ar and 3%CF$_3$H/CCl$_4$+20%(C$_2$H$_2$+2.5O$_2$)+Ar. For the reference mixtures 3.5/10/15/20%(C$_2$H$_2$+2.5O$_2$)+Ar were investigated.

Similarly to hydrogen-oxygen mixtures, ignition times in acetylene were just slightly increased in presence of CF$_3$H admixture and CCl$_4$ had considerable

inhibiting effect. The contrast to previously studied detonation of acetylene [12] which was indifferent to CF$_3$H admixture but was dramatically accelerated in presence of CCl$_4$ is notable.

As GRI-Mech mechanism included acetylene-related reactions is nevertheless declared to be unsuitable for modeling of pure acetylene combustion, a comprehensive kinetic scheme of acetylene oxidation provided in [13] was used during analysis. Calculated values of ignition delay times are shown in Fig. 4 as lines. One can see, that there is good agreement between experimental and modeling result for 3.5%(C$_2$H$_2$+2.5O$_2$)+Ar mixture, but for less diluted mixtures measured induction times occur to be much shorter than predicted ones.
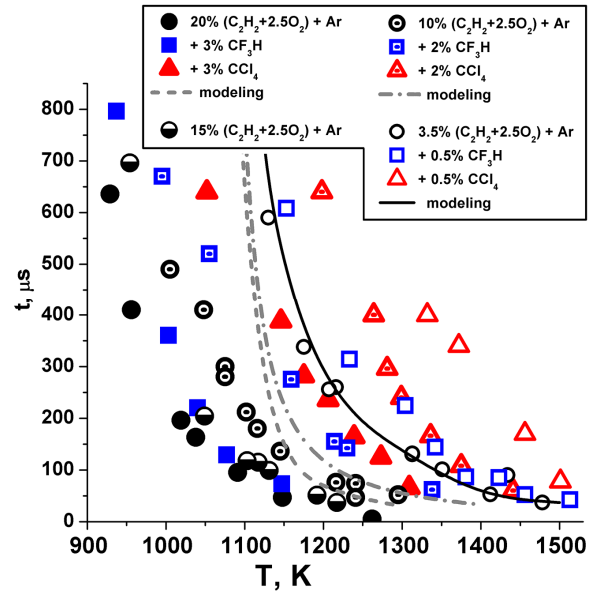

Fig. 4. Experimental (dots) and modeled (lines) temperature dependencies of ignition delay times in acetylene-oxygen mixtures doped with haloalkanes at pressures 2.0-2.6 bar

It's notable that among the data reviewed in [13] there is a work [14] where authors reported ignition delay times which also weren't satisfactorily described by suggested kinetic mechanism and were much shorter than ones predicted by general heuristic dependence of ignition delay time (measured in microseconds) on temperature and mixture components concentration:

$$t = 10^{-7.035}exp(9770/T)[C_2H_2]^{-0.236}[O_2]^{-0.701}[Ar]^{0.015} \quad (8)$$

Authors of [13] suggest that such results were caused by impurity, but one should note that it's the only one of 9 sources and 20 datasets providing data in 950-1200 K region and the study was performed behind the reflected shock waves in moderately diluted 10.8%C$_2$H$_2$+8.5O$_2$+Ar mixture, while C$_2$H$_2$ concentration do not exceeds 3.0% in all other works. Notable that 20%-diluted hydrogen-oxygen and methane-oxygen stoichiometric mixtures studied in present work at the same conditions seems to be not strongly affected by such flaws in spite of comparable

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energy release. Thus, we cautiously conclude that obtained results indicate actual kinetic features of C_2H_2 oxidation, decomposition and polymerization leading to ignition accelerating. An indirect evidence of such kinetic processes is the considerable pressure rise during the induction time (see Fig.2) registered in acetylene-oxygen mixtures only, while inert gases and hydrogen- and methane-oxygen mixtures of same dilution demonstrates just the very minor pressure rise behind the reflected wave which is the common feature of shock tube.

Methane

On the first stage of experiments the ignition of $20\%(CH_4+O_2)+Ar$ mixture was investigated in a wide range of pressures behind the reflected shock wave. Aluminum and copper diaphragms of various thicknesses were used to obtain pressures in range 1.5-17 bar at the same temperature range 1300-1900 K. Pressure range 4.2-5.2 bar was chosen as the most thoroughly experimentally investigated one. All obtained values of ignition delay times are presented in Fig. 5 as dots. Modeling values of induction times obtained in kinetic modeling using GRI-Mech 3.0 kinetic scheme [11] shown as lines. One can see quite good agreement observed in the whole investigated range of parameters. Thus, GRI-Mech 3.0 kinetic mechanism was used as a base for following analysis of haloalkanes influence.
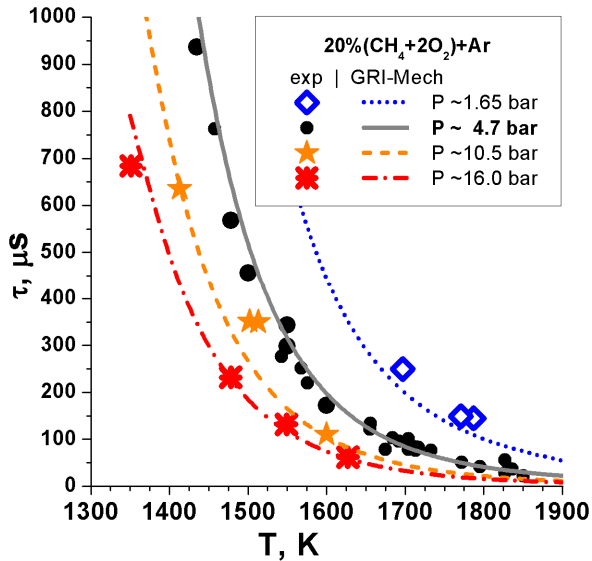

Fig. 5. Experimental (dots) and modeled (lines) temperature dependencies of ignition delay times in $20\%(CH_4+O_2)+Ar$ mixture at various pressures

In contrast to hydrogen- and acetylene-oxygen mixtures, methane ignition was significantly accelerated in presence of studied haloalkanes. Experimentally measured induction times in mixtures $0.5/3.0/10\%CF_3H/CCl_4+20\%(CH_4+O_2)+Ar$ are shown in Fig. 6 as dots.

Preliminary analysis has shown that the key reactions involving products of haloalkanes

decomposition are $Cl + CH_4 \rightarrow CH_3 + HCl$ and $CF_2 + O_2 \rightarrow COF + O$, where the formation of active radicals subsequently initiating chain combustion reactions occurs. Thus, our task was specified as developing of simplified kinetic mechanisms allowing accurate modeling of CF_2 and Cl formation.
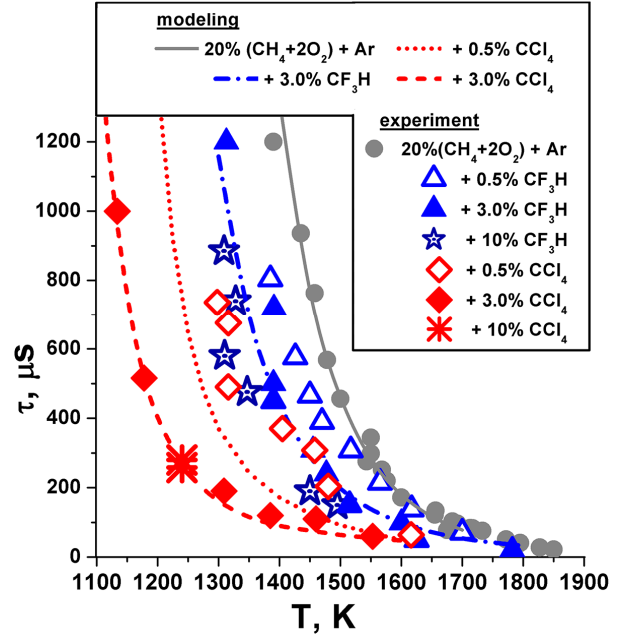

Fig. 6. Experimental (dots) and modeled (lines) temperature dependencies of ignition delay times in $20\%(CH_4+O_2)+Ar$ mixture doped with haloalkanes at various concentrations at pressures 4.2-5.2 bar

Kinetics of fluoroform decomposition and secondary reactions involving CF_2 was quite thoroughly studied in recent works [15-17]. Main and the only channel of CF_3H pyrolysis is

$$CF_3H (+M) \rightarrow CF_2 + HF (+M) \qquad (9)$$

Resulting concentration of CF_2 radicals also affected by reactions of their recombination and dissociation

$$CF_2 + CF_2 (+M) \leftrightarrow C_2F_4 + HF (+ M) \qquad (10)$$
$$CF_2 + M \leftrightarrow CF + F + M \qquad (11)$$
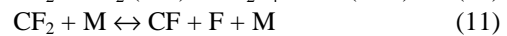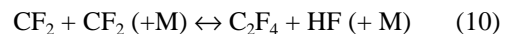
In presence of oxygen CF_2 subsequently oxidizes to COF_2 and CO in reactions

$$CF_2 + O_2 \rightarrow COF + O \qquad (12)$$
$$CF_2 + O \rightarrow COF + F \qquad (13)$$
$$COF + COF \rightarrow COF_2 + CO \qquad (14)$$
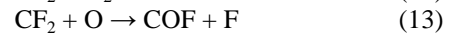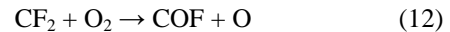
The value of rate constant of the key reaction (12) measured experimentally in work [18] was used.

Pyrolysis of CCl_4 is less investigated as it proceeds in a much more complex way. It was assumed that main channel of CCl_4 decomposition and atomic chlorine release is

$$CCl_4 \rightarrow CCl_3 \rightarrow CCl_2 \rightarrow C_2Cl_4 \rightarrow C_2Cl_2 \rightarrow C_2+2Cl \quad (15)$$
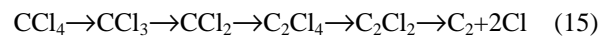
Reaction $CCl_4 \xrightarrow{k_1} CCl_3+Cl$ was well studied in work [19], but due to obvious experimental hardship of

CCl$_3$ radical decomposition study there are quite a few reliable data about CCl$_3 \xrightarrow{k_2}$ CCl$_2$+Cl reaction, which is no less important for determination of atomic chlorine release. A cautious estimation $k_2 = 0.1k_1$ given in [20] was applied. The value of rate constant of the key reaction Cl + CH$_4 \rightarrow$ CH$_3$ + HCl measured experimentally in work [21] was used. Most important secondary reactions as well as limited number of reactions of interaction of chlorine species with active radicals H, O, OH and HO$_2$ was collected from several literature sources [22-24].

Values of ignitions delay times obtained during kinetic modeling are shown in Fig. 6 as lines. One can see that suggested kinetic mechanism provides remarkably well agreement between experimental and modeling results and allows describing the main features of promoting activity of haloalkanes at elevated temperatures.

Conclusions

Influence of haloalkanes CF$_3$H and CCl$_4$ on temperature dependencies of ignition delay times in diluted hydrogen-, acetylene- and methane-oxygen mixtures was experimentally studied. Induction times observed in reference mixtures were in good agreement with the predictions of modern comprehensive kinetic schemes. Minor inhibiting effect of CF$_3$H was observed in hydrogen and acetylene combustion; presence of CCl$_4$ increases ignition delay times significantly. Contrary, combustion development in methane-oxygen mixtures was significantly accelerated in presence of both haloalkanes. The performed kinetic analysis indicated that in the methane-oxygen ignition the promoting species formed by admixtures pyrolysis are correspondingly CF$_2$ and atomic chlorine, which produce active radicals in reactions CF$_2$ + O$_2 \rightarrow$ COF$_2$ + + O and Cl + CH$_4 \rightarrow$ CH$_3$ + HCl, initiating the chain reactions of ignition. Results of kinetic modelling performed using the suggested mechanism agree well with experimental data.

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