



Research Article

The features of combustion of hydrogen and methane in oxygen and air in the presence of difluorodichloromethane additives

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Abstract

It is shown that the inhibitor limit of ignition of the premixed methane-air mix makes 1 vol% difluorodichloromethane at 1 atm. It means that difluorodichloromethane is an effective inhibitor to prevent undesirable ignition of methane-air mixes at atmospheric pressure. It is experimentally shown that the concentration limits of the initiated combustion known from literature are meaningful only for previously prepared mixes. If the mixes are prepared just before the experiment, then the existence or the lack of ignition is determined by both an order of injection of mixture components, and the geometry of an installation. Therefore, the inhibition with halons can hardly be used to address the challenges of safety in mines. Thus, the influence of gasdynamic factors on the efficiency of inhibition is revealed. It is shown that the active centers of hydrogen and methane combustion determining the development of combustion process have the different chemical nature. Vibrationally excited molecules of hydrogen fluoride ($v = 2, 3$) are for the first time detected in the products of combustion of hydrogen and methane in the presence of difluorodichloromethane by means of hyper spectrometers of visible and near infrared spectral range. It can be promising phenomenon in laser chemical applications. It is shown that in methane oxidation, the reaction with difluorodichloromethane leading to the formation of hydrogen fluoride ($v = 2,3$) has to include the active center of methane combustion.

Keywords Ignition · Combustion · Inhibition · Hydrogen · Methane · Air · Oxygen · Chemical mechanism · Halon · Hyperspectrometer · High speed filming

1 Introduction

The method of inhibition of flammable gas mixes is widely used in practice to provide fire and explosion safety of the equipment [1–3]. This problem is complicated by the Montreal Protocol on the restriction of the use of allegedly ozone-depleting substances, to which effective inhibitors of combustion—fluorochlorocarbons (named halons in applications of safety, or freons, if they are considered as coolants) were assigned.

Despite the ban, the ozone gap over Antarctica found in 1985 remains now almost as big as it was when the Montreal Protocol was signed in 1987. It is excessive to note that the global industrial factories and, especially, refrigeration units, are missing in Antarctica. However, the production of widely used chlorine-substituted halons such as promising combustion inhibitor and a coolant dufluorodichloromethane CF_2Cl_2 was stopped [4]. In particular, for consumers, it led to a significant increase in the cost of the equipment and prices for installation and service works [5].

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Not only halons are promising fire inhibitors. It is known that some organophosphorus compounds [6] and organometallic compounds [4] inhibit combustion of hydrocarbons more efficiently than e.g. halon CF_3Br by a factor of about 100. However, they ignite in air and they are toxic, and therefore, they can be used only in places where human personnel are absent.

As compared with organophosphorus and organometallic compounds, chlorine-substituted halons do not ignite in the air under normal conditions, and they are safe for human personnel; these are only unbreathable. Among them difluorodichloromethane is the cheapest and safe one [7]. Unfortunately, due to the ban, the data on the inhibitor efficiency of CF_2Cl_2 are limited and contradictory.

The mechanism of flame inhibition by means of halons has not been fully understood. It is known that combustion and explosion are branched chain processes, in which the cycle of reactions (so-called a reaction chain) results in the reproduction of the active centers of the combustion [8]. If the additive, which reacts with the active centers, is injected into a zone of combustion then reaction chains are terminated; it leads to the inhibition of combustion. Notice that the specific reaction of branching (or the set of the reactions) in the course of methane combustion has not yet been established [9].

Thus, the termination with a molecule of inhibitor can be rather effective if the molecule reacts with the active center, which participates in a branching [10] or propagation [11] reaction step of a reaction chain. It is possible to find out the reaction only by means of kinetic or spectroscopic methods on the basis of direct measurement of the reaction rate of this active center with an inhibitor.

Another experimental possibility of establishment of the chemical nature of the elementary steps, which are responsible for branching and termination of reaction chains, is the analysis of the limit phenomena in inhibition of gas flames, as these phenomena are caused by the competition of branching and termination of active centers via reaction with the inhibitor. It is shown in [12] that the most effective “ozone-safe” inhibitor is C_4F_{10} ; its minimum effective concentration makes 6 vol%. However, the concentration of methane in the stoichiometric mix makes about 9 vol%, i.e. the concentration of fuel is comparable with that of inhibitor. In that case the additive may cause the change in fuel composition and withdraw the mixture out of the ignition area. Thus, the term “inhibitor” is inapplicable and it is necessary to use the terms “diluent”, “retardant” or “suppressant”.

It should be noted that the vast majority of the accidents involving methane explosion take place at atmospheric pressure. Hence, it is important to have an effective (less than 10 vol% to fuel) and a safe inhibitor to reduce the risk of accidents. However, as can be seen from above,

the effective amount of the perfluorinated halon additive is ≥ 6 vol% being comparable with fuel concentration.

The establishment of the mechanism of halon inhibition in the case of the reaction of hydrogen oxidation or CO oxidation in the presence of hydrogen is a relatively clear problem because a reaction of chain branching in these processes is known: $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$. (the comma indicates a free valence) [8]. Atoms H participate in this reaction; therefore, the reactions of H atoms with halon or the products of its decomposition can be the competing reactions of chain termination, because reactions $\text{O} + \text{halon}$ or $\text{OH} + \text{halon}$ do not lead to chain termination; when only OH is terminated, the branching is even maintained.

In addition, there is no reason to consider that atoms H play the leading role in methane oxidation. Really, in the works [13, 14] it is assumed that the role of H atoms in hydrocarbon oxidation is not determining one and consists, at least, in participation in longer chains, than at hydrogen oxidation.

Notice that the estimate of a rate constant at room temperature of termination via CF_2Cl_2 is given in [15]: $k(\text{H} + \text{CF}_2\text{Cl}_2) = 5 \times 10^{12} \exp(-9500/\text{RT}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It means that hydrogen atoms react with halon molecules in the primary center of ignition at 1000 K (experimental value of gas temperature in a spark ignition zone [14]); it can provide inhibition [14].

The work is aimed at the establishment of the inhibition efficiency of CF_2Cl_2 additives in the reactions of hydrogen and methane combustion in air and oxygen as well as identification of influence of gas dynamic factors on the efficiency of inhibition. The latter is important in practical applications: e.g. in mines, the premixed methane-inhibitor mix cannot be created anyway, because methane can leak out of the place, unknown in advance. A traditional optical emission spectroscopy and hyper spectrometers of visible and near infrared spectral range were used for the establishment of the nature of the light emitting particles in the presence of halon additive in order to obtain new data on the chemical mechanism of the action of the additive.

2 Experimental

In experiments, two installations were used. In the first installation (installation 1), both hyper spectrometers and a high-speed color digital camera were used for registration of light emission. The analysis of optical and NIR spectra of combustion of hydrogen and methane in oxygen and air at atmospheric and reduced pressures was carried out. Hyper spectrometers allowed to perform 4D measurements, namely, the 1st dimension is time, 2nd one—wavelength, 3rd one—spectral intensity at this

wavelength, 4th one—coordinate of the fragment of an emitting source. In the second installation (installation 2), the spectrograph with crossed dispersion equipped with a digital video camera was used for emission recording. The spectrograph had higher resolution than an optical hyper spectrometer; it allowed to carry out the exact assignment of spectra.

The stainless steel reactor 25 cm long and 12 cm in diameter was supplied with a tangential gas input (noted by a blue circle in Fig. 1a, b), removable covers and an optical quartz window. Experiments were performed at initial room temperature. The pumped-out reactor was filled with a gas mix from the high pressure buffer volume up to the necessary pressure; flame initiation was carried out with a spark discharge (1.5 J). If a gas mixture was prepared immediately in the reactor, the components of the mix were injected via the open valve of the tangential input. Because of a sharp pressure difference in the buffer volume and the reactor, a gas whirl occurs in the reactor leading to the reduction of mixing time [16, 17].

The pressure in the process was recorded by means of the tensoresistive Carat DI sensor, from which the signal was transmitted to the computer via A/D converter. The value of the extent of expansion of combustion products ε_T was determined by the value of the maximum pressure P_b developed in the course of combustion of the mix [1, 3]: $P_b/P_0 = 1 + \gamma(\varepsilon_T - 1)$, the value of normal velocity of flame propagation U_n was determined from a ratio [1, 3]: $U_n = V_v/\varepsilon_T$. P_0 is initial pressure, γ is an isentropic exponent of an initial mix, V_v —a visible flame velocity. Before each experiment the reactor was pumped out to

10^{-1} Torr. Pressure in the reactor was controlled with a standard vacuum gage, and in the buffer volume—with a standard pressure gage. Gases (H_2 , O_2 , CH_4 , CF_2Cl_2) were of chemically pure grade.

Fuel mixtures were mainly stoichiometric ones (see below), and the inhibitor was added in an amount of X vol%. The inhibitor concentration limit was considered as a mean inhibitor concentration X vol%, further X %; at $(X + 0.1X)$ % the initiated ignition occurs, at $(X - 0.1X)$ % it does not occur, all other things being equal. The pump-down time between experiments was 2 h.

Recording of the light emission during combustion was carried out by means of the spectrograph with crossed dispersion STE-1 supplied with the color Sony DCR_SR200E video camera (installation 2); or a hyper spectrometer and a color high-speed movie camera Casio Exilim F1 Pro through an optical window in a removable cover (Fig. 1). Hyper spectrometers sensitive over 400–970 nm range and over the near infrared range 970–1700 nm [18] were used. The experiments on high-speed filming were performed with gas mixes $(H_2 + air)_{stoich} + 10\% CF_2Cl_2$, $(CH_4 + air)_{stoich} + 0 \div 10\% CF_2Cl_2$, $(H_2 + O_2)_{stoich} + 10\% \div 15\% CF_2Cl_2$, $(CH_4 + O_2)_{stoich} + 10\% \div 15\% CF_2Cl_2$, $7\%CH_4 + air + 0 \div 1\% CF_2Cl_2$, $11\%CH_4 + air + 0 \div 1\% CF_2Cl_2$. The obtained data were processed and stored in computer memory for the further analysis.

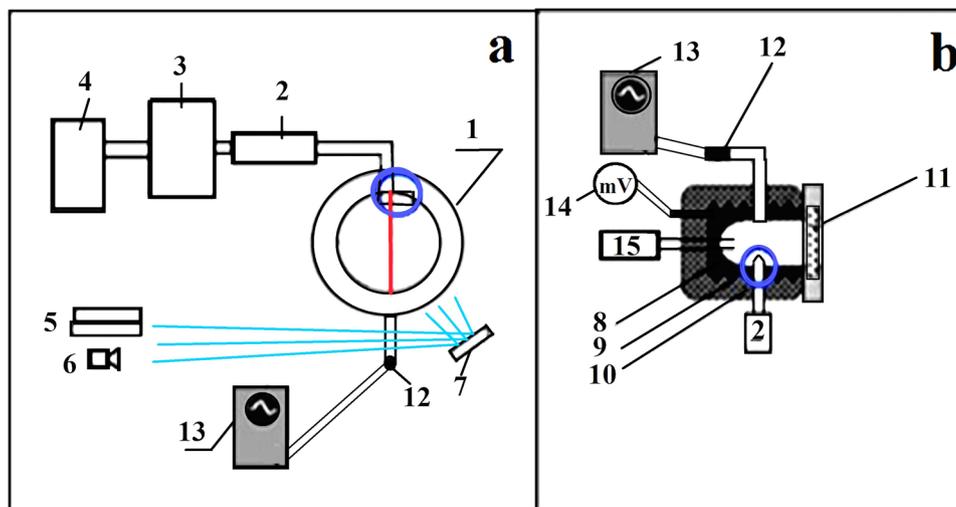


Fig. 1 Installation 1. **a** Scheme of experimental installation; **b** scheme of the reactor. The warmed-up reactor 1, electromagnetic valve 2, buffer volume 3, cylinder with a gas mix 4, hyper spectrometers 5, digital video camera 6, rotary mirror 7, internal asbestos isolation 8, heater 9, external asbestos isolation 10, optical window 11,

pressure sensor 12, A/D converter and computer for data storage and analysis 13, millivolt meter and thermocouple 14, spark ignition 15. The red line, on which 4D-spectral shooting is carried out is shown in **a**. The width of this line is about 1 mm. The blue circle notes the tangential input of gas into the reactor

3 Results and discussion

It was shown that 10% CF_2Cl_2 additive does not have a noticeable inhibiting effect on the combustion of the previously prepared mix H_2 —air in consent with [19]. If an estimate of the rate constant of the reaction $\text{H} + \text{CF}_2\text{Cl}_2 \rightarrow \text{HCl} + \text{CF}_2$ $5 \times 10^{12} \exp(-9500/\text{RT}) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [15] is true one, H atoms are terminated via halon molecules in the primary center of ignition at 1000 K (experimental value of gas temperature in a spark ignition zone [14, p. 93]). The observed weak inhibition means that CF_2Cl_2 molecules participate also in some competing reactions of the development of reaction chains.

However, just 2% CF_2Cl_2 additive in the previously prepared stoichiometric mix of methane with air completely inhibits the initiated ignition. The experiments on the preparation of a gas mix immediately in the reactor were

performed. It was shown that the gas mixture prepared by the first injection of 2% CF_2Cl_2 and then stoichiometric mix $\text{CH}_4 + \text{air}$ up to 1 atm, cannot be ignited. However, if the mix is prepared in reverse order (first stoichiometric mix $\text{CH}_4 + \text{air}$ is injected, and then CF_2Cl_2 to 1 atm), then ignition occurs already at 4% CF_2Cl_2 (Fig. 2a, b).

Notice that in the presence of halon the pressure jump is higher, than in its absence (Fig. 2 right at the top). As this pressure jump is caused by heat release in the combustion [20], it means that at methane oxidation in the presence of halon, additional heat is released, i.e. halon does not act as a diluent, it participates in the combustion.

Thus, the concentration limits of the initiated combustion known from the literature are meaningful only for previously prepared mixes. If the mixes are prepared just before the experiment, then the existence or the lack of ignition is determined by both an order of injection of

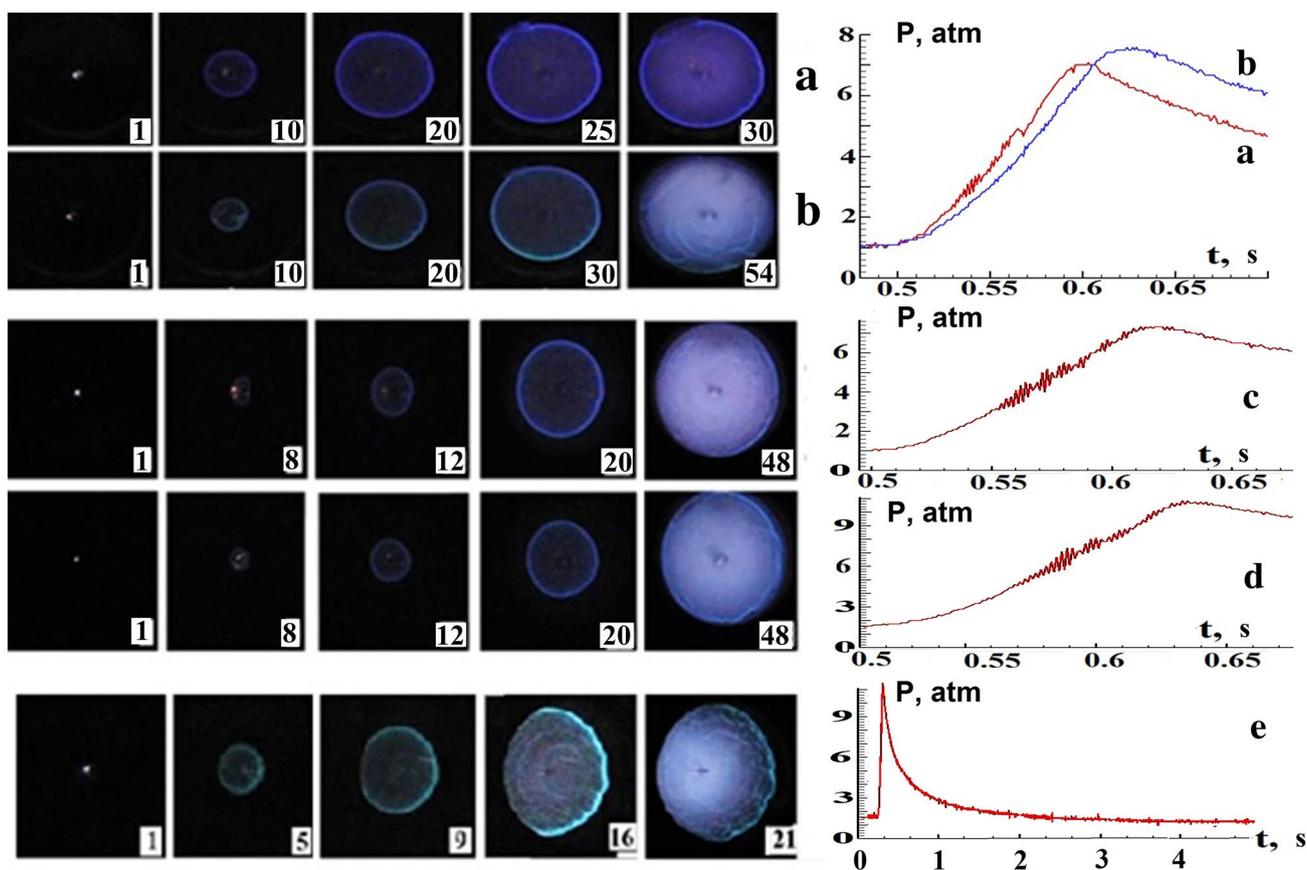


Fig. 2 High-speed filming of the flame front propagation initiated by a spark discharge in the gas mix: **a** $(\text{CH}_4 + \text{air})_{\text{stoich}}$, initial pressure is 1 atm, **b** $(\text{CH}_4 + \text{air})_{\text{stoich}} + 4\% \text{CF}_2\text{Cl}_2$. First methane mix with air is injected, then 4% CF_2Cl_2 to 1 atm. The mix, prepared in reverse order, does not burn. Oscillograms of pressure changes at the initiated ignition of mixes **a** and **b** are shown on the left. **c** ignition of previously prepared mix $(\text{CH}_4 + \text{air})_{\text{stoich}} + 1\% \text{CF}_2\text{Cl}_2$, initial pressure 1 atm. **d** ignition of the same mix at initial pressure 1.5 atm. Oscil-

lograms of pressure change at the initiated ignition are shown on the right. **e** premixed mixture 40% $\text{H}_2 + \text{air}$ in the presence of 10% CF_2Cl_2 . Initial pressure 1.5 atm. The video camera is located on the side of the reactor; in front of the reactor there hyperspectrometers are placed. Pressure change dependency on time during ignition is shown on the right. The figure on a shot corresponds to a number of a shot after initiation, 600 frames/s

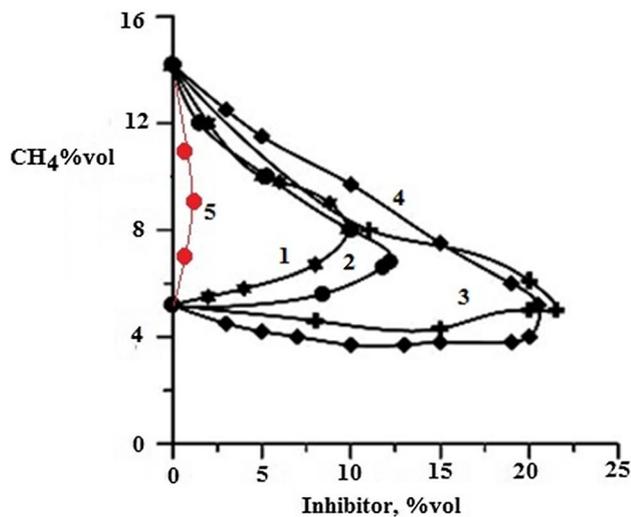


Fig. 3 Influence of various inhibitors on the flammability limits of methane in air: 1— $C_2F_4Br_2$, 2— C_2F_5H , 3—NAFS-III (mixture of fluorinated hydrocarbons), 4— CHF_3 , 5— CH_2F_2 . 1–4 experimental data from [19], 5—this work

mixture components, and the geometry of an installation. Therefore, the inhibition with halons can hardly be used to solve the problems of safety in mines: there a premixed methane-inhibitor mix cannot be created anyway, because methane can leak out of the place, unknown in advance. It was shown that in the reactor, which is not treated by ignitions, it is possible to initiate the ignition of a previously prepared mix $(CH_4 + air)_{stoich} + 1\% CF_2Cl_2$ (Fig. 2c); it is possible to ignite this mix at 1.5 atm only after 30 min pumping (Fig. 2d). Thus, even small amounts of reaction products, e.g. of water vapor, make considerable impact on the value of the limit of the initiated ignition. The visible flame velocity at the limit is lower than that of the mix without inhibitor; the flame front in the presence of inhibitor has cellular shape. As is seen in Fig. 2 (down on the right), the flame propagation is followed by flame pressure oscillations, i.e. has unstable character.

Pressure oscillations and the cellular flame shape indicate the proximity of the mix containing 1% CF_2Cl_2 to the limit of the initiated ignition [1, 20]. In this case CF_2Cl_2 is not a retardant, but an effective inhibitor, which operating concentration is almost 10 times less than fuel concentration. Indeed, in that case the additive cannot cause the change in fuel composition and withdraw the mixture out of the ignition area. The results of the experiment on ignition of leaner and richer non-stoichiometric mixtures showed that inhibitor limits make 0.5% for 7% methane-air and 0.5% for 11% methane-air mixes; these values in comparison with the data [20] indicate the high effectiveness of CF_2Cl_2 additives (Fig. 3).

Thus, under conditions of the same installation, the inhibitor limit of the mix $(H_2 + air)_{stoich}$ in the presence of CF_2Cl_2 exceeds 10%; at the same time the inhibitor limit of the mix $(CH_4 + air)_{stoich}$ makes 1% CF_2Cl_2 . It means in consent with [12, 21], that in the work, the evidence is obtained that the active centers of methane and hydrogen combustion, which determine flame propagation, have different chemical nature.

In Fig. 4, visible and near IR emission spectra of combustion of the mix $(H_2 + air)_{stoich}$ in the presence of 10% CF_2Cl_2 are shown. It is seen in Fig. 4a that the most intensive visible bands are observed over the range 850–1000 nm; these can be assigned to HF ($v=3$) [22]. Notice that as the flame propagates with a visible velocity 210 cm/s, and $\varepsilon=12.5$ from Fig. 2e, the normal flame velocity is 16.8 cm/s (see experimental). It is about 15 times less than the normal velocity of flame propagation without halon additive [3]. Thus, the warming up in the flame front is comparably small; therefore, the bands of alkali metals (Na and K) characteristic of hot flames have low intensity in the spectrum.

In Fig. 4b, near IR emission spectrum of combustion of the mix $(H_2 + air)_{stoich}$ in the presence of 10% CF_2Cl_2 is shown. We carried out the line assignment, using the data [23] presented in Fig. 4c. It follows from the comparison of Fig. 4b, c that the bands at 1.25 μm and 1.32 μm relate to vibrationally excited molecules HF ($v=2$). The wide band at 1.4 μm is caused by H_2O radiation [23]. This assignment is illustrated in Fig. 4d, in which a near IR emission spectrum of the mix $(H_2 + air)_{stoich}$ in the presence of 10% CF_2Cl_2 (red curve), imposed on a near IR emission spectrum of the mix $(H_2 + air)_{stoich}$ is presented. As is seen, Fig. 4d adequately approximates the spectrum shown in Fig. 4b.

Thus, in combustion products of the mix $(H_2 + air)_{stoich}$ in the presence of 10% CF_2Cl_2 , the molecules HF ($v=2$) and ($v=3$) are detected. Notice that molecules HF in the zero vibrational state were observed in [24] in this reaction. It should be noted that IR data [24] of the products of $H_2 + O_2 + CF_2Cl_2$ combustion allow identifying HF ($v=0$), CF_4 , COF_2 and CF_3Cl . HCl was not detected. FTIR data [25] of the products of $CH_4 + O_2 + CF_3Br$ allow identifying HF ($v=0$), CF_4 , COF_2 , H_2O and CO_2 . HBr bands are very weak, i.e. the amount of halogen hydrides (except HF) in the products is probably small; it must be taken into account in considering the mechanism of inhibition with halons.

We also detected molecules HF ($v=3$) at inhibition of natural gas combustion with octadecafluorodecahydronaphthalene ("artificial blood", perfluorodecaline $C_{10}F_{18}$) [26]. The reaction, in which enough energy can be emitted ($11,100\text{ cm}^{-1} = 1.38\text{ eV} = 37\text{ kcal/mole}$) to provide vibrational excitation of HF molecules ($v=3$), is almost a thermally neutral reaction [14, 26, 27]:



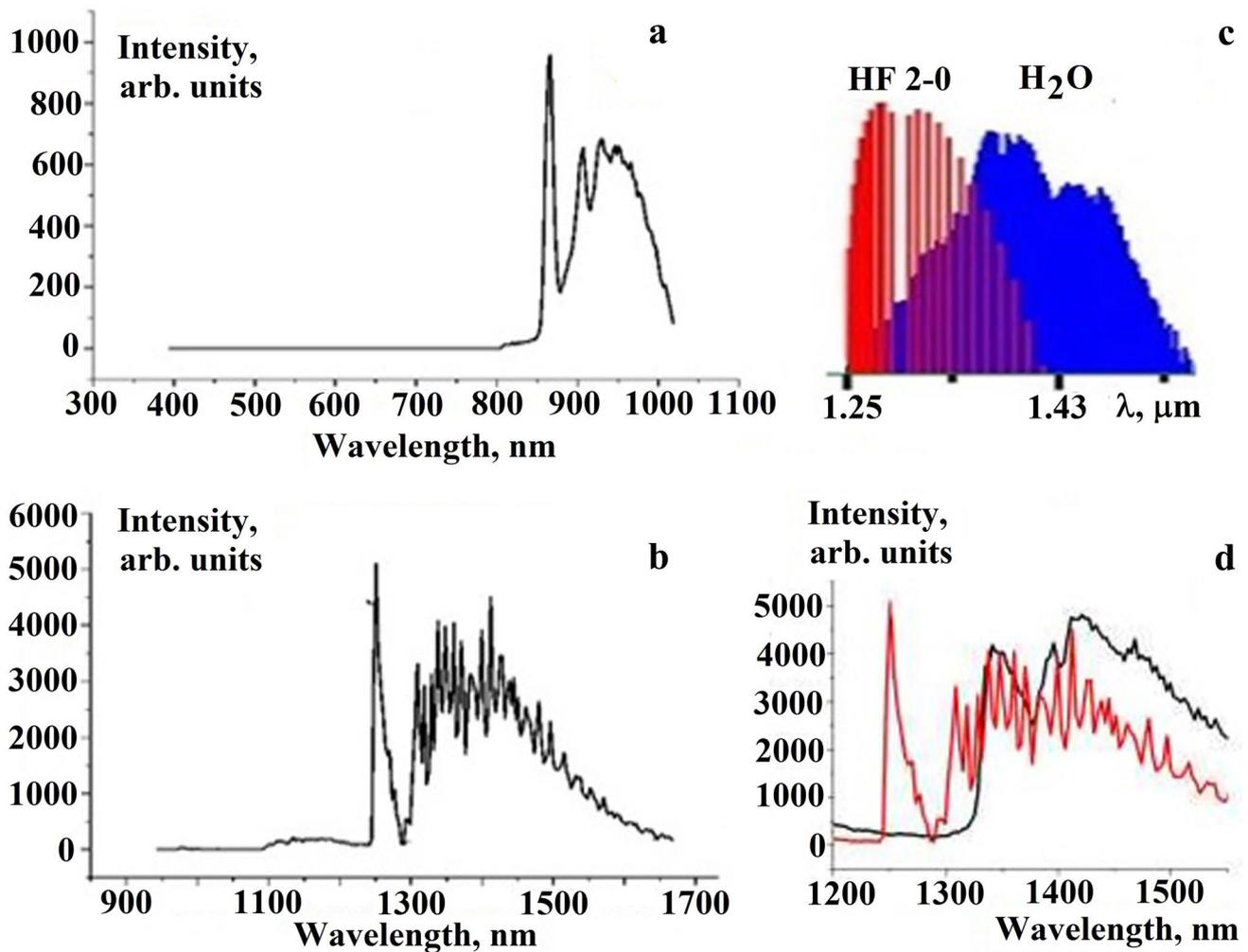


Fig. 4 Emission spectra of combustion of the mix $(\text{H}_2 + \text{air})_{\text{stoich}}$ in the presence of 10% CF_2Cl_2 at 1.5 atm in visible (**a**) and near IR area (**b**), recorded with hyper spectrometers, **c** near IR emitting bands of HF ($v=2$) and H_2O according to [23], **d** a near IR emission spec-

trum of the mix $(\text{H}_2 + \text{air})_{\text{stoich}}$ in the presence of 10% CF_2Cl_2 (red), imposed on a near IR emission spectrum of the mix $(\text{H}_2 + \text{air})_{\text{stoich}}$

Since the inhibitor concentration limit of the stoichiometric methane-air mixture is about 1% CF_2Cl_2 , the intensity of HF emission is indeed rather low to compare with HF intensity at hydrogen combustion in the presence of the same amount of halon. To increase the sensitivity of the technique by means of addition of greater amounts of halon, oxygen mixes instead of air mixes were used.

We draw the attention of the reader to the fact, that the measurement of the inhibitor concentration limit is especially relevant for fuel–air combustion at atmospheric pressure, that is, for conditions where the issue of explosion safety arises. In the experiments, when oxygen was used instead of air, the formation of excited particles in the combustion processes studied was investigated; explosion safety issues and, accordingly, inhibitor concentration

limits upon combustion in oxygen under reduced pressure were not considered.

In addition, we showed that the inhibitor limit of the mix $(\text{CH}_4 + \text{air})_{\text{stoich}}$ makes 1% CF_2Cl_2 , while, as is shown below, the mix $(\text{CH}_4 + \text{O}_2)_{\text{stoich}} + 15\% \text{CF}_2\text{Cl}_2$ can be ignited at 100 Torr. It provides a rough estimate of the inhibitor concentration limits of methane-oxygen mixtures, which are significantly greater than those of methane-air mixtures (Rev#1).

In the experiments described below, gas mixes $2\text{H}_2 + \text{O}_2 + 10\% \div 15\% \text{CF}_2\text{Cl}_2$ and $(\text{CH}_4 + \text{O}_2)_{\text{stoich}} + 10\% \div 15\% \text{CF}_2\text{Cl}_2$ were used. In Fig. 5, the results of experiments in installation 2 are presented; the assignment of spectral bands of HF ($v=3$) on the basis of a spectrum with higher resolution is carried out.

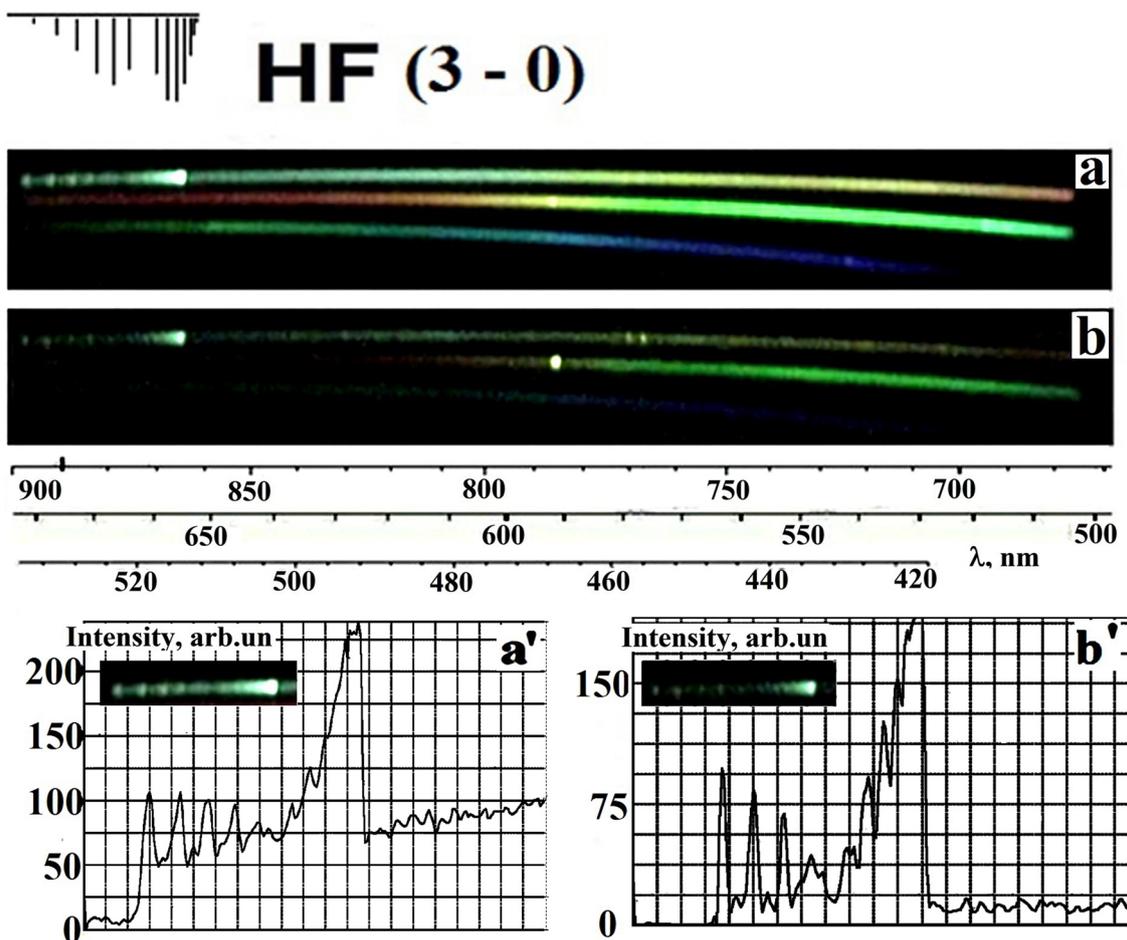


Fig. 5 Emission flame spectra at initial pressure 100 Torr: **a** $(\text{CH}_4 + \text{O}_2)_{\text{stoich}} + 10\% \text{CF}_2\text{Cl}_2$, **b** $(\text{H}_2 + \text{O}_2)_{\text{stoich}} + 10\% \text{CF}_2\text{Cl}_2$, **a'** the region of the spectrum **a**, corresponding to the emission of HF ($\nu=3$) 0.87–0.91 μm processed by means of the Hesperus 3.0 program **b'** the region of the spectrum **b**, corresponding to the emis-

sion of HF ($\nu=3$) 0.87–0.91 μm processed by means of the Hesperus 3.0 program. The emission spectrum of HF ($\nu=3$) [31] is shown on top. Three lines on each spectrum from top to bottom belong to spectral intervals 910–670 nm, 680–500 nm, 550–420 nm respectively

In the following series of experiments, the dependence of the change of a signal intensity of HF ($\nu=2$) and ($\nu=3$) on concentration of CF_2Cl_2 was investigated. In Fig. 6, the emission spectra of the mixes $2\text{H}_2 + \text{O}_2 + 10\%$ and $15\% \text{CF}_2\text{Cl}_2$ and $(\text{CH}_4 + \text{O}_2)_{\text{stoich}} + 10\%$ and $15\% \text{CF}_2\text{Cl}_2$ recorded over intervals 400–970 nm (Fig. 6a, b) and 970–1700 nm at an initial pressure of 100 Torr are shown (Fig. 6c, d). The spectrum with maximum intensity was chosen from the time sequence of the spectra for each experiment.

As is seen from Fig. 6, the emission of HF ($\nu=2, 3$) is also observed in the combustion of the stoichiometric methane–oxygen mix in the presence of $10\% \text{CF}_2\text{Cl}_2$; in addition, the maximum intensity of HF bands ($\nu=2, 3$) in methane combustion is higher, than in $2\text{H}_2 + \text{O}_2$ combustion in the presence of the same amount of halon.

It appears unlikely that the maximum concentration of H atoms in CH_4 combustion is larger than in H_2 combustion. In addition, the active centers of the combustion of hydrogen and methane determining the development of the combustion process differ from each other. It means that the reaction with CF_2Cl_2 leading to formation of HF ($\nu=2, 3$) in methane combustion includes the active center of methane combustion rather than hydrogen combustion. As CF_2Cl_2 is an effective inhibitor of methane combustion, this active center has to participate in the elementary act of branching or propagation of a reaction chain as well as to contain a hydrogen atom to form HF molecule.

The data on rate constants of elementary reactions, which are accessible in the literature are limited and contradictory, i.e. the available material is not nearly enough to make reasonable assumptions about the mechanism of halon action. According to the latest data, the rate

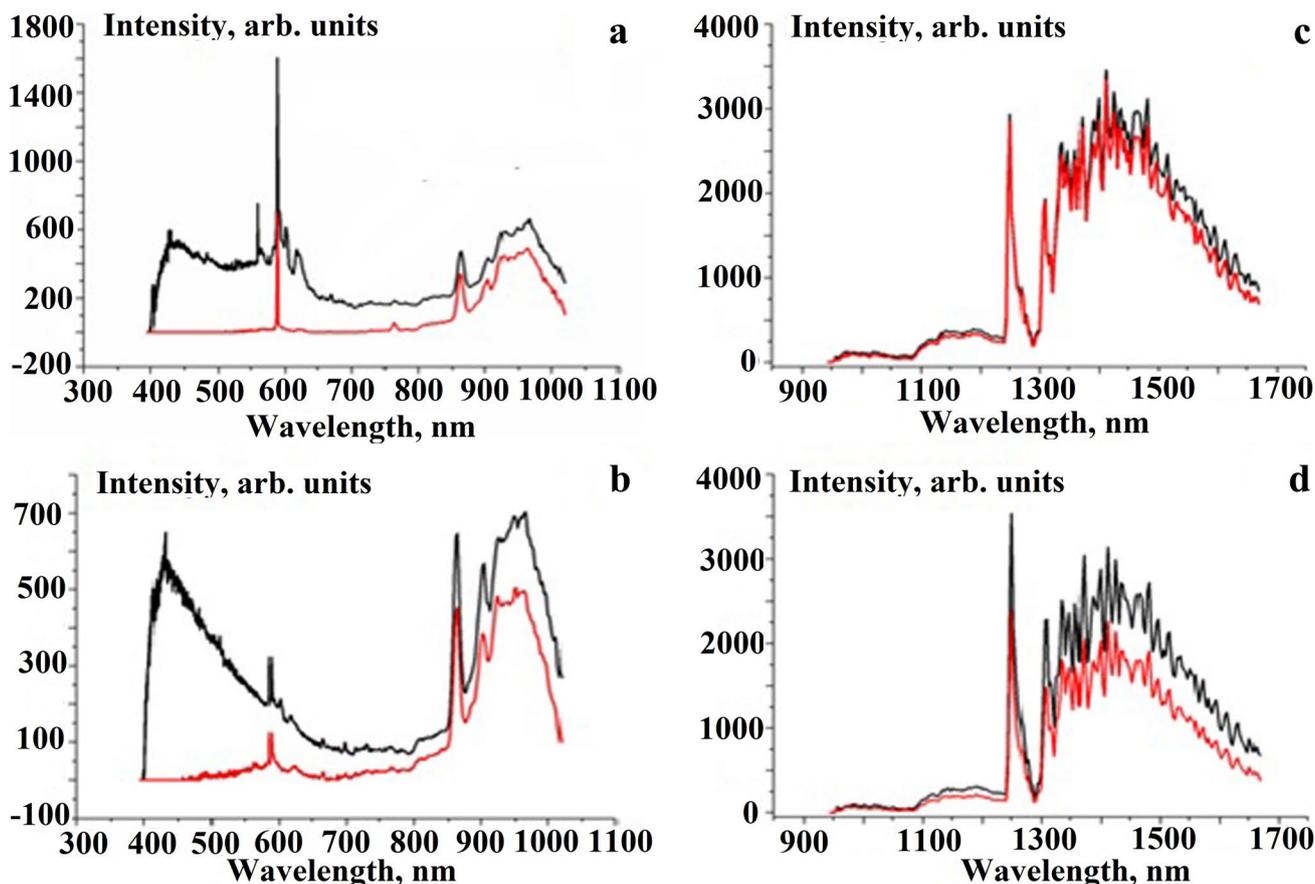
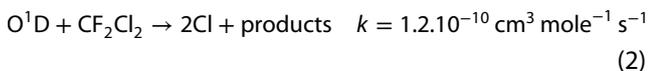


Fig. 6 Emission spectra of ignition. **a** $(H_2+O_2)_{stoich} + 10\% CF_2Cl_2$ and $(CH_4+O_2)_{stoich} + 10\% CF_2Cl_2$, obtained for a spectral interval 400–970 nm. **b** $(H_2+O_2)_{stoich} + 15\% CF_2Cl_2$ and $(CH_4+O_2)_{stoich} + 15\% CF_2Cl_2$, obtained for a spectral interval 400–970 nm, **c** $(H_2+O_2)_{stoich} + 10\% CF_2Cl_2$ and $(CH_4+O_2)_{stoich} + 10\% CF_2Cl_2$,

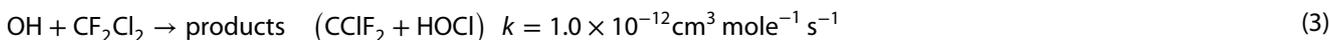
obtained for a spectral interval 970–1700 nm, **d** $(H_2+O_2)_{stoich} + 15\% CF_2Cl_2$ and $(CH_4+O_2)_{stoich} + 15\% CF_2Cl_2$, obtained for a spectral interval 970–1700 nm. Initial pressure is 100 Torr. The spectrum with the maximum intensity is chosen from the time sequence of spectra for each experiment

constant of the reaction of atoms of oxygen with halon [28]



i.e. (2) is a rather fast reaction, however, in this reaction HF is not formed.

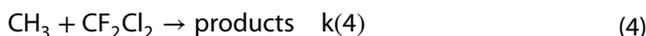
In [29] an estimate of the reaction rate constant is given (in [30], however, it is claimed that this reaction practically does not occur)



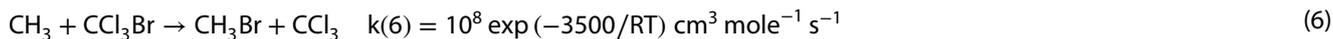
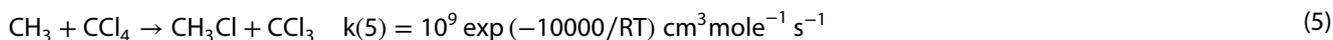
In this fast reaction, formation of HF is not also considered. However, if the molecules HF are formed in this reaction (for example, in almost thermoneutral reaction $OH + CF_2Cl_2 \rightarrow COFCl + HF + Cl$ [27]), it could not explain weak inhibition of hydrogen oxidation and strong

inhibition of methane oxidation with halon. Notice that in the above reactions, the formation of experimentally detected CF_2O is not discussed at all.

Let's consider the possible reactions of CH_3 radical. In the reaction of a chlorine atom separation from CCl_4 , $CFCl_3$ and CF_2Cl_2 with CH_3 radicals at 128 °C [31], the reaction rate values obtained for these three reactions are in the relation 1:24:126. The data of [32] allow estimating a rate constant of the reaction (if the results [31, 32] are true ones)



In [32] the rate constants of the following reactions are measured



The estimate of the rate of reaction (4) makes $k(4) \approx 126 \times k(5)$, in the assumption that the activation energy of a rate constant of the reaction (4) makes some average of activation energies of reactions (5) and (6), i.e. $k(4) \approx 10^9 \exp(-5000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The obtained value of $k(4)$ corresponds to a rather slow reaction, which cannot be responsible for effective inhibition of gas-phase methane oxidation.

It should be noted also that completely fluorinated hydrocarbons are worse inhibitors, than CF_2Cl_2 . For example, as is stated above, the most effective "ozone-safe" inhibitor is C_4F_{10} , its minimum effective concentration makes 6% [11]. In addition, we showed earlier that 0.9% perfluorodecaline $\text{C}_{10}\text{F}_{18}$ does not completely inhibit oxidation of stoichiometric methane-air mix; it is required to dilute this mix with carbon dioxide (15%) for complete inhibition [33].

It means that, as well as in case of hydrogen oxidation, inhibition of methane oxidation with CF_2Cl_2 is caused by some cycle of reactions, which nature as well as the values of their rate constants, requires a substantial clarification.

4 Conclusions

It is established that the concentration limit of ignition of a premixed H_2 -air mix in the presence of CF_2Cl_2 at 1 atm exceeds 10%, whereas the inhibitor limit of ignition of the premixed methane-air mix makes 1% CF_2Cl_2 . It means that CF_2Cl_2 is an effective inhibitor to prevent undesirable ignition of methane-air mixes at atmospheric pressure. It is experimentally shown that the concentration limits of the initiated combustion known from literature are meaningful only for previously prepared mixes. If the mixes are prepared just before the experiment, then the existence or the lack of ignition is determined by both an order of injection of mixture components, and the geometry of an installation. Therefore, the inhibition with halons can hardly be used to address the challenges of safety in mines. Thus, the influence of gasdynamic factors on the efficiency of inhibition is revealed.

It is shown that the active centers of hydrogen and methane combustion determining the development of combustion process have a different chemical nature.

Vibrationally excited molecules HF ($\nu=3$) and HF ($\nu=2$) are for the first time detected in the products of combustion

of hydrogen and methane in the presence of CF_2Cl_2 . It can be promising phenomenon in laser chemical applications.

It is experimentally shown that the intensity of HF ($\nu=3$) and HF ($\nu=2$) bands in methane combustion in oxygen is higher than in $2\text{H}_2 + \text{O}_2$ combustion in the presence of the same amount of halon. It means that the reaction with CF_2Cl_2 leading to HF ($\nu=2, 3$) formation in methane combustion has to include the active center of methane combustion. Besides, as CF_2Cl_2 is an effective inhibitor of methane combustion, this active center has to participate in the elementary act of chain branching or chain propagation as well as to contain a hydrogen atom to form HF molecule.

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

1. Hastie JW (1973) Molecular basis of flame inhibition. *J Res Natl Bur Stand A Phy Chem* 77:735–764
2. Coward HF, Jones GW (1952) Limits of flammability of gases and vapors. Bulletin 503. Bureau of Mines, Washington
3. Zabetakis MG (1965) Flammability characteristics of combustible gases and vapors. Bulletin 627. Bureau of Mines, Washington
4. Linteris GT, Rumminger MD, Babushok V, Tsang W (2001) Flame inhibition by ferrocene and blends of inert and catalytic agents. In: Proceedings of the 28th international symposium on combustion, London, pp 33–47
5. Kopylova OA, Romanov VV, Prochorova AI, Kopylov IS (2017) Review of thermodynamic characteristics of R-134A, R-410A and R-407C coolants for the air conditioning system. *Young Scientist*. <https://moluch.ru/archive/160/45004>. Accessed 19 July 2019
6. Jayaweera TM, Melius CF, Pitz WJ, Westbrook CK, Korobeinichev OP, Shvartsberg VM, Shmakov AG, Rybitskaya IV, Curran HJ (2001) Flame inhibition by phosphorus-containing compounds over a range of equivalence ratios. In: Proceedings of the joint meeting combustion The Institute Oakland, California, pp 33–44
7. Emergency and continuous exposure limits for selected airborne contaminants (1984) National Academy Press Committee on Toxicology Board on Toxicology and Environmental Health Hazards Commission on Life Sciences, National Research Council Washington DC 2:34–40

8. Semenov NN (1958) On some problems of chemical kinetics and reaction ability, 2nd edn. Academy of Sciences of the USSR, Moscow (**in Russian**)
9. Karasevich YuK (2009) Kinetics of chemical ionization in shock waves. IV. Kinetic model of ionization at acetylene oxidation. *Kinet Catal* 50:617–626
10. Azatyan VV, Baklanov DI, Merzhanov AG et al (2001) Inhibition of developed detonation of hydrogen-air mixtures. *Dokl Phys Chem* 376:1–4
11. Rubtsov NM, Azatyan VV, Borodulin RR (1980) Rate constants of chain origination and propagation in nitrogen trichloride decomposition. *Bull Acad Sci USSR Div Chem Sci* 29:1165–1170
12. Golov NV (2017) Features of ignition and burning of combustible gases and vapors in various oxidizing environments. Dissertation, Institute of Fire Safety VNIPO Russian Federation (**in Russian**)
13. Rubtsov NM, Tsvetkov GI, Chernysh VI (2008) Different effects of active minor admixtures on hydrogen and methane ignitions. *Kinet Catal* 49:344–351
14. Rubtsov NM (2016) The modes of gaseous combustion. Springer, Cham
15. Babushok VI, Linteris GT, Meier OC, Pagliaro JL (2014) Flame inhibition by CF_3CHCl_2 (HCFC-123). *Combust. Sci Technol* 186:792–814
16. Troshin KYA, Shamshin IO, Smetanyuk VA, Borisov AA (2017) Self-ignition and combustion of gas mixtures in a medium with vortex flow. *Russ J Phys Chem B* 11:952–962
17. Borisov AA, Knorre VG, Kudrjashova EL, Troshin KYA (1998) On temperature measurement in an induction period of the ignition of homogeneous gas mixtures in rapid mixture injection static setup. *Chem Phys Rep B* 17:105–109
18. Rubtsov NM, Vinogradov AN, Kalinin AP, Chernysh VI et al (2016) Cellular combustion and delay periods of ignition of a nearly stoichiometric H_2 -air mixture over a platinum surface. *Mendeleev Commun* 26:160–162
19. Azatyan VV, Shebeko YuN, Bolodyan IA, Navtsenya VYu (2006) Effect of diluents of various chemical nature on the flammability limits of gas mixtures. *Combust Explos Shock Waves* 6:708–714
20. Lewis B, Von Elbe G (1987) Combustion, explosions and flame in gases. Acad Press, New York
21. Rubtsov NM (2017) Key factors of combustion. From kinetics to gas dynamics. Springer, Cham
22. Herzberg G. (1950) Molecular spectra and molecular structure. In: Spectra of diatomic molecules, vol 1, 2nd ed, Van Nostrand, New York
23. Hole OM (2011) In situ HF-concentration measurements in combustion environments using diode laser absorption spectroscopy. A theoretical investigation. Bachelor Project in Physics University of Lund, Lund
24. Grytsinin S, Korchagina EG, Kossyi IA, Misakyan MA, Silakov VP, Tarasova NM, Temchin SM (2001) Decomposition of chlorine and (or) fluorine-bearing substances in a gas mixture ignited by a slipping surface discharge. *Plasma Sources Sci Technol* 10:125–133
25. McNesby KL, Daniel RG, Widder JM, Miziolek AW (1995) Spectroscopic investigation of atmospheric pressure counterflow diffusion flames inhibited by Halons. U.S. Army Research Laboratory ATTN: AMSRL-WT-PC Report number ARL-TR-857 Aberdeen Proving Ground, MD 21005-5066
26. Rubtsov NM, Seplyarskii BS, Tsvetkov GI, Chernysh VI (2010) Thermal ignition of coal powders in the presence of natural gas, oxygen and chemically active additives. *Mendeleev Commun* 20:98–100
27. Luo YR (2007) Comprehensive handbook of chemical bond energies. CRC Press, Boca Raton
28. Brasseur GP, Jacob DJ (2017) Modeling of atmospheric chemistry. Cambridge University Press, Cambridge
29. Belikov Y, Nikolayshvili S (2016) The role of the dipole interaction of molecules with charged particles in the polar stratosphere. *J Earth Sci Eng* 6:115–149
30. Atkinson R, Hansen DA, Pitts JN Jr (1975) Rate constants for the reaction of OH radicals with CHF_2Cl , CF_2Cl_2 , CFCl_3 , and H_2 over the temperature range 297–434 K. *J Chem Phys* 63:1703–1706
31. Hauteclouque S (1977) Réactions des radicaux CH_3 avec les molécules CCl_4 , CFCl_3 et CF_2Cl_2 . *J Photochem* 7:83–89
32. Macken KV, Sidebottom HW (1979) The reactions of methyl radicals with chloromethanes. *Int J Chem Kinet* 11:321–330
33. Rubtsov NM, Tsvetkov GI, Chernysh V., Seplyarsky BS, Azatyan VV (2009) Patent of the Russian Federation RU 2 368 410 C1: 27 09 2009 Bul No 27 (**in Russian**)

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