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VARIOUS INFLUENCE OF ACTIVE CHEMICAL ADDITIVES ON HYDROGEN AND HYDROCARBONS COMBUSTION

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ABSTRACT

It is experimentally revealed that the methane combustion inhibitor CCl_4 *shows no effect on the lower ignition limit of hydrogen combustion. It is established that small amounts (~*10^{-1} *%) of chromium hex carbonyl promote combustion of* $2H_2 + O_2$ *mixture, which manifests itself in increase in the propagation velocity of the flame, thus inhibition of oxidation of isobutene by this additive takes place. Therefore the role of hydrogen atoms in hydrocarbon oxidation is not significant and may result at least in participating in longer reaction chains than in hydrogen oxidation. It means that the kinetic mechanism of inhibiting combustion of hydrocarbons by carbonyls suggested in the literature based on accounting for termination of hydrogen atoms should be refined.*

Keywords: Combustion, Flame, Propagation, Critical, Inhibitor, Hydrogen, Hydrocarbon, Explosion, Safety.

1. INTRODUCTION

The problem of ensuring the explosion safety of hydrogen–air and methane–air mixtures is among the technological challenges in fuel power engineering. One promising solution to such a problem is employing small quantities of chemically active additives (inhibitors) [1-3].

Obtaining key parameters, which determine critical conditions of ignition and flame propagation can be useful in understanding of influence of small chemically active additives on combustion. It allows simplifying kinetic model and obtaining estimates of kinetic parameters as well. E.g. earlier [4, 5] we suggested an approximate analytical method for calculation of velocities and flame propagation limits (FPL) in hydrogen-air mixtures at atmospheric pressure in the presence of inhibitors. The method was based on a narrow reaction zone model [6] and gave a qualitative description of experimental characteristics of hydrogen combustion in the presence of inhibitor. These were both occurrence of FPL in the absence of thermal losses into reactor walls and the dependence of FPL on the chemical nature of inhibitor.

For efficient use of chemical additives, it is necessary to understand the mechanism of their action, including the estimates of rate constants of their reactions with chain carriers. For example, when studying the activity of unsaturated hydrocarbons as active additives for suppressing hydrogen flames [2], it should be expected that isobutene ($(CH_3)–C(CH_3)=CH_2$), as compared to propene ($CH_3–CH=CH_2$), will offer greater steric hindrance for approaching hydrogen atoms. At the same time, the energy barrier in the reaction between isobutene and H must be lower owing to the stronger inductive effect of the two methyl groups in isobutene.

In this regard we will briefly consider organ metallic compounds (OMC). Production of the effective and widely used inhibitor of combustion of hydrocarbons CF_3Br (Halon 1301) and some other halons was stopped because these substances promote destruction of the ozone layer [1, 7] though in our opinion it was only an occasion to replace earlier used halons with the new line of these compounds. Anyway the search for alternative inhibitors became topical. For example, it is known that some organ phosphorus compounds [8] and OMC [1, 7, 9] inhibit combustion of hydrocarbons more efficiently than CF_3Br by a factor of ~100 [1, 2]. However, they ignite in air and they are toxic, and therefore, they can be used only in places where human personnel are absent.

It was found [10] that addition of OMC (for example, iron carbonyl $Fe(CO)_5$ or ferrocene $Fe(C_5H_5)_2$) to hydrocarbon flames under 1 atm in an amount above several hundred ppm decreases the combustion rate by ~ 50%. However, the mechanism of the effect of OMC is not revealed experimentally [1, 11, 12]. Establishing the nature of inhibition of hydrocarbon combustion by OMC additives will allow revealing the mechanisms of the effect of highly efficient inhibitors with the purpose of searching for new nontoxic inhibiting compounds. The mechanism of inhibition by $Fe(CO)_5$ was suggested in [13] and is based on the recombination of hydrogen atoms with participation of carbonyl molecules.

The purposes of the work are the following:

- to investigate experimentally effect of small additive (at a level of 100 ppm) of $Cr(CO)_6$ vapor on the oxidation of hydrogen and isobutene (iso-C_4H_8), which will allow establishing the applicability of inhibition mechanisms based on termination of H and O atoms.
- to compare the efficiency of additives of vapors of ferrocene $Fe(C_5H_5)_2$, butyrylferrocene $C_{14}H_{16}FeO$, $Cr(CO)_6$, as well as combined inhibitors based on mixtures of chromium carbonyl with sulfur hexafluoride SF_6 and halogenated hydrocarbons (CF_2Cl_2, C_4H_9J, CCl_4, $CHCl_3$) on combustion of mixtures of natural gas with air.
- to establish correlation between the inhibition efficiency and the features of the chain combustion mechanism by studying the influence of methane combustion inhibitors on hydrogen combustion and the influence of hydrogen combustion inhibitors on methane combustion in stoichiometric mixtures $2H_2 + O_2$ and natural gas (NG) + $2O_2$ in the presence of small additives of C_3H_6, iso-C_4H_8, CCl_4, and SF_6.

Note that the aforementioned OMC are not self-inflammable in air and are relatively low-toxic since they have a low vapor pressure.

2. EXPERIMENTAL

Experiments were carried out under static conditions [14] in three types of reactors. Reactor

I was a quartz cylinder of 8 cm in diameter and 12 cm in length (Fig.1, in the center). It had inputs for bleeding-in and pumping out the gases and was equipped with optical quartz windows. In some experiments ignition was initiated by spark discharge. The reactors were blown with hydrogen for 1 min and then evacuated to 10^{-3} Torr prior to each experiment. Combustible mixtures $2H_2 + O_2$, iso-$C_4H_8 + O_2$, $C_3H_6 + O_2$, $CH_4 + O_2$ and NG + O_2 were prepared preliminarily. Initially, carbonyl vapors having the smallest vapor pressure were admitted first into evacuated reactors up to necessary pressure of 0.05–0.17 Torr. Then the combustible mixture was added up to necessary pressure and held in the reactor for 10 min in order to be well mixed. Light emission in the course of combustion in the reactors was detected using a FEU-39 photomultiplier with a spectral sensitivity of 200–600 nm equipped with an interference filter (306 ± 10 nm) to detect OH ($A^2\Sigma^+$ - $X^2\Pi$) emission [15]. Emission spectra of initiated ignition were detected using OSA-500 optical spectral analyzer (Germany) sensitive in a region of 200–900 nm (0.2 nm per channel). The result of the required number of scans (1 scan = 500 channels per 32 ms) was stored in computer memory. For simultaneous detection of the emission kinetics at three wavelengths (OH, a resonance line of chromium (425.4, 427.4, and 429 nm), blackbody radiation), we separately used two monochromators equipped with FEU-39 and FEU-62 (spectral sensitivity of 600–1300 nm) photomultipliers. Kinetic measurements at 1 atm and 298 K for the initiated ignition were carried out in a stainless steel cylinder of 13 cm in diameter and 15 cm in length equipped with end-face optical quartz window 12 cm in diameter (reactor II). The reactor was pumped out to 10^{-2} Torr, and initially the vapors of the active additive and then fuel and air were admitted up to 1 atm. Combustion was initiated in the center of reactor II. Reactor III was a heated quartz cylinder 3.6 cm in diameter and 35 cm in length. It was used at pressures of 5–100 Torr and temperatures of 845–973 K (set with an accuracy of 0.5 K). Preliminarily prepared stoichiometric mixtures of hydrogen and natural gas (NG) with oxygen and additives (if necessary) were examined. Integral light emission in all reactors was monitored using FEU-71 photomultiplier (spectral sensitivity of 200–600 nm). Emission spectra of ignition were recorded with the crossed dispersion spectrograph equipped with a CCD camera sensitive over the range of 420–900 nm. The spectra were analyzed using the AmLab Hesperus 3.0 beta program package. Combustion was also recorded by means of the Casio Exilim F1 Pro color high-speed digital camera (1200 frames/s), sensitive over the spectral range of 420–740 nm; each set of frames was stored in computer memory. Gas pressure was monitored with a piezoelectric transducer. Signals from the pressure transducer and photomultiplier were recorded by means of the digital C9-8 oscilloscope and stored in computer memory. The emission from electronically excited OH radicals at 306 nm was recorded using an interference filter and FEU-71 photomultiplier by means of the digital C9-8 oscilloscope. In addition the synchronization input of the oscilloscope received the signal from the opt couple which detected the moment of the gas admission into the evacuated reactor. This enabled us to measure delay times of ignition. The lower ignition limit P_1 was determined by the bleed-off method [16]. Experiments with $2H_2 + O_2$ mixtures containing additives were performed in the reactor III coated with magnesium oxide MgO, and experiments with NG + $2O_2$ mixtures were performed over quartz surface. According to gas chromatography data, NG contained 98% methane and 2% (propane + butane). Gases H_2, O_2, C_3H_6, iso-C_4H_8, CO_2,

SF_6, and CF_2Cl_2 were chemically pure; $Cr(CO)_6$, ferrocene $Fe(C_5H_5)_2$, butyrylferrocene $C_5H_5FeC_5H_4COC_3H_7$, C_4H_9J, CCl_4, $CHCl_3$ $TiCl_4$, J_2 and MgO were of special purity grade.

3. RESULTS AND DISCUSSION

3.1. Effect of Reactive Additives on the Initiated Ignition of H_2 and Hydrocarbons in Oxygen

Propagation of iso-C_4H_8 + O_2 flame recorded with the speed color camera in the presence and in the absence of $Cr(CO)_6$ were compared with $2H_2 + O_2$ flame in the reactor I (Fig.1 a,b). The results presented in Fig.1a demonstrate inhibiting effect of $Cr(CO)_6$ and agree with the literature data [5]. One can suggest that $Cr(CO)_6$ molecules decompose in the flame front with the formation of metal atoms, which rapidly interact with O_2. As is stated in [11] condensation of oxides leads to the formation of nanoparticles and to the appearance of the developed surface in the reactor volume. This leads to the inhibition effect due to an increase in the rate of heterogeneous termination of reaction chains which is rather high [17].On the basis of [13], we should expect the inhibiting effect of $Cr(CO)_6$ on the oxidation reaction of hydrogen because the inhibiting effect is concerned with termination of H atoms on carbonyl molecules according to [13] ; on the other hand H atoms are the main chain carriers in hydrogen combustion. However in agreement with our earlier results [18], the effect of $Cr(CO)_6$ additives turned out to be promoting as is seen in Fig.1b. It means that the kinetic mechanism of inhibition of combustion of hydrocarbons by carbonyls [13] based on the account of termination reactions with participation of H atoms requires correction.

For both of the systems studied, initiated ignition in the presence of $Cr(CO)_6$ is accompanied by intense emission. The visible emission spectrum is shown in Fig.2a. In the emission spectrum CrO bands with distinct heads [19] were detected as well as atomic emission of alkali metals (Na, K) usually observed in flames. It means that metal oxide actually forms in flame. Hydrogen atoms also occur in these flames. As is seen from Fig.2 b,c where the features of the emission spectra of $2H_2 + O_2$ and NG + $2O_2$ combustion in the presence of CF_2Cl_2 are compared, molecules HF (v=3) are formed in the course of combustion. These high vibrationally excited molecules can arise only in almost thermally neutral reaction $H + CF_2Cl_2$ □ HF (v=3) +$CFCl_2$. It means that H atoms participate in hydrocarbons combustion as well. It should be noted that HF (v=3) signal intensity in hydrogen flame is less than in NG-oxygen one due to smaller time of exposure of the matrix of the camera at the expense of the higher speed of hydrogen oxidation.

Intense resonant lines of Cr atoms (425.4, 427.4, and 429 nm [19]) are also observed in the emission spectrum (Fig. 2a, Fig. 3). Notice that excitation of chromium atoms is of chemical nature since the self-heating during the combustion of the stoichiometric mixture $2H_2 + O_2$ under our conditions is not above 2000 K [20] and is insufficient for thermal excitation of Cr atoms. In the emission spectrum of stoichiometric NG + $2O_2$ mixture in the presence of the $Cr(CO)_6$, the lines of Cr atoms are less intense by a factor of ~ 10 than in $2H_2 + O_2$ one (Fig. 3). Fig. 4 shows emission kinetics of initiated ignition in the mixture $2H_2 + O_2$ at 120 Torr in the presence of 0.15 Torr $Cr(CO)_6$ at three wavelengths, namely, radicals OH (306 nm), resonant line of the atomic chromium at 427.4 nm, and the wavelength of 635 nm, which corresponds to the head of CrO spectrum. It is evident from Fig. 4 that OH radicals occur at the initial stage of combustion; then the band of chromium atoms appears; and, finally, the oxide arises. These results lead to the following conclusion about the sequence of transformations in the combustion wave. During the combustion in the presence of $Cr(CO)_6$, metal carbonyl in the combustion front decomposes with the formation of metal atoms, which oxidize with the formation of oxide particles. These latter condense. As is seen from the aforesaid the establishment of detailed mechanism of OMC action needs further investigation. The detection of the promoting effect of $Cr(CO)_6$ on the oxidation process of hydrogen, in which H atoms are the main carriers of reaction chains, indicates that the inhibition mechanism described in [13], which is based on taking into account termination of H atoms *via* inhibitor molecules needs essential changes. The observation of promotion of oxidation of hydrogen by metal carbonyls also indicates that the role of hydrogen atoms in the development of the chains during the combustion of hydrocarbons is not determining and involves at least participation in longer chains than during the oxidation of hydrogen, which is in contrast with certain modern notions [21]. Although the rate of disappearance of hydrogen atoms on a massive surface of oxide is high [17], the nanoparticles containing metal atoms apparently react in another way with the chain carriers of H_2 oxidation. This way can be similar to the promoting effect of platinum sponge on this reaction [22, 23]. Indeed, H atoms, owing to their high reaction ability, prevent oxidation of metal atoms. Therefore, metal particles exert the promoting effect on the combustion of hydrogen. However, during oxidation of hydrocarbons, where the amount of hydrogen atoms is not so large, the developed surface of particles of metal oxide manifests the inhibiting effect. Really, as is seen in Fig. 3 the amount of metal atoms in the hydrocarbon flame is smaller by an order of magnitude. The results obtained in this part of the work demonstrate the possible ability of nanoparticles forming during the thermal decomposition of $Cr(CO)_6$ both to promote the combustion of hydrogen (metal nanoparticles) and to inhibit the combustion of hydrocarbon (metal oxide nanoparticles).

3.2. Effect of Small Chemically Active Additives on the Combustion of Mixtures of Natural Gas with Air at 1 Atm

It should be noted that up to now the most important elementary reactions in the mechanism of combustion of methane in which the development of reaction chains occur, have not been reliably established. It is known [24] that, during oxidation of methane, two determining sets of reactions are distinguished, namely, oxidation of methane into CO and oxidation of CO into CO_2. An effective inhibitor should retard both of these processes. Therefore, to suppress the combustion of methane, combined inhibitors should be used to influence on the elementary reactions of each of the two stages in the combustion mechanism. In this work, we made an effort to determine the effect of various combined inhibitors on the lower concentration limit (LCL) of initiated ignition of NG-air mixtures.

The experiments on determining the efficiency of inhibitors were performed as follows. Preliminarily, LCL was determined to be 4.66 ±0.05% in reactor III at 1 atm and 298 K. This value was the arithmetic mean between such concentrations of NG in air at the lower of which initiated ignition was not observed and at the larger of which it was observed. According to [20], the LCL of NG is lower than the LCL of pure methane. In the next series of experiments, the value of LCL of mixtures of NG with air was determined in the presence of the vapors of $Cr(CO)_6$, ferrocene $Fe(C_5H_5)_2$, and butyrylferrocene $C_5H_5FeC_5H_4COC_3H_7$.

It was shown that ferrocene and butyrylferrocene have similar efficiency. It was also found that the mentioned OMC in concentration of ~ 0.04%, which approximately corresponds to the pressure of their saturated vapors, possess a comparable efficiency and increase the LCL by no more than 10%. This means that these OMC are weakly efficient inhibitors in the LCL region for mixtures of NG with air. It illustrates Fig.5 where dependencies of delay times of initiated ignition of lean NG-air mixtures with and without $Cr(CO)_6$ additives at 1 atm on the content of NG in the mixture are shown.

The comparison of inhibiting efficiency of combined inhibitors (halogen-substituted hydrocarbons CF_2Cl_2, C_4H_9J, CCl_4, $CHCl_3$, and SF_6 in the presence of the same amount of $Cr(CO)_6$ (0.17 Torr)) on NG - air combustion in LCL region is shown in Fig. 6. We used the delay time τ of ignition and the integrated intensity of light emission I as the measure of efficiency of the additive. It is evident from Fig. 6 that the addition of $Cr(CO)_6$ noticeably increases the efficiency of using CCl_4 as the inhibitor. From Fig. 6, it is also evident that the addition of SF_6 manifests the highest efficiency, and the least effective inhibitor is $CHCl_3$.

These results allow us concluding that the presence of H atoms in the molecule of the active additive does not provide any increase in inhibiting efficiency. Notice that individual additives SF_6, CF_2Cl_2, and CCl_4 taken in amounts greater than 2 vol % do not display additional increase in the inhibiting efficiency but, to the contrary, promote combustion of NG with air, which agrees with the results [24], where the effect of additives of CF_3J, CF_3Br, $C_2F_4Br_2$, and $C_2F_4Br_2$ on the combustion of methane–air mixtures was investigated. The promoting effect obtained with the amount of inhibiting additives of more than 2 vol % is a consequence of the fact that the oxidation of additives containing halogen and oxygen is accompanied by the formation of active intermediate particles participating in reactions of the development of reaction chains.

As is mentioned above, metal carbonyls are effective inhibitors of hydrocarbon combustion, but these are extremely toxic. In this study, we used a mixed inhibitor containing metal chloride much less toxic than the carbonyls (specifically, $TiCl_4$) and J_2. J_2 is offered in [1]. We demonstrate in Fig. 7 that 0.4% of complex inhibitor (the vapor of saturated solution of J_2 in $TiCl_4$) reduces the natural gas oxidation rate (determined as the increase rate in pressure signal or I) by a factor greater than 10. Thus, the very exothermic combustion process at atmospheric pressure can be inhibited by a small amount of the chemically active additive which is not OMC.

3.3. Thermal Ignition of Hydrogen and Natural Gas Mixtures with Oxygen in the Presence of Chemically Active Additives

It was shown above that Cr $(CO)_6$, which inhibits hydrocarbons combustion, promotes hydrogen combustion. It evidently means that the role of H atoms in a chain unit in hydrocarbons combustion is not limited to the reaction cycle of only H_2 oxidation: $H + O_2$ □ $H + OH$; $O + H_2$ □ $O + OH$; $OH + H_2$ □ $H + H_2O$. Propene is an effective inhibitor of H_2 combustion

[2], CCl_4 is methane combustion inhibitor [1]. SF_6 is a chemically inert combustion suppressant [20].

Carrying out the oxidation of H_2 and NG in the presence of these additives enabled us to verify the different role of H atoms in both combustion processes. $CH_4 + O_2$ mixture ignites at higher temperatures than $2H_2 + O_2$ one because methane combustion is a less intensive process. Furthermore, the delay period in methane combustion near the lower thermal ignition limit P_1 is longer than 10 min [25]. This causes serious difficulties in P_1 measurements. For this reason the delay time $\square^0$ of ignition was measured at given values of pressure and temperature. Thus $\square^0$ values for the NG + $2O_2$ mixtures were somewhat smaller than the same values measured for $CH_4 + 2O_2$ mixtures [26]. This discrepancy is due to the presence of more readily ignitable hydrocarbons such as propane and butane (see **Experimental**) in NG. As it stated above, the lower concentration limit LCL was determined to be 4.66 ±0.05% (Fig.5) as compared to 5% for methane oxidation.

Experiments were performed in the reactor II. At 960 K, $\square^0$ for the NG + $2O_2$ mixture was reproducibly determined to be 21 ±2 s. In the presence of 1% CCl_4, we measured $\square^{CCl4} = 62 \pm 5$ s at 963 K. The fact that the delay time of thermal ignition is observed experimentally means that the inhibitor (CCl_4 in this case) influences on the rate of one of the steps of the chain unit of methane oxidation [27].

By contrast, in the presence of 2% SF_6, $\square^{SF6} = 20 \pm 4$ s; that is, $\square^{SF6} \approx \square^0$. This indicates that SF_6 is not an inhibitor, but a combustion suppressant that takes part in termolecular chain termination. On the other hand, 1% C_3H_6 additive reduces the delay time of ignition to 15 ±4 s at the same temperature; that is, C_3H_6 is a promoter of methane combustion.

Temperature dependencies of P_1 for $2H_2 + O_2$ mixture over MgO surface in the absence and in the presence of the above mentioned active additives are shown in Fig. 8 a,b. First, comparison with our data [27], [Fig.1] shows that the P_1 values do not depend on reactor length (25 cm in [27]). It means that in both cases the influence of reactor both-ends is negligible. Therefore our values of upper limits of the rate constants of the reactions of H atoms with propene and isobutene molecules [27] estimated by the ignition limit method [28]: ((1.0 ± 0.3) $10^{-11}\exp(-1450 \pm 400/T)$ and (0.8 ± 0.3) $10^{-11}\exp(-550 \pm 200/T)$ cm^3 $molecule^{-1}$ s^{-1}, respectively), in the temperature range of 840–950 K seem to be reproducible. As is seen unsaturated hydrocarbons exert a marked inhibiting effect on the ignition of the $2H_2 + O_2$ mixture. At the same time, neither CCl_4 nor SF_6 has an appreciable effect on P_1. The experimentally detected opposite effects of the additives C_3H_6 and CCl_4 on the self-ignition of H_2 and NG suggest that H atoms do not play a crucial role in hydrocarbons oxidation.

4. CONCLUSIONS

It is shown that small additive (~10^{-1}%) of $Cr(CO)_6$ promotes combustion of $2H_2 + O_2$ mixture buts inhibits oxidation of isobutene. This means that the role of H atoms in oxidation of hydrocarbons is not determining and results in at least the participation in longer chains than in hydrogen oxidation. Therefore, the kinetic mechanism of inhibition of hydrocarbons combustion by carbonyls based on the account of termination reactions of hydrogen atoms should be refined.

An increase in efficiency of combined inhibitors on the combustion of mixtures of natural gas with air is established. It is shown that methane combustion inhibitor CCl_4 exerts no effect on the lower limit of hydrogen thermal ignition; it also is evidence to the fact that the role of H atoms in hydrocarbon oxidation is not significant.

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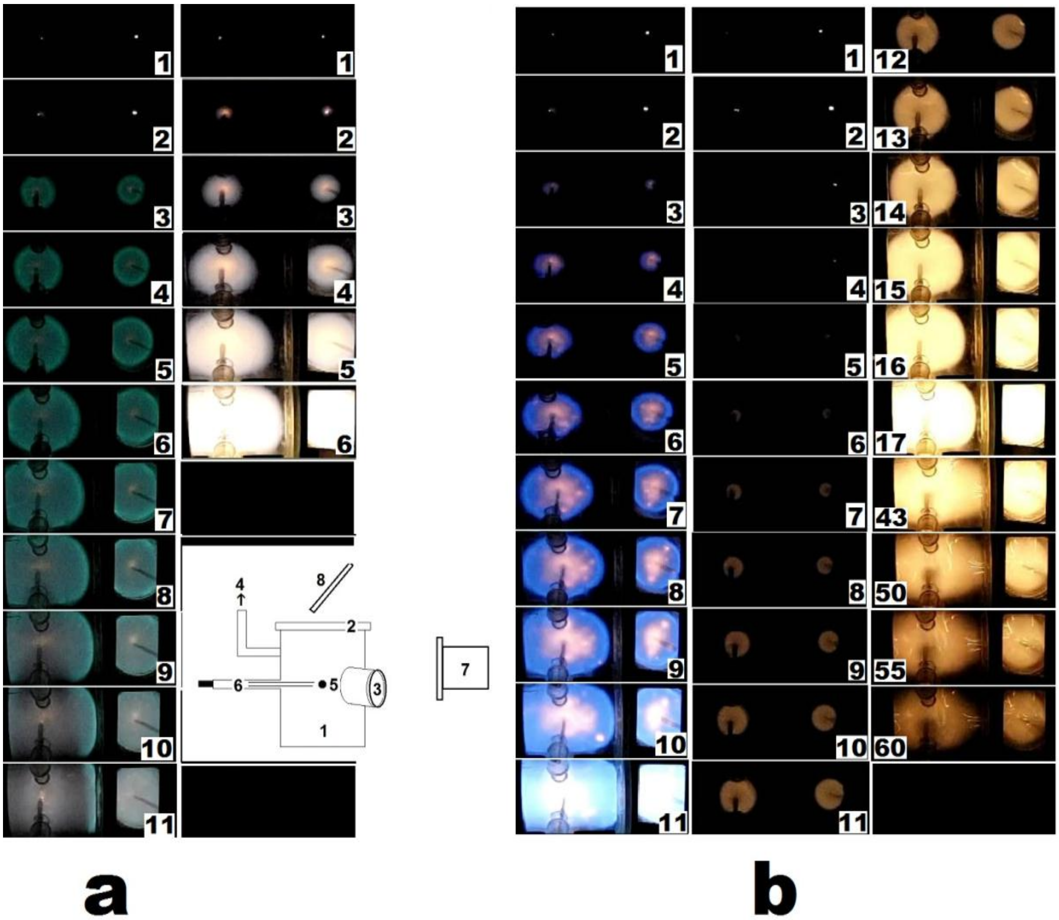
Figures

Fig-1. Sequences of video images of the spatial development of initiated ignition at 1200 shots/s.



(a) in 45 Torr $2H_2 + O_2$ + 5 Torr CCl_4 + 50 Torr CO_2 (left)

in 45 Torr $2H_2 + O_2$ + 5 Torr CCl_4 + 50 Torr CO_2 + 0.17 Torr $Cr(CO)_6$ (right)

(b) in 85 Torr (isobutene + O_2) $_{\text{stoichiometric}}$ + 15 Torr CO_2 (left column)

in 85 Torr (isobutene + O_2) $_{\text{stoichiometric}}$ + 15 Torr CO_2 + 0.17 Torr $Cr(CO)_6$ (two right columns).

In the center - experimental installation : (*1*) cylindrical quartz reactor I, (*2*) removable top, (*3*) optical window, (*4*) outlet for reactor evacuation, (*5*) piezoelectric gage, (*6*) ignition electrodes, (*7*) high-speed video camera and (*8*) rotary mirror.

Fig-2. Emission spectra of (*a*) initiated ignition of $2H_2 + O_2$ in the presence of 0.17 Torr $Cr(CO)_6$, P = 100 Torr (*b*) initiated ignition of 80 Torr $2H_2 + O_2$ + 20 Torr CF_2Cl_2 and (*c*) initiated ignition of 80 Torr (isobutene+ O_2)$_{\text{stoichiometric}}$ + 20 Torr CF_2Cl_2. On the top – the emission spectrum of CrO.

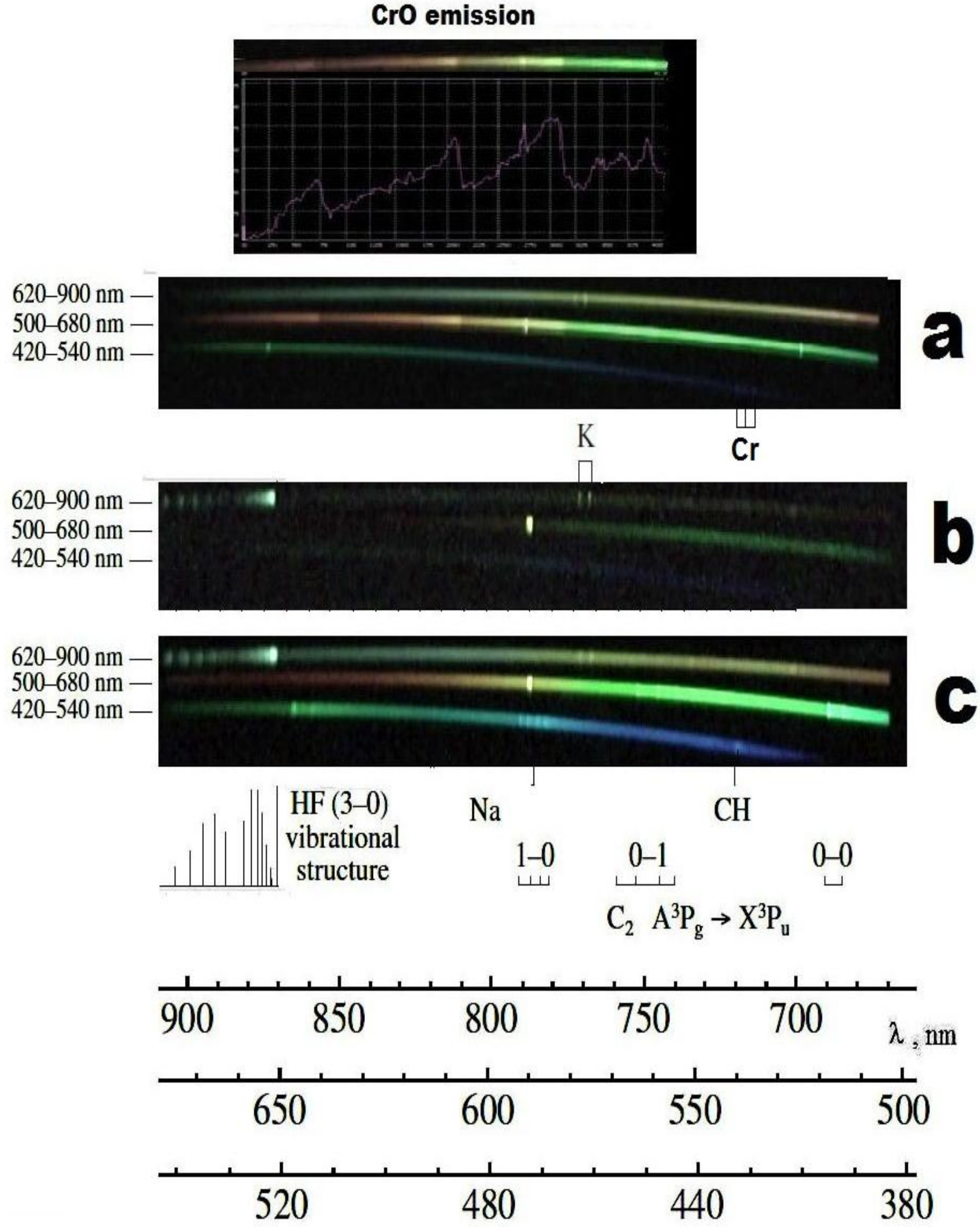


Fig-3. Emission spectra of initiated ignition in the reactor I: (a) stoichiometric mixture $2H_2 + O_2$ in the presence of 0.17 Torr $Cr(CO)_6$, P = 200 Torr; (b) NG + $2O_2$ in the presence of 0.17 Torr $Cr(CO)_6$, $P = 200$ Torr.

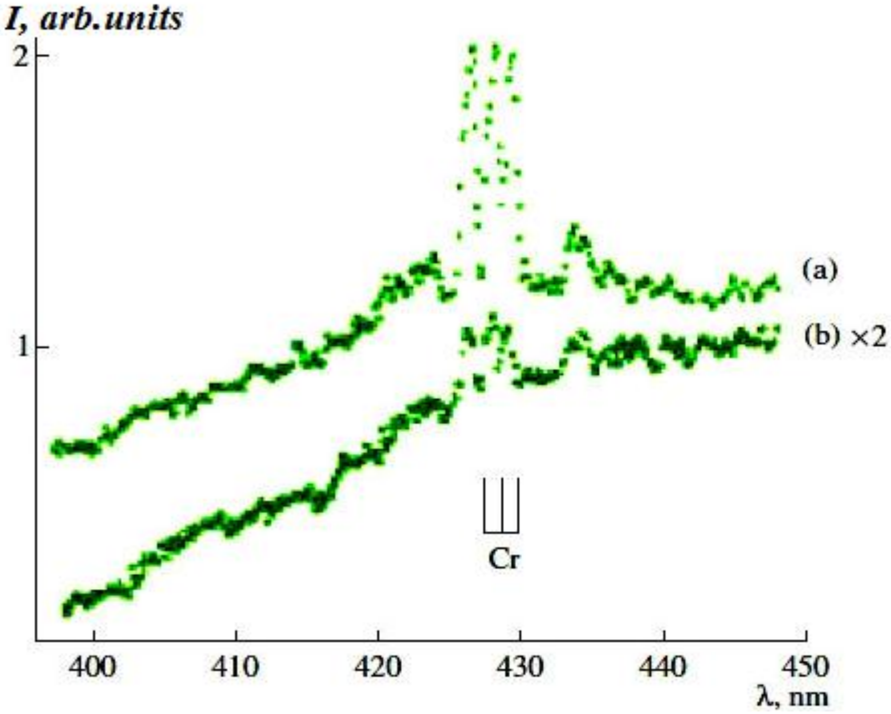


Fig-4. Emission kinetics in the initiated ignition of 120 Torr $2H_2 + O_2$ in the presence of 0.15 Torr $Cr(CO)_6$ at 306 nm (OH radicals) (*1*), resonant line of atomic chromium 427.4 nm (*2*), and the wavelength at the head of CrO band 635 nm (*3*).

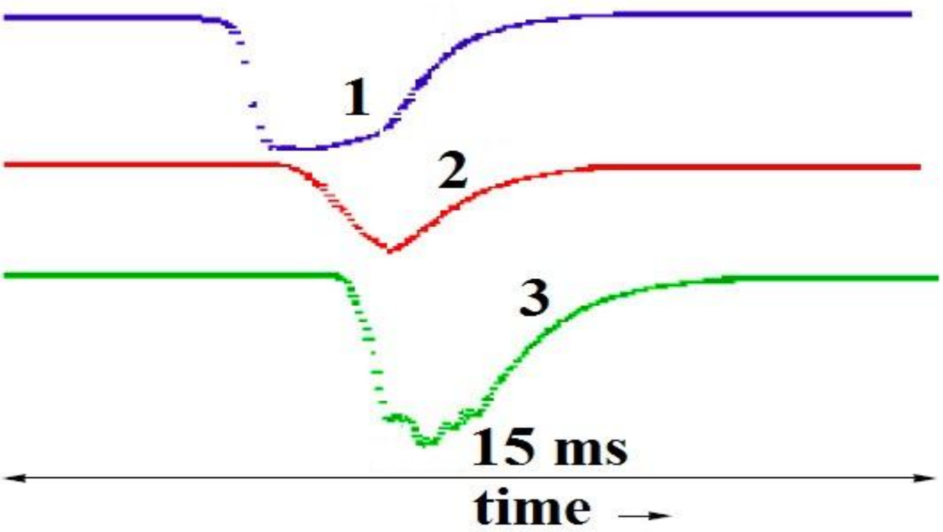


Fig-5. Dependencies of delay times of initiated ignition of lean NG-air mixtures with OMC at 1 atm on the content of NG in the mixture. Blue curve - NG + air; red curve - NG + air + 0.14 Torr of ferrocene; green curve - NG + air + 0.17 Torr of $Cr(CO)_6$. There is no initiated ignition at 4.96% NG in air in the presence of OMC.

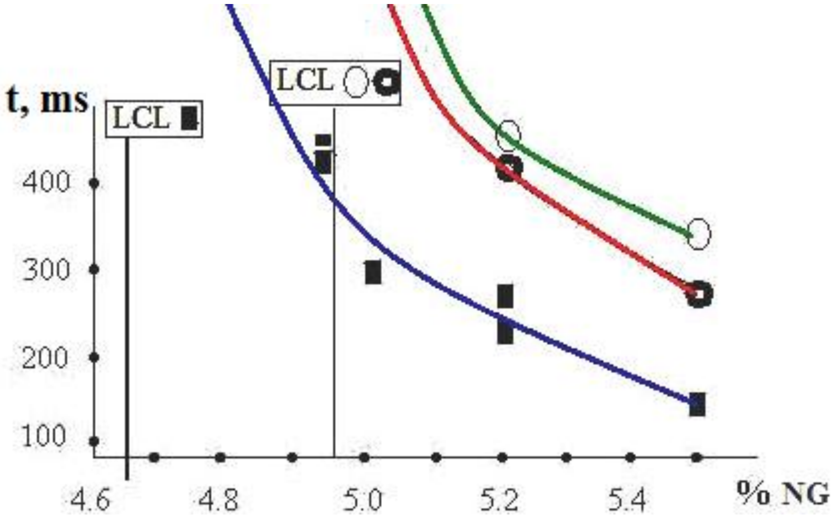


Fig-6. Delay times of combustion and intensities of light emission for initiated ignition of mixtures of natural gas with air in the presence of SF_6 and a series of halogenated hydrocarbons. In all experiments (excluding purple points), the same additive 0.17 Torr $Cr(CO)_6$. $P = 750$ Torr. The curve is plotted through the points corresponding to the mixture 0.17 Torr $Cr(CO)_6$ + 2% CCl_4.

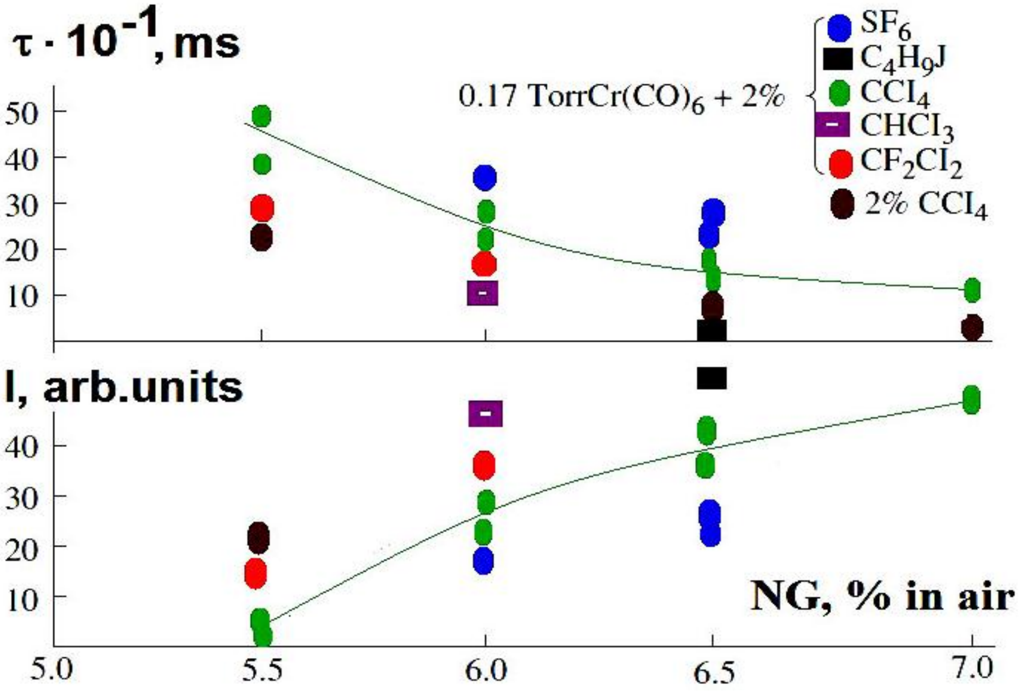


Fig-7. Oscillograms of initiated ignition of natural gas in air: (a) 7.5% NG + air, P = 1 atm, T = 298 K; (b) 7.5% NG + 0.4% ($TiCl_4$+J_2) + air, P = 1 atm, T = 298 K. (*1*) Time profile of light emission intensity (I_{CL}). (2) Time profile of pressure (□P).

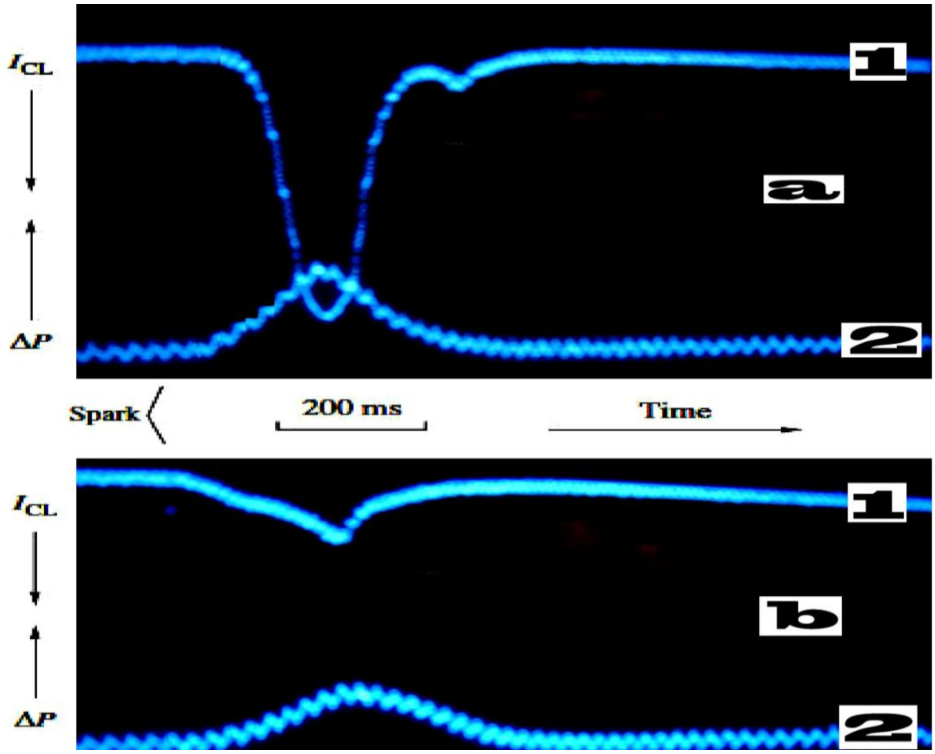


Fig-8. Combustion of the $2H_2$ +O_2 mixture over MgO surface in the presence of C_3H_6, *iso*-C_4H_8, CCl_4, and SF_6: (a) temperature dependencies of P_1 in the presence of (*1*) *iso*-C_4H_8, (*2*) CCl_4, and (*3*) SF_6 (isobutene concentrations are indicated at the curves);

(b) temperature dependencies of P_1 in the presence of C_3H_6 (propene concentrations are indicated at the curves).