

Combustion Characteristics of Gaseous Mixtures of Combustible Gases with Air and Ozone-Safe Inhibitors

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ABSTRACT

An experimental investigation of influence of various inhibitors (CF_3H , $\text{C}_2\text{F}_5\text{H}$, $\text{C}_3\text{F}_7\text{H}$, $\text{C}_3\text{F}_6\text{H}_2$, CF_2ClH , $\text{C}_2\text{F}_5\text{Cl}$, $\text{C}_2\text{F}_5\text{I}$, C_4F_8 , C_4F_{10} , $\text{C}_2\text{F}_4\text{Br}_2$, Inh A₁) on combustion characteristics of hydrogen - air and methane - air mixtures in closed vessel has been carried out. Flammability limits, maximum explosion pressure, maximum pressure rise rate have been determined. An effect of chemical induction has been revealed, when combustion of lean hydrogen - air and methane - air mixtures promotes oxidation of fluorinated halons with an appropriate elevation of maximum explosion pressure and maximum pressure rise rate. It has been found, that inhibitor Inh A₁, proposed by Institute of Structural Macrokinetics of Russian Academy of Sciences, influences on upper flammability limit of hydrogen in air more strong in comparison with diluents investigated in this work (except $\text{C}_2\text{F}_5\text{I}$). This phenomenon allows to consider Inh A₁ as a perspective substitution of halons for explosion prevention of hydrogen - air mixtures.

INTRODUCTION

Up to now brominated halons were widely used for fire extinguishing, explosion prevention and explosion suppression [1-3]. But according to the well known Montreal convention an application of brominated halons, which can strongly destroy the ozone layer of the Earth, must be gradually finished. Therefore a problem of search of inhibitors, which can substitute brominated halons, arises. Many works are aimed on a decision of this problem (see, for example, [1-10]).

An action of halons on flames at halons can be explained not only as a result of dilution, but firstly as consequence of inhibition of combustion processes passing by chain-branching mechanism. Inhibitor's molecules react efficiently with active intermediate products (atoms, radicals), which are carriers of reaction chains, producing products, which are not able to regenerate carriers of reaction chains.

Halons, in which number of halogen atoms is not less, than number of hydrogen atoms, are as a rule noncombustible. On the other hand, combustion of gaseous mixture can at some conditions cause an oxidation of halons. If combustion of a halon is exothermic enough, associated oxidation of main combustible and the halon takes place. This effect of chemical induction has been revealed in our work.

This work is aimed on an experimental investigation of influence of inhibitors, which are safe for the ozone layer of Earth, on combustion characteristics of gaseous mixtures.

EXPERIMENTAL

Experiments have been carried out on a set-up called "Variant", which is described in detail in [11]. The set-up has a spherical reaction vessel with internal diameter 20 cm (volume 4.2 dm³) made from stainless steel. An initial pressure of gaseous mixture in this set-up can reach 4 MPa. The set-up includes also system for preparing of combustible mixture, which ensures evacuation of the reaction vessel till residual pressure not higher than 0.5 kPa, and formation of combustible mixture in it by partial pressure. A fused nichrom wire with diameter 0.2 and length 3 ± 1 mm placed in the centre of the reaction vessel was used as an ignition source at supplying of voltage 42 V on it. System of registration of a flame propagation consists from a pressure detector "Saphire-22" with a time constant $3 \cdot 10^{-3}$ sec, a remembering oscilloscope S9-8 and connecting lines providing a synchronization of a mixture ignition and a recording on oscilloscope. It was accepted, that flame propagates in a mixture of a given composition, if pressure increase in the closed reaction vessel exceeds 30 kPa. Experimental data have been processed according to standard [12]. The following inhibitors were investigated: CF₃H, C₂F₅H, C₃F₇H, C₃F₆H₂, CF₂ClH, C₂F₅Cl, C₂F₅I, C₄F₈ (perfluorocyclobutane), C₄F₁₀, NAF S-III, Inh A₁. The combustible gases were methane and hydrogen. Experiments were executed at room temperature and atmospheric pressure. Except pressure elevation in the reaction vessel at a gaseous mixture combustion, rarefaction pressure ΔP_V after cooling of combustion products to room temperature and steam condensation was measured. The ΔP_V value characterises both a combustion completeness and an extent of participation of inhibitor in combustion processes.

Relative error in measurements of all parameters did not exceed 10 %.

RESULTS AND DISCUSSION

The main results of our experiments are presented in Figs. 1-4. In Fig. 1 flammability limits in mixtures of combustible gas (methane, hydrogen) - air - diluent are presented.

In Figs. 2, 3 typical dependencies of maximum explosion pressure ΔP_{\max} and maximum explosion pressure rise rate $(dp/dt)_{\max}$ for combustible mixtures of various compositions on a diluent concentration [Inh]. For convenience these data are presented in dimensionless form by normalization on maximum explosion pressure $\Delta P_{\max o}$ and maximum explosion pressure rise rate $(dp/dt)_{\max o}$ of gaseous mixtures without inhibitors. The normalization constants $\Delta P_{\max o}$ and $(dp/dt)_{\max o}$ are the following:

- for mixtures CH₄ - air - C₂F₅H $\Delta P_{\max o} = 300, 600, 600$ kPa at CH₄ concentration in its mixture with air 5.5, 10, 12 % (vol.);

- for mixtures H₂ - air - C₄F₈ $\Delta P_{\max o} = 290, 460, 640, 610, 520$ kPa at [H₂] in air 10, 20, 30, 40, 50 % (vol.);

- for mixtures CH₄ - air - C₄F₁₀ $(dp/dt)_{\max o} = 1.7, 7.4, 10.2, 11.0$ MPa/s at [CH₄] in air 6, 8, 10, 12 % (vol.);

- for mixtures H₂ - air - CF₂ClH $(dp/dt)_{\max o} = 3.6, 98, 155, 230, 240$ MPa/s at [H₂] = 10, 20, 30, 50 % (vol.).

In Fig. 4 the values of rarefactions in the reaction vessel after a cooling of combustion products and steam condensation are presented in the dimensionless form. The normalization constants ΔP_{V_0} are the following:

- for mixtures CH₄ - air - CF₃H $\Delta P_{V_0} = -8.8, -11.5, -14.5, -12.5$ kPa at [CH₄] in air 6, 8, 10, 12 % (vol.);

- for mixtures H₂ - air - C₃F₇H $\Delta P_{V_0} = -14, -27, -41, -29$ kPa.

Let us analyze the presented above results.

Minimum inertization concentrations of diluents investigated in our experiments are higher for hydrogen in comparison with methane. This result coincide qualitatively with data published elsewhere (see, for example, [12] and cited there works). But for C₃F₇H and C₄F₈ we have obtained the opposite result. A reason of this phenomenon is not clear.

At a transition from diluents with one carbon atom (CF₃H, CF₂ClH) to inhibitors with two C atoms the inhibition effectiveness increases, because minimum inertization concentrations (MIC) of diluents decrease. But a transition from inhibitors with two carbon atoms to diluents with three and four C atoms does not give a sufficient change in MIC. An availability of Cl atom in an inhibitor molecule causes a reduction in MIC, because energy of a chemical bond C-Cl is lower, than for chemical bond C-F.

Minimum inertization concentration of C₂F₅I in relation to methane is sufficiently lower, than MIC of C₂F₅H, but in relation to hydrogen we have the opposite situation. Thus a change in C₂F₅H of H atom on I atom cause not only a change of inhibition effectiveness of diluent, but also a preferential action on hydrogen - and methane - air flames. At the same time we should note a very strong influence of C₂F₅I on the upper flammability limit (UFL) of hydrogen in air. On this parameter the inhibitor C₂F₅I exceeds significantly all diluents investigated by us except Inh A₁, which has a comparable action on UFL of hydrogen. It should be noted, that combustible mixtures at inertization points are lean in all ternary gaseous compositions investigated by us. In the case of hydrogen this results agrees with the known data published in literature (see, for example, [13]). But for methane and diluents investigated earlier mixtures at inertization points are close to stoichiometric one [14]. This difference is caused probably by an active participation of fluorinated diluents in combustion processes.

In Fig. 1 we can see a strong influence of Inh A₁ on UFL of hydrogen. This influence higher, that for C₂F₄Br₂, which is one of the most strong inhibitors of combustion

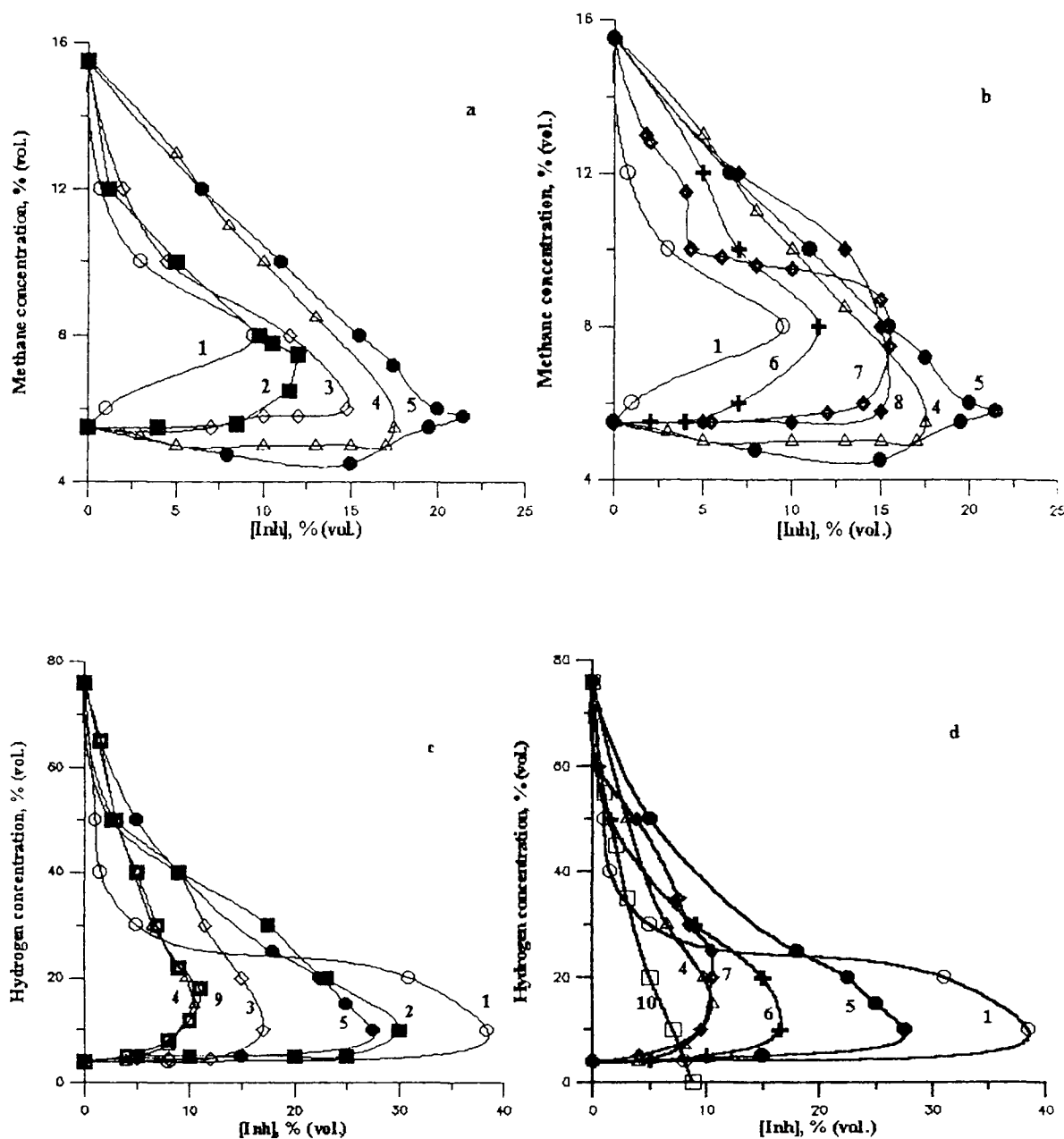


FIGURE 1. Flammability limits in mixtures combustible gas (methane (a,b), hydrogen (c,d)) - air - diluent (Inh).

1 - C₂F₅I; 2 - CF₃H; 3 - CF₂ClH; 4 - C₂F₅H; 5 - C₂F₅Cl; 6 - C₃F₇H; 7 - C₄F₁₀; 8 - C₄F₈; 9 - C₂F₄Br₂; 10 - Inh A₁.

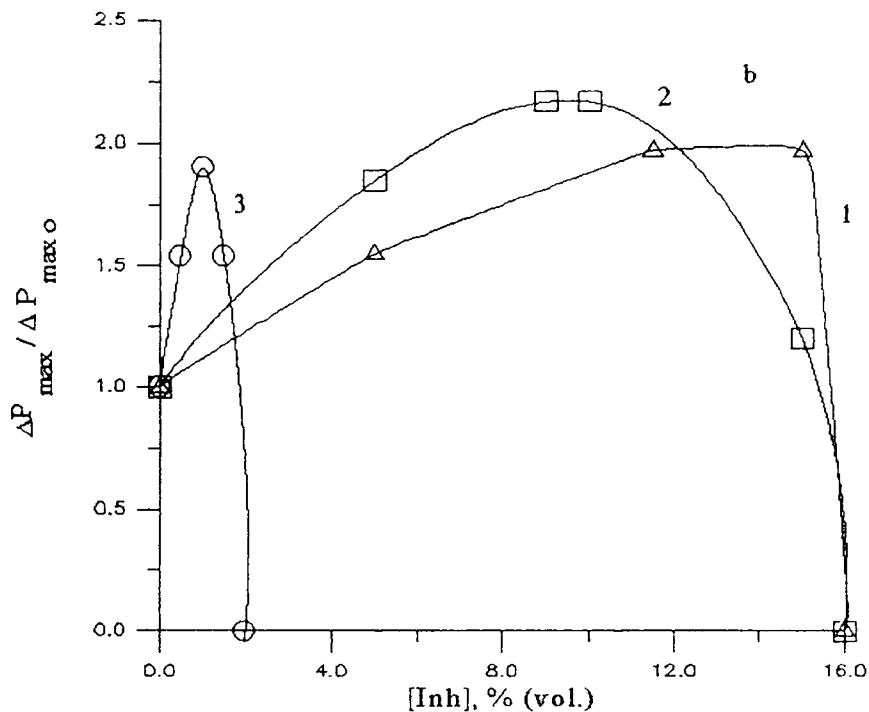
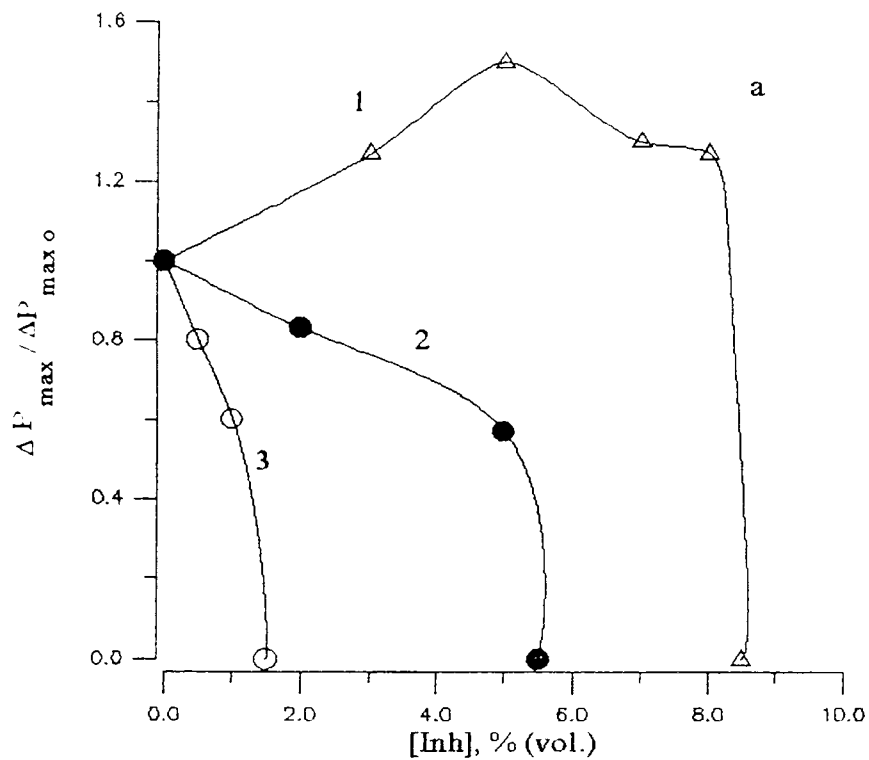


FIGURE 2. Typical dependence of maximum explosion pressure of gaseous mixtures on inhibitor concentration: a - combustible - methane (1 - $[\text{CH}_4]=5,5\%$ (vol.), 2 - $[\text{CH}_4]=10\%$ (vol.), 3 - $[\text{CH}_4]=12\%$ (vol.)); diluent - $\text{C}_2\text{F}_5\text{H}$; b - combustible - hydrogen (1 - $[\text{H}_2]=10\%$ (vol.), 2 - $[\text{H}_2]=20\%$ (vol.), 3 - $[\text{H}_2]=50\%$ (vol.)); diluent - C_4F_8 (perfluorocyclobutane).

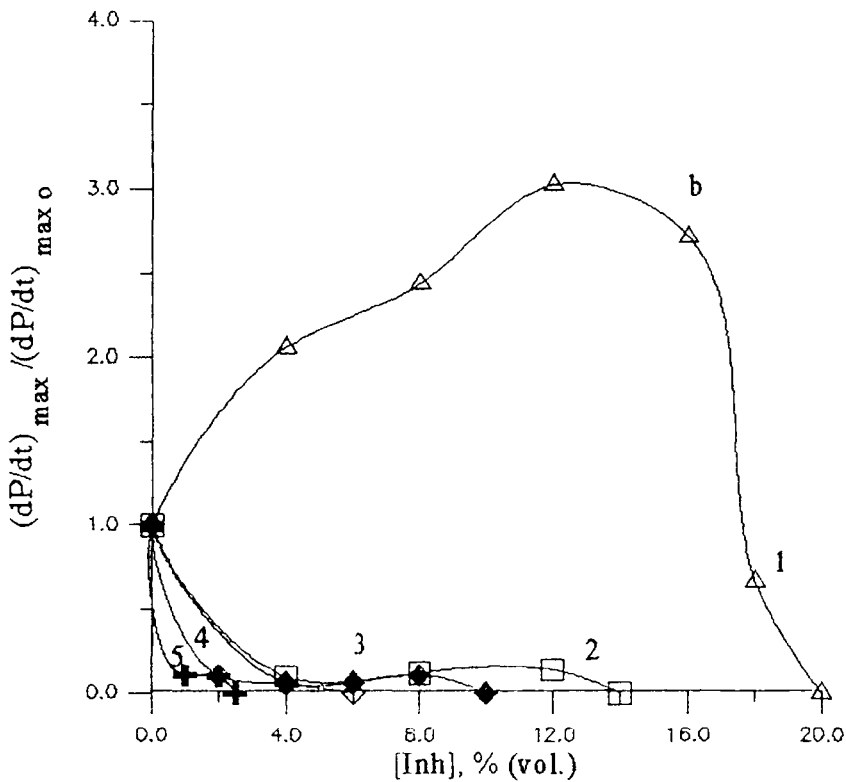
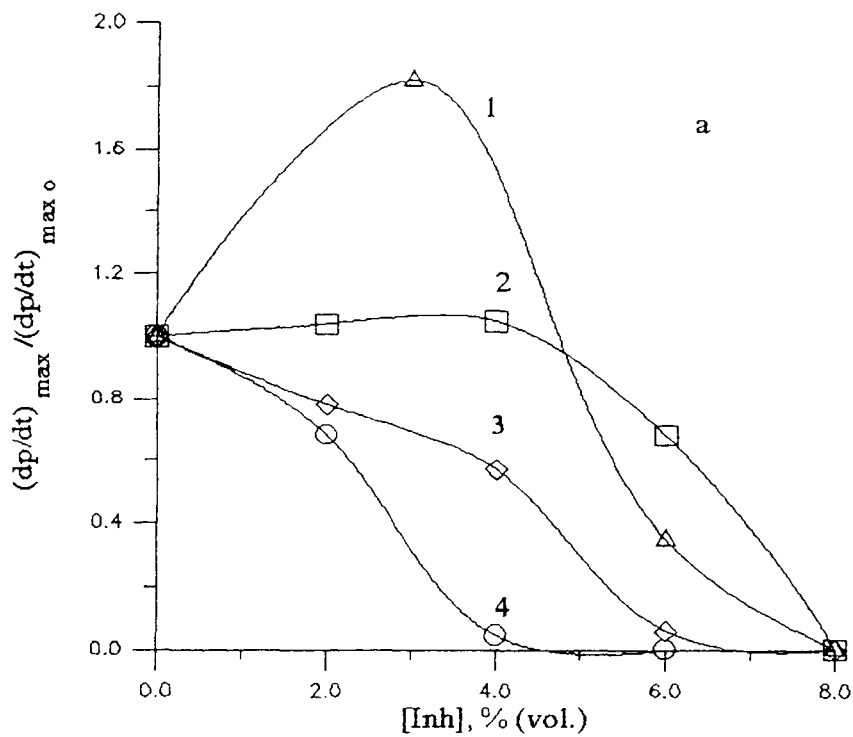


FIGURE 3. Typical dependence of maximum explosion pressure rise rate of gaseous mixtures on inhibitor concentration: a - combustible - methane (1 - $[CH_4]=6\%$ (vol.), 2 - $[CH_4]=8\%$ (vol.), 3 - $[CH_4]=10\%$ (vol.), 4 - $[CH_4]=12\%$ (vol.)), diluent - C_4F_{10} ; b - combustible - hydrogen (1 - $[H_2]=10\%$ (vol.), 2 - $[H_2]=20\%$ (vol.), 3 - $[H_2]=30\%$ (vol.), 4 - $[H_2]=40\%$ (vol.), 5 - $[H_2]=50\%$ (vol.)), diluent - CF_2ClH .

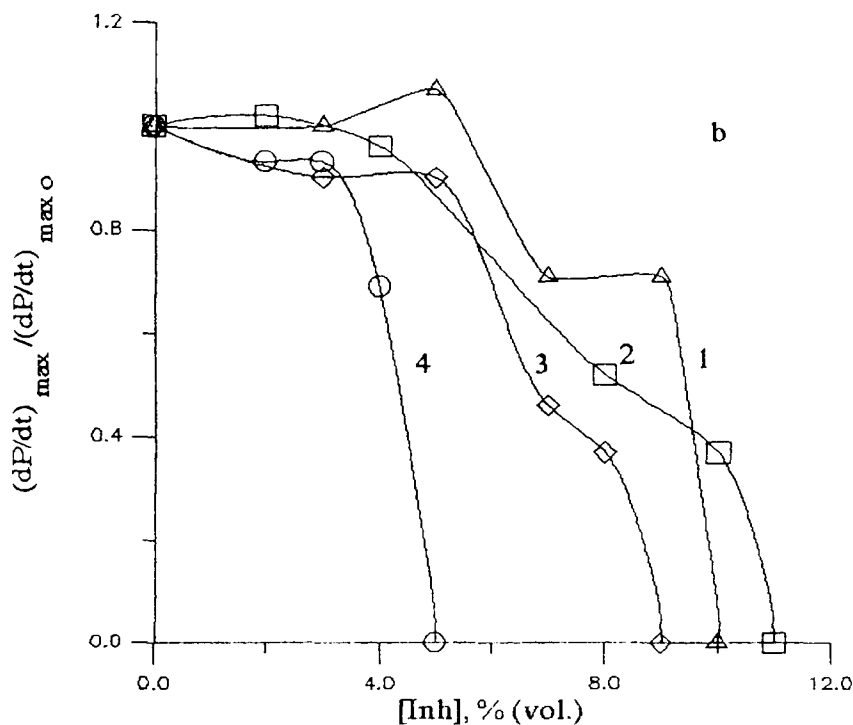
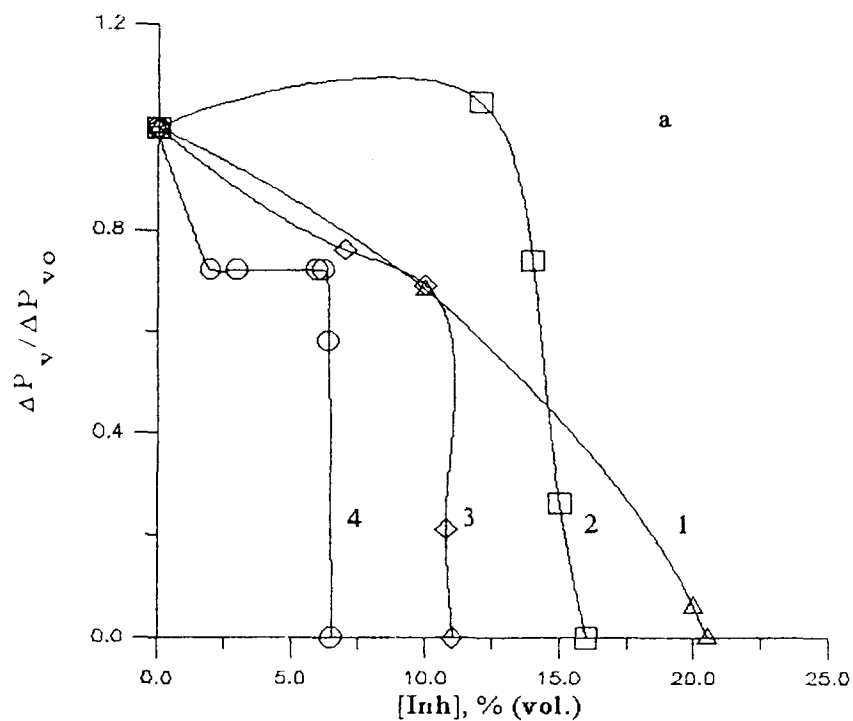


FIGURE 4. Typical dependence of rarefaction pressure in the closed vessel after a cooling of combustion products and steam condensation.

a - combustible - methane (1 - $[\text{CH}_4]=6\%$ (vol.), 2 - $[\text{CH}_4]=8\%$ (vol.), 3 - $[\text{CH}_4]=10\%$ (vol.), 4 - $[\text{CH}_4]=12\%$ (vol.), diluent - CF_3H ; b - combustible - hydrogen (1 - $[\text{H}_2]=10\%$ (vol.), 2 - $[\text{H}_2]=20\%$ (vol.), $[\text{H}_2]=30\%$ (vol.), 4 - $[\text{H}_2]=50\%$ (vol.), diluent - $\text{C}_3\text{F}_7\text{H}$).

processes, and comparable with the action of $\text{C}_2\text{F}_5\text{I}$, despite of Inh A_1 is a combustible gas. The reason of this phenomenon is a more high effectiveness of a chain termination

in the chain-branching process of combustion of hydrogen. Because it is a combustible gas, it should be used for explosion prevention of hydrogen - air mixtures with H_2 concentrations not lower than 15 % (vol.)

An interesting effect revealed in this work is an availability of maxima in dependencies of ΔP_{max} and $(dp/dt)_{max}$ on inhibitor concentration for lean combustible mixtures, despite of all diluents investigated in the work are noncombustible (except Inh A₁). This effect is caused by an active participation of fluorinated halons in combustion processes with a heat release at their conversion in a flame front. A position of these maxima for ΔP_{max} as a function of [Inh] is displaced as a rule to the minimum inertization concentration of inhibitor.

At a dilution of lean H_2 - air mixtures by C_3F_7H and C_4F_8 anomalous high maximum explosion pressures reaching 1000 kPa are observed. Such high ΔP_{max} do not realize even at a combustion of near-stoichiometric hydrogen - air mixtures in a closed vessel. This result is also caused by an active participation of fluorinated inhibitors in a heat release in a flame front.

A character of influence of C_2F_5I on maximum explosion pressure ΔP_{max} and maximum explosion pressure rise rate $(dp/dt)_{max}$ of hydrogen - air mixtures is rather unusual (see Fig. 5, for which values $\Delta P_{max \circ}$ and $(dp/dt)_{max \circ}$ are presented above). The value of ΔP_{max} as a function of $[C_2F_5I]$ has a maximum, but at the same time the value of $(dp/dt)_{max}$ does not have such a maximum. This effect demonstrates an active role of C_2F_5I in a flame front and a sufficient influence of this inhibitor on a laminar burning velocity.

The peculiarity of curves in Fig. 4 is a rather slow change of the ΔP_v value at low inhibitor contents. Only at [Inh] close to minimum inertization concentration the remarkable change of ΔP_v begins.

Thus we reveal the phenomenon of chemical induction, when combustion of fluorinated halons is induced by the process of hydrogen or methane oxydation in lean combustible mixtures containing relatively high oxygen concentrations. It means, that the chemical reaction limiting induction passes with participation of oxygen and active intermediate products (atoms and radicals) forming at combustion of hydrogen or methane. Two of these intermediate products (O and OH) react with fluorinated halons rather slow because chemical bonds O - F and HO - F forming in these reactions have relatively low break energies. But reaction of separation of halogen atom from a halon molecule by atomic hydrogen is exothermic enough. Halogen radical, which is produced in this reaction, reacts with O_2 , and this stage is probably limiting.

One of the possible mechanisms of a heat release in a flame front at combustion of fluorinated hydrocarbons is their conversion firstly to C_2F_4 by means of active radicals. Then tetrafluoroethylene takes part in combustion process and stipulates a heat release. As it is known [15], tetrafluoroethylene is a combustible gas having flammability limits.

It should be noted, that the phenomenon of combustion of fully fluorinated hydrocarbons induced by a hydrogen flame has been revealed in [16]. In this work combustion of $H_2 - O_2 - C_2F_6$ mixture was investigated. It has been found, that neither $C_2F_6 - O_2$ mixture nor $C_2F_6 - H_2$ mixture are not able to combustion. At the same time the $H_2 - O_2 - C_2F_6$ mixture can propagate flame at some concentrations of components and in combustion at some products of C_2F_6 conversion are present (such as CF_4 , COF_2 etc.), and the initial reactants are absent. This means, that C_2F_6 burns in such flame.

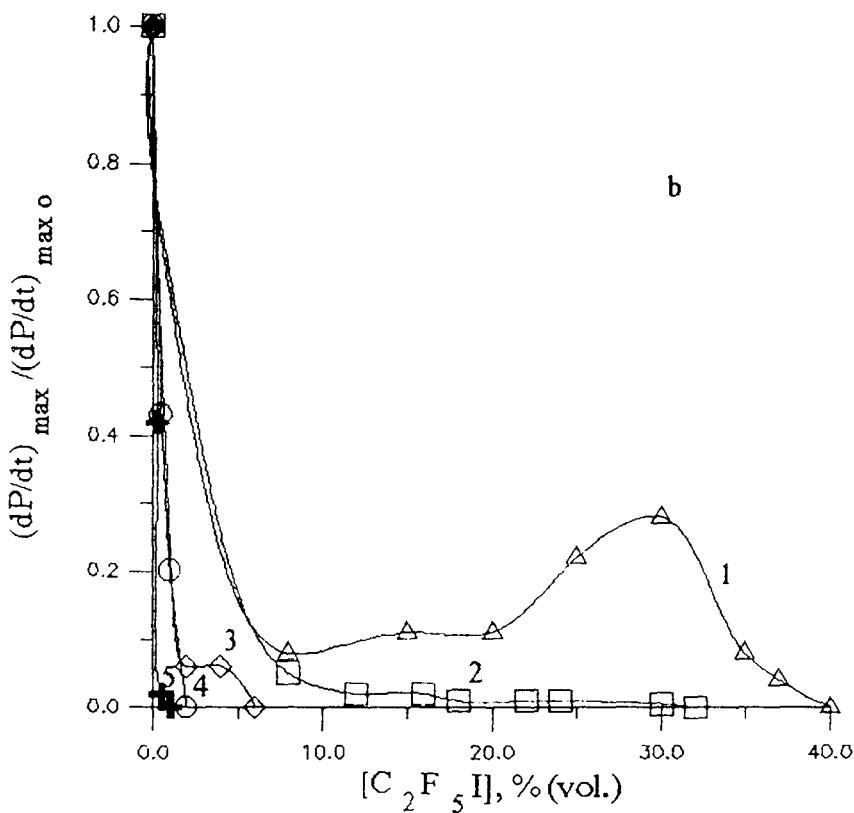
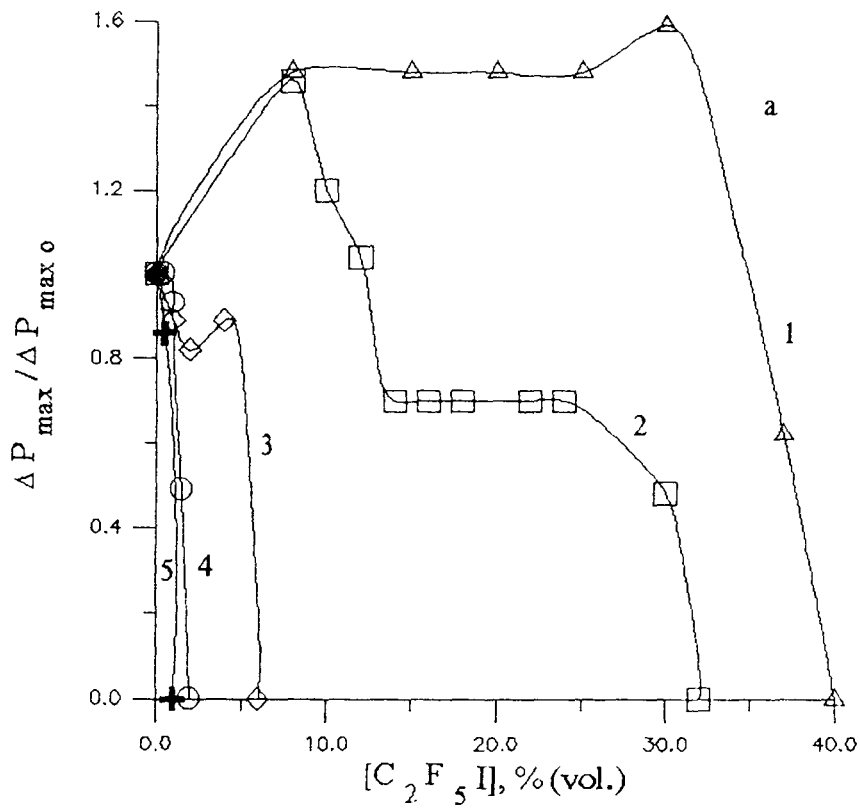


FIGURE 5. Dependence of maximum explosion pressure ΔP_{\max} (a) and maximum explosion pressure rise rate $(dP/dt)_{\max}$ (b) of hydrogen - air mixtures on C_2F_5I concentration.

CONCLUSIONS

An experimental investigation of an influence of various inhibitors (mainly fluorinated hydrocarbons) on combustion of methane - air and hydrogen - air mixtures has been carried out in this work. Flammability limits, maximum explosion pressures, maximum explosion pressure rise rates and rarefaction pressures in a closed vessel after a cooling of combustion products to a room temperature and steam condensation have been determined. A phenomenon of induction of combustion of fluorinated halons by lean hydrogen - air and methane - air flames has been revealed. These halons inhibit combustion of hydrogen and methane at concentrations of these combustibles near upper flammability limits and promote combustion of H_2 and CH_4 in lean mixtures. The availability of effect of promotion does not mean that investigated inhibitors can not use in reach mixtures, where their effectiveness is high enough.

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