

Characteristics of the Development of a Chain Thermal Explosion when Burning Gas Mixtures under Atmospheric Pressure

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Abstract—An experimental study of the features of the critical transition between two kinetic combustion regimes of gas-air mixtures reacting by a chain mechanism is carried out. The presence of two radically different combustion modes is experimentally confirmed by the example of the combustion of propane–air mixtures, both containing an inhibitor (trifluoromethane) and without it, and in complete agreement with the predictions of the theory of A chain thermal explosion (CTE). It is shown that the pattern observed in this work is characteristic not only for slow-burning but also for fast-burning gas mixtures of various compositions. The two distinct and radically different regions observed on the pressure–time variation curve during the combustion of gas mixtures are a manifestation of the general laws which combustible gas mixtures reacting by the chain mechanism follow in a wide range of pressures. It is found that fluorine-containing hydrocarbon is capable of induced oxidation in rich combustible gas mixtures. Trifluoroethane CF₃H has an inhibitory effect on the chain combustion process of the propane–air mixture before it enters the CTE and promotes combustion in the CTE mode. If the transition to the CTE is not possible during the propane–air mixture combustion, the fluorinated agent has only an inhibitory effect on combustion.

Keywords: chain thermal explosion, inhibition, promotion, induced oxidation

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INTRODUCTION

As is known [1, 2], the condition for thermal ignition (thermal explosion) consists of the simultaneous fulfillment of the following relations, ensuring the accumulation of thermal energy in a system with progressive self-acceleration:

$$\dot{q}_+ \geq \dot{q}_-, \quad (1)$$

$$d\dot{q}_+/dT \geq d\dot{q}_-/dT, \quad (2)$$

where \dot{q}_+ is the heat arrival rate, \dot{q}_- is the heat removal rate, and T is temperature. This condition is general; i.e., it is not limited by the nature and mechanism of the reactions.

The condition for branched-chain ignition is the excess of the reproduction rate of active intermediate particles over the rate of their death [2, 3]:

$$f \geq g - 2(w_0k)^{0.5}, \quad (3)$$

where w_0 is the chain nucleation rate and k is the reaction rate constant of the nonlinear branching of the chains.

The author of [4] first drew attention to the fact that, since quantity \dot{q}_+ is equal to the product of the rate of a chemical reaction and its thermal effect, the

extremely strong non-Arrhenius temperature dependence of the rate of the chain process creates particularly favorable conditions for the development of a thermal explosion. It was argued a developing avalanche and self-heating of the process, that mutually reinforce each other, can lead to an explosion even at low pressures [4]. The process of the combustion of gaseous media, in which the mixture is ignited first by the fulfillment of condition (3), then, as the chain avalanche develops, self-heating intensifies (condition (1)) and, when conditions (1) and (2) are fulfilled, a thermal explosion occurs, is called the chain thermal explosion (CTE) [4].

From the proposed CTE concept, there are two different kinetic regimes of the developed gas-phase chain combustion between which there is an abrupt transition: the first one, which occurs when conditions (3) and (1) are met simultaneously is characterized by a relatively low pressure increase that developed during combustion; and the second one arises when conditions (1)–(3) are fulfilled simultaneously; in it the pressure that developed during combustion (and, therefore, self-heating) is much higher, and the process proceeds more intensively.

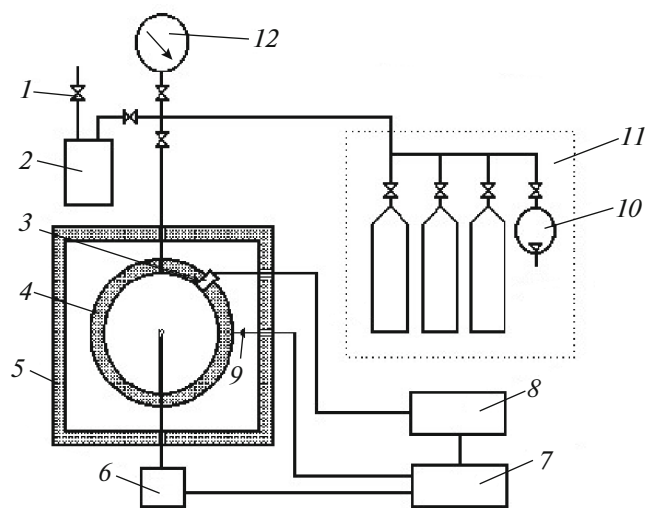


Fig. 1. Experimental installation Variant: (1) valve; (2) steam generator; (3) pressure meter; (4) reaction vessel; (5) thermostat; (6) ignition device; (7) control panel; (8) oscilloscope; (9) thermocouple; (10) vacuum pump, (11) gas injection system; (12) vacuum gauge.

The predicted various kinetic regimes were observed both at low initial pressures of combustible gas mixtures (see, Fig. 4.XI and Section 3 of Chapter XI in [5]), and at the initial pressures close to atmospheric [5, 6]. At high pressures, the effect is most easily detected by burning gas mixtures containing an inhibitor. In Fig. 11.XI from [5], which shows the dependence of the maximum pressure developing during the combustion of a hydrogen–air mixture containing 40% H_2 on the presence of inhibitors in the mixture, kinks are visible on curves 2 and 3: with an increase in the content of the inhibitors above the values to the right of the abscissa of dots a_1 and a_2 , the burning rate (ΔP_{\max} is the maximum pressure that develops during combustion) drops spasmodically due to the violation of condition (2).

At atmospheric pressure, two different kinetic regimes of the developed gas-phase chain combustion were also observed in uninhibited hydrogen–air and methane–air mixtures [6]. As follows from the data presented in Fig. 3.2 from [6], at a hydrogen concentration in the mixture of 17 vol %, a sharp change in the combustion mode is observed: if, as $[H_2]_0$ increases from 15 to 17 vol %, the value ΔR_{\max} increases by 20%, then at the same hydrogen content in the mixture of 17 vol %, a random change in the initial composition of the system, which is within the experimental error, leads to ΔP_{\max} increasing by 260%. A similar picture occurs in rich mixtures at $[H_2]_0 = 60$ vol %.

It should be noted that the difference between the two observed kinetic regimes of the gas-phase chain combustion was evaluated primarily by the difference in values ΔP_{\max} [5, 6] (in [5], also on the change in

chemiluminescence). In the present work, a detailed study of the features of the critical transition between two kinetic combustion regimes of gas–air mixtures reacting by a chain mechanism is carried out.

EXPERIMENTAL DESCRIPTION

The experiments were carried out at the initial atmospheric pressure and initial temperature room at the Variant installation, the scheme of which is shown in Fig. 1. This installation is designed to measure the concentration limits of flame propagation, the maximum pressure developed during combustion (ΔP_{\max}), and the maximum rate of increase in pressure during combustion, $(dP/dt)_{\max}$, in the pressure range 0.1–4.0 MPa. The reaction vessel of the installation has a spherical shape and is made of stainless steel. Its diameter is 20 cm and the volume is 4.2 L. The installation has a system for preparing gas mixtures for partial pressures and a vacuum system. The required gas mixture is formed by the partial pressures in the reaction vessel, previously evacuated to 0.5 kPa. Flame propagation was recorded using a Sapphire-22 pressure transducer designed for continuous pressure measurement with an error of not more than 0.25% [7] and recorded on a digital oscilloscope. It was assumed that flame propagation occurs if the pressure increase exceeds 30 kPa. Relative errors in determining the concentration limits of the effect of additives on flame propagation, the maximum explosion pressure, and the maximum explosion pressure rise rate did not exceed 10%.

In the experiments, mixtures of propane and air were used, both with the addition of an inhibitor, trifluoroethane (CF_3H), and without it. The propane–air mixture was chosen because of the relatively low normal rate of its combustion (0.39 m/s [8]), which should facilitate the visualization of the transition of the gas-phase combustion to the CTE mode. The required gas mixtures were made directly in the reaction vessel. The mixture was allowed to mix for 30 min. The correspondence of the pressure in the reaction vessel to atmospheric pressure was controlled before the experiment on the vacuum gage. The mixture was ignited at atmospheric pressure in the reaction vessel using a spark ignition source with an energy of 2 J, located in the center of the reaction vessel. During the experiment, the maximum explosion pressure and the maximum growth rate of the explosion pressure in the reaction vessel were recorded. For each composition of the initial mixture, the experiment was repeated at least five times.

RESULTS

As follows from Fig. 2, when the propane content is 8 vol % in the propane–trifluoromethane–air mixture, a sharp change in the combustion regime at $[CF_3H]$ 2 vol % is detected depending on the maximum pressure developing during combustion on the

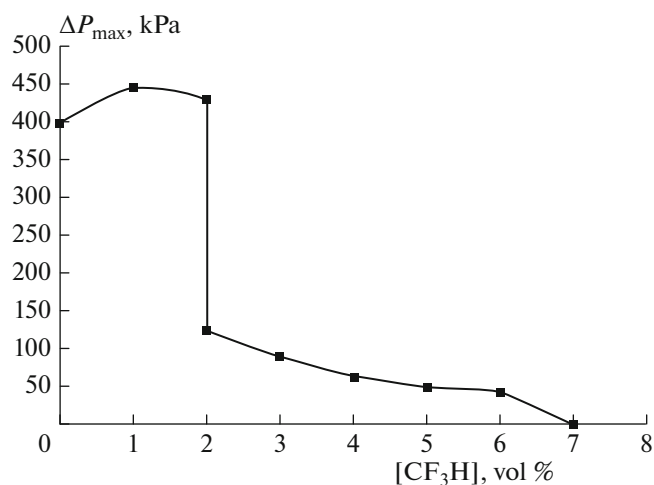


Fig. 2. Dependence of the maximum pressure on the concentration of trifluoromethane during combustion of the developing propane (8% vol.)–trifluoromethane–air mixture.

concentration of trifluoromethane. However, in our opinion, the direct experimental data on measuring the change in the pressure that develops during combustion as a function of time shown in Fig. 3 are of greater interest. As follows from these data, at $[CF_2H]$ -2, 4, and 6 vol %, in the mixture with propane (8 vol %) and air, the dependence of pressure on time has two distinct and radically different regions: the initial region I, which is an *S*-shaped curve with access to a certain plateau, characterized by a small increase in pressure of up to 16 kPa; and region II, with a significantly higher combustion rate, in which pressures develop that are 2.6–26.9 times higher than the pressures in the initial section. At a propane concentration of 8 vol % and the CF_3H content in the mixture of 2 vol %, the random change in the initial composition of the system, which is within the experimental error (0.1 vol %), leads to ΔP_{\max} increasing 3.44 times (Fig. 3a). In our opinion, the experimentally observed picture cannot be described from the standpoint of the classical thermal theory of combustion and is a visualization of the transition of the chain combustion to the CTE mode: the initial section of the pressure growth curve (region I in Fig. 3) during the combustion of a propane–trifluoromethane–mixture air corresponds to a chain process accompanied by self-heating (simultaneous fulfillment of conditions (3) and (1)), and the region of more intense combustion (region II in Fig. 3) corresponds to a CTE (simultaneous fulfillment of conditions (1)–(3)). The existence of a sharp transition from region I to region II in the dependences shown in Fig. 3 also indicates the existence of a critical transition temperature in the CTE, which fully corresponds with the concept of the CTE described in the book [5].

Let us consider in more detail the effect of the addition of trifluoromethane on the transition of the

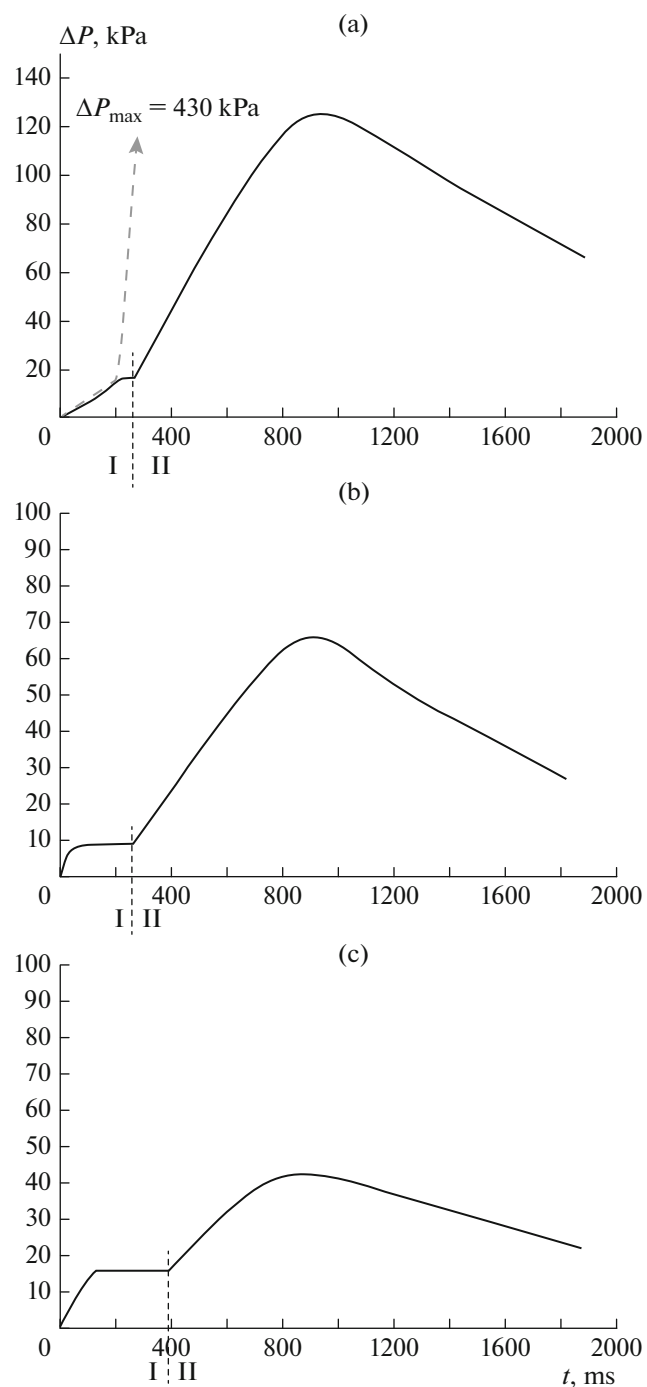


Fig. 3. Dependence of the pressure on time during combustion of mixture of 8 vol % propane–trifluoromethane–air at concentrations of trifluoromethane of 2 (a), 4 (b), and 6 vol % (c).

combustion of a propane–air mixture to the CTE mode. A number of fluorocarbons, including CF_3H , are known and widely used gas suppression agents for the gas-phase combustion. However, these products have a dual effect on the combustion process: together with the inhibitory effect on the gas combustion pro-

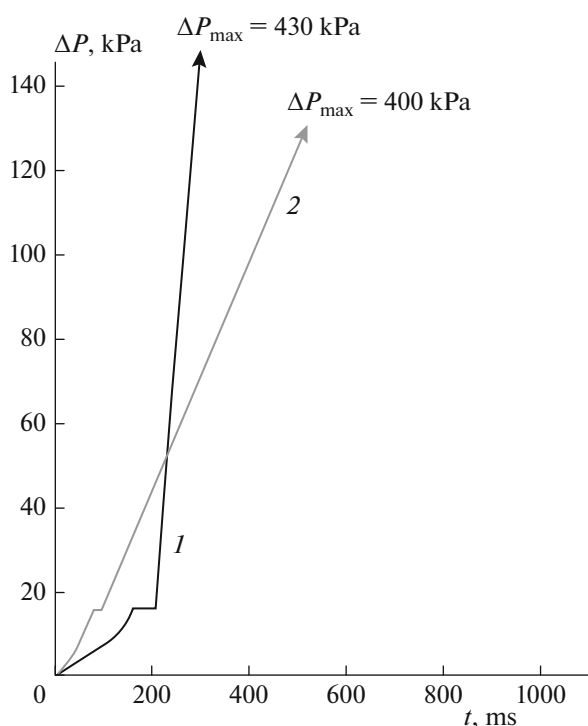


Fig. 4. Features of the effect of trifluoromethane on the combustion of a mixture of 8 vol % propane–air: (1) 2 vol % CF_3H ; (2) 0 vol % CF_3H .

cess, which manifests itself most strongly when exposed to rich mixtures consisting of the interaction of fluorocarbons and the products of its conversion with atomic hydrogen [6, 9], fluorocarbons can themselves turn into flames, providing additional heat during combustion. In particular, it was established [6, 9] that, when added to poor hydrogen–air and methane–air mixtures, CF_3H , $\text{C}_2\text{F}_5\text{H}$, and $\text{C}_3\text{F}_7\text{H}$ are capable of induced oxidation with heat release, which intensifies the combustion of the main (hydrogen–air or methane–air) mixture and significantly reduces the inhibitory effect of fluorocarbons on the combustion process. In general, we can conclude that the effect of fluorocarbons on the combustion of gas mixtures is determined by the competition of two components of the same process: the inhibitory effect of fluorocarbons on the gas-phase combustion and heat generation accompanying the process of their chemical transformation into flames.

The described phenomena certainly manifest themselves upon the action of trifluoromethane on the combustion of a propane–air mixture containing 8 vol % C_3N_8 ; however, the experimentally observed picture is much more complicated than that described in [6, 9]. In contrast to the data presented in these works, which show that the effect of the induced oxidation of fluorocarbons appears only in poor hydrogen–air and methane–air mixtures when exposed to

CF_3H on the combustion of a rich propane–air mixture, it was found that the addition of trifluoromethane in quantities of 1 to 2 vol % increases ΔP_{max} by 7.5–11% compared to burning a propane–air mixture without the addition of CF_3H . It is important to note that such an increase (by about 10%) in the maximum pressure developed during combustion, due to the heat released during the conversion of trifluoromethane into a flame, does not explain the presence of the second region with the peak pressure in Fig. 3 (the pressure increase several times in relation to the initial portion of the curves). Thus, the possible explanation presented in Fig. 3 of the experimental picture, linking the presence of region I with the combustion of a strongly inhibited propane–air mixture, and region II, with the conversion of a fluorine-substituted hydrocarbon, turns out to be unjustified.

As follows from Fig. 4, the addition of 2 vol % CF_3H has an inhibitory effect on the process of the chain combustion of a propane–air mixture before its transition to the CTE: the maximum rate of increase of the pressure in a mixture containing trifluoromethane is half the value of $(dP/dt)_{\text{max}}$ when a propane–air mixture burns without the addition of fluorocarbon. However, in the area of the developed CTE, the situation changes significantly: the additional heat release due to the conversion of fluorocarbon added to the propane–air mixture provides the maximum pressure to rise at a rate that is faster by a factor of 5.3 in the mixture compared to the propane–air mixture without additives; and the maximum pressure is 30 kPa greater than that developed during burning. We also note that with an increasing concentration of trifluoromethane in the mixture, the values ΔP_{max} and $(dP/dt)_{\text{max}}$ decrease significantly (see Fig. 3), and in the situation where only the simultaneous fulfillment of conditions (3) and (1) and the transition to a CTE are impossible, only the inhibitory effect of trifluoromethane is observed.

The picture experimentally observed in this work is not something unique, inherent only in the combustion process of a propane–air mixture. In [10], in which, in the initial atmospheric pressure, the photochemically induced combustion of a mixture of 1,1-difluoroethane with chlorine in the presence of an oxygen inhibitor was studied, just as in the present work, the dependence of the temperature on time at different concentrations of oxygen has two different regions. With the accurate recording of the experimental results, a similar characteristic dependence of pressure or temperature on time is also observed during the combustion of fast-burning mixtures (for example, hydrogen–air) at high (about atmospheric) initial pressures. In particular, in our analysis of the published data, such a dependence was found in Fig. 10.XI from the book [5], which shows the oscillograms of chemiluminescence and pressure during the transition of the combustion of a mixture of 30% H_2

with air in the CTE: the initial portion of the time-dependent pressure developing during combustion in the interval 0–10 ms has the characteristic S-shaped form with access to a plateau (0.25 atm); then there is a transition to the CTE, characterized by a sharp increase in pressure. Another example is the data in Fig. 3.1 from the thesis [6], from which it follows that, if conditions (2) can be satisfied, together with conditions (3) and (1), when burning hydrogen–air mixtures at the initial atmospheric pressure, two regions are observed, the first of which corresponds to the simultaneous fulfillment of conditions (3) and (1); and the second, to the simultaneous fulfillment of conditions (1)–(3). If condition (2) cannot be fulfilled during the combustion process, only the region corresponding to the simultaneous fulfillment of only conditions (3) and (1) is observed.

Thus, we can conclude that the experimental picture observed in the present work during the combustion of a propane–air mixture with or without the addition of fluorocarbon is characteristic of the combustion of gas mixtures reacting at the initial atmospheric pressure by the chain mechanism. The dependences of pressure or temperature on time observed during the combustion of such mixtures can be explained only based on the CTE concept and are its obvious experimental confirmation.

CONCLUSIONS

In the present work, a detailed study of the features of the critical transition between two kinetic combustion regimes of gas–air mixtures reacting by a chain mechanism is carried out. By the example of the combustion of propane–air mixtures, both with an inhibitor (trifluoromethane) additive and without it, in complete agreement with the predictions of the CTE theory, the existence of two radically different combustion modes was experimentally confirmed, one of which is characterized by a relatively small increase in pressure and corresponds to chain combustion accompanied by self-heating without the simultaneous fulfillment of both conditions of thermal ignition, while the other one has a significantly higher combustion rate and corresponds to the CTE. If the simultaneous fulfillment of the conditions of thermal ignition is not possible during the combustion of a gas mixture, only

the first mode of its combustion is observed without transition to the CTE.

Based on the analysis of the experimental data of other works, it is shown that the picture experimentally observed in this work is characteristic not only for slow-burning but also for fast-burning gas mixtures of various compositions. Thus, we can conclude that the two clearly defined and radically different regions observed on the time dependence of pressure during the combustion of gas mixtures are a manifestation of general laws which combustible gas mixtures reacting by the chain mechanism follow in a wide range of pressures (from low (about 20 Torr) to high (atmospheric)).

It was also first discovered in the work that a fluorine-containing hydrocarbon is capable of induced oxidation not only in poor but also in rich combustible gas mixtures. Trifluoromethane has an inhibitory effect on the chain combustion process of the propane–air mixture before it enters the CTE and promotes combustion in the CTE mode. If, during the combustion of the propane–air mixture, transition to the CTE is not possible, the fluorinated agent has only an inhibitory effect on combustion.

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