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# Effect of Olefin + Carbon Dioxide Admixtures on the Ignition of Methane–Air Mixtures

**V. V. Azatyan, G. R. Baimuratova, and S. K. Abramov**

*Institute of Structural Macrokinetics and Materials Research Problems, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*

*e-mail: azatyan@ism.ac.ru*

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**Abstract**—Experimental data are reported on the kinetics and mechanism of methane–air combustion in a closed space at atmospheric pressure and on the effects of inhibitor admixtures and inert gases. Ignition arises and develops as a result of a chain avalanche occurring in the mixture, and self-heating is significant only in developing chain combustion. Admixtures containing propene or isobutene and carbon dioxide (5% olefin + 20% $CO_2$) efficiently prevent the ignition and combustion of methane–air mixtures of any composition.

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Understanding the influence of reactive admixtures on the combustion of methane–oxygen (air) mixtures is essential for solving the problems of explosion prevention and combustion process optimization in power engineering, including engines, and for chemical kinetic theory. The publications devoted to the inhibition of methane combustion mostly consider the effect of admixtures on the flame structure (see, e.g., [1–5]). Most of these studies deal with organophosphorus compounds as inhibitors. There have been numerical simulations of the process based on a hypothetic reaction mechanism (see, e.g., [5]). At the same time, there have been only a few works devoted to the influence of admixtures on the concentration limits of flame propagation and on combustion intensity, and only halogenated hydrocarbons have been examined as admixtures (see, e.g., [6–10]). These admixtures are, however, corrosive and toxic. Furthermore, these compounds are much heavier than air (the molecular weight of tetrafluorodibromoethane is 260) and settle in the course of time, and for this reason alone they are unsuitable as preventers. The manufacturing of many freons, including tetrafluorodibromoethane and trifluorobromoethane, the most popular ones, has been stopped to meet the recommendations of a number of international conventions and to reduce environmental hazards.

It was demonstrated in earlier works [10, 11] that perfluorobutane (12%) prevents the ignition of methane–air mixtures of any composition at atmospheric pressure. The same effect is exerted by the perflurobutane–propane–butane–propylene mixture (8%). The mechanism of the action of organic halides on methane combustion was not investigated. The necessity of use of large amounts of admixtures made it difficult to distinguish the role of reaction chain termination under the action of the admixture from the role of mixture dilution. General drawbacks of these compounds are their low effectiveness and expensiveness.

Here, we report the discovery and study of the prevention of methane–air ignition and combustion under the action of propene– and isobutene–carbon dioxide mixtures and the effect of propene and $CO_2$ on the methane combustion intensity.

## EXPERIMENTAL

The combustion reaction was carried out in a closed cylindrical stainless steel reactor 12.6 cm in diameter and 25.2 cm in height. The hydrocarbons and $CO_2$ were 99% pure. Working mixtures were prepared in the reactor using a partial pressure technique. The relative error in the $CO_2$ and methane concentrations did not exceed 1%. The relative error in the inhibitor concentrations was 4%. The components were admitted into the vacuumized reactor in the following order: olefin, methane, $CO_2$, and air. The initial mixture pressure and temperature were 1.0 bar and 293 K, respectively. The mixture was ignited with a spark produced between electrodes mounted at the bottom of the reactor and charged from a capacitor bank. The energy of the initiating pulse was 3.6 J, which is above the minimum necessary value. Ignition was initiated 15 min after gas admission into the reactor, a time sufficient for the components to mix completely.

From the initiation of combustion until the completion of the process, we simultaneously recorded the mixture pressure and chemiluminescence. The signal from the piezoelectric pressure sensor was amplified and was recorded by a S9-8 double-beam memory oscilloscope with a discretization time of 2 μs. The

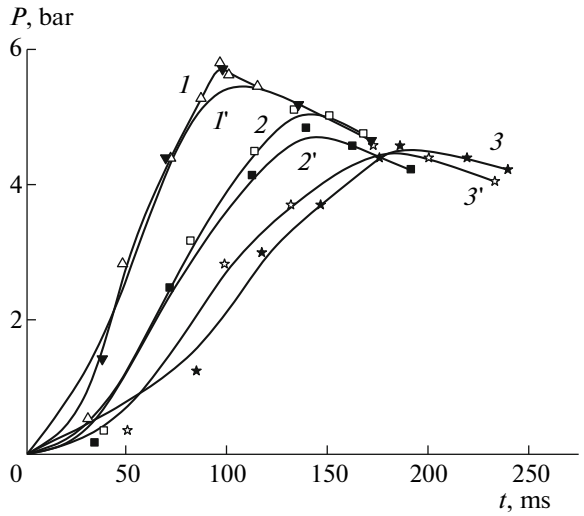


**Fig. 1.** Pressure variation in replica experiments on the combustion of methane–air mixtures with methane concentrations of (*1*, *1'*) 10, (*2*, *2'*) 8.0, and (*3*, *3'*) 7.0%.

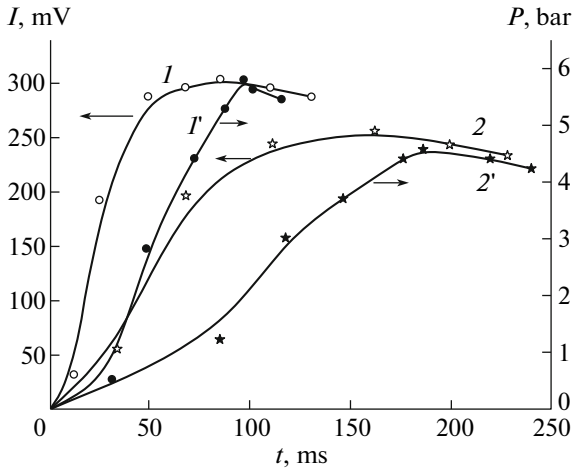


**Fig. 2.** (*1*, *2*) Luminescence and (*1'*, *2'*) pressure variation in the combustion of methane–air mixtures with methane concentrations of (*1*, *1'*) 10 and (*2*, *2'*) 7.0%.

clock frequency of the pressure sensor was 300 kHz. The chemiluminescence of the flame in the 300–600 nm range was recorded with an oscilloscope using a photosensor. After the completion of the reaction, we measured the residual pressure of the mixture. After each experiment, the reactor was pumped down to ≅2 Pa. Ignition was detected as peaks in pressure and chemiluminescence oscillograms and as a pressure drop after the completion of combustion.

Combustion is accompanied by a marked intermediate pressure rise (Fig. 1) as a result of the increase in the gas temperature. Obviously, the gas temperature in the propagating flame zone, which is the place where heat evolution occurs, is higher than the temperature of the unburned gas. Accordingly, the pressure rise ($\Delta P$) characterizes the reactor volume–average temperature rise (and the averaged temperature). This temperature rise is due to the fact that the rate of heat evolution in combustion exceeds the rate of heat removal from the reactor.

The shorter the characteristic reaction time as compared to the characteristic heat removal time, the greater the temperature rise and the closer the average temperature to the combustion zone temperature. Thus, the $\Delta P$ value and its growth rate characterize the heat evolution intensity and, accordingly, the rate of the combustion reaction. It is due to this fact that the chemiluminescence intensity and pressure vary with time in the same way, as can be seen from the oscillograms presented in Fig. 2: both grow at an increasing rate (are concave upwards), pass through a maximum, and then descend comparatively slowly. The duration of the decline of the luminescence intensity after the maximum depends considerably on the duration of light emission by the water and $CO_2$ molecules forming in the flame. The pressure decrease kinetics is largely determined by the gas cooling time after combustion. The olefin concentrations did not exceed the lower concentration limits of flame propagation for the olefin–air mixtures.

## RESULTS AND DISCUSSION

The pressure variation carves presented in Fig. 1 by way of example, which refer to three different methane–air mixtures, illustrate the good reproducibility of our experiments. The highest self-heating and the maximum combustion rate are observed for near-stoichiometric mixtures, in which the methane concentration is ≈9.5% (Fig. 3).

The kinetic curves plotted in Fig. 2 demonstrate that, for both mixtures, the maximum growth rate of

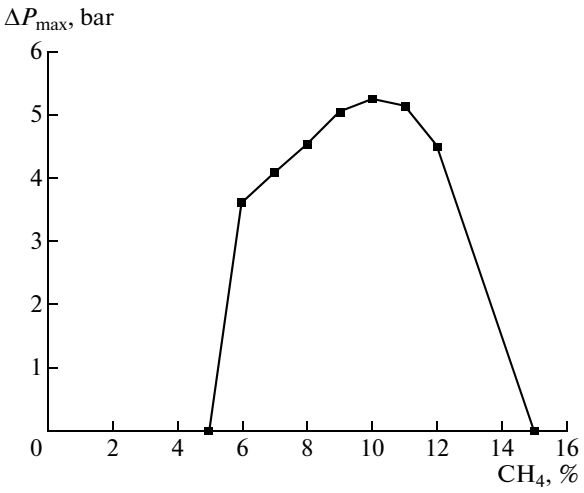


**Fig. 3.** Maximum pressure rise during the combustion of methane–air mixtures as a function of the initial methane concentration.

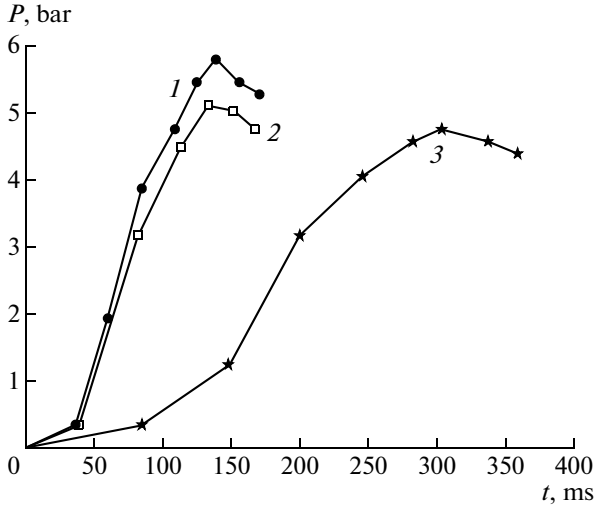


**Fig. 4.** Pressure variation in the combustion of the (*1*) 8% $CH_4$ + 2% $C_3H_6$ + air, (*2*) 8% $CH_4$ + air, and (*3*) 8% $CH_4$ + 15% $CO_2$ + air mixtures.

the chemiluminescence intensity ($I$), indicated by the maximum slope of the luminescence curve, is reached sooner than the maximum pressure growth rate ($\Delta P$), i.e., the highest self-heating. Therefore, ignition arises and develops as a result of a chain avalanche occurring in the mixture, and self-heating is significant only in developing chain combustion. This is also indicated by the fact that the $I$ maxima are observed earlier than the $\Delta P$ maxima (Fig. 2). Our analysis of data of other authors [5] demonstrated that further evidence in favor of the branched chain mechanism of methane combustion is the hydrogen atom concentration reaching 1.5% of the initial $O_2$ concentration. Indeed, taking into account the experimental data for the hydrogen atom concentration in the methane flame (which can be high as 0.09% of the entire mixture [3, 4]), the rate constants of the reaction

$$H + O_2 = OH^{\bullet} + O, \qquad (I)$$

and of the intermolecular reaction between $CH_4$ and $O_2$ ($1.9 \times 10^{14}\exp(-8350/T)$ and $2 \times 10^5 T^{2.745}\exp(-26\,040/T)$ cm$^3$ mol$^{-1}$ s$^{-1}$, respectively [12–14]), and the fact that the gas temperature in the combustion zone does not exceed 1800 K [3, 4], one can readily see that the rate of reaction (I) in the methane flame is higher than the rate of the molecular reaction between $O_2$ and $CH_4$ by a factor of several hundreds. Therefore, $O_2$ is consumed in reaction (I), which yields O atoms and $OH^{\bullet}$ radicals, to an incomparably greater extent than in its molecular reaction with methane. Reaction (I), which multiplies free valences, is the initial event of chain branching. It is followed by fast reactions of the resulting O atoms and $OH^{\bullet}$ radicals with methane:

$$OH^{\bullet} + CH_4 = H_2O + CH_3^{\bullet}, \qquad (II)$$

$$O + CH_4 = OH^{\bullet} + CH_3^{\bullet}. \qquad (III)$$

The $CH_3^{\bullet}$ radicals at typical methane combustion temperatures (above 1500 K) are largely involved in the reactions

$$CH_3^{\bullet} + O_2 = CH_2O + OH^{\bullet}, \qquad (IV)$$

$$CH_3^{\bullet} + O_2 = CH_3O + O. \qquad (V)$$

These reactions are followed by the formation of CO and the regeneration of H atoms:

$$CH_2O + O_2 = HCO^{\bullet} + HO_2^{\bullet}, \qquad (VI)$$

$$HCO^{\bullet} + O_2 = HO_2^{\bullet} + CO, \qquad (VII)$$

$$CO + OH^{\bullet} = CO_2 + H. \qquad (VIII)$$

It is these multiply recurring reactions that constitute the branched reaction chain. Another significant reaction in the flame is

$$H + HO_2^{\bullet} = 2OH^{\bullet}. \qquad (IX)$$

Leaving aside the other reactions in the methane combustion mechanism, note that, in the absence of an inhibitor, chain termination involves the $CH_3^{\bullet}$ and $HO_2^{\bullet}$ radicals and products of their recombination reactions. Reaction

$$H + CH_4 = H_2 + CH_3^{\bullet} \qquad (X)$$

replaces hydrogen atoms with a much less reactive chain carrier. Therefore, to the extent to which the methyl radical causes chain termination, this reaction is a chain termination and methane combustion self-inhibition step. This is indicated by the fact that minor methane admixtures inhibit the ignition of hydrogen–air mixtures.

In the presence of an olefin, there is additional efficient chain termination, which is primarily due to the addition of an H atom to the olefin (RH) molecule:

$$H + RH = R_1^{\bullet}, \qquad (XI)$$

where $R_1^{\bullet}$ is the alkyl radical mainly responsible for chain termination. The activation energy of reaction (XI) is no higher than 6.5 kJ/mol [13, 15]. Because of this, reaction (XI) competes efficiently with free valence multiplication reaction (I). The alkyl radical resulting from reaction (XI) reacts with an oxygen molecule:

$$R_1^{\bullet} + O_2 = R_1O_2^{\bullet}. \qquad (XII)$$

A considerable part of the alkyl peroxy radicals decompose under combustion conditions to regenerate the olefin:

$$R_1O_2^{\bullet} = RH + HO_2^{\bullet}. \qquad (XIII)$$

Note that, when ignition is prevented by an inhibitor, no reaction takes place and $O_2$ is not consumed, as was mentioned above. Accordingly, the inhibitor is not consumed either. Thus, preventing ignition, the inhibitor does not lead to oxygen consumption. This is evidence that ignition prevention is not due to only oxygen consumption in the inhibitor–oxygen reaction. Therefore, the fact that the radicals forming from the initial inhibitor during combustion react with $O_2$ is not

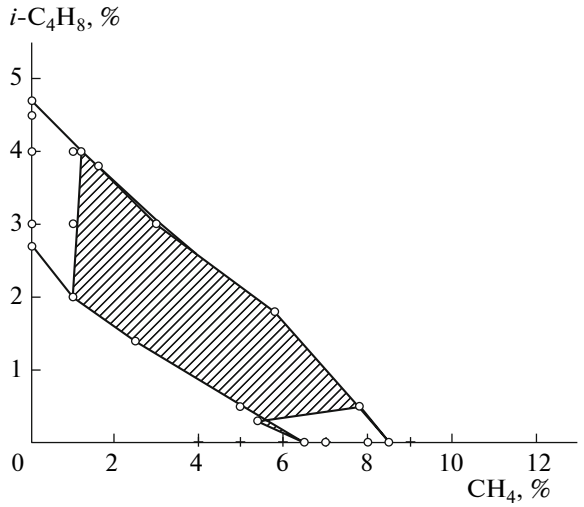


**Fig. 5.** Concentration region of the ignition of the $CH_4$ + $i$-$C_4H_8$ + 20% $CO_2$ + air mixture.

the consequence of only oxygen consumption. This work is aimed at preventing methane ignition and, in some cases, reducing the intensity of methane combustion.

After producing a spark, neither a pressure change nor chemiluminescence is detected in such mixtures. No pressure change in the mixture is also observed after the run. A similar effect is exerted by isobutene–$CO_2$ admixtures. The results of some experiments are presented in Fig. 4.

Our experiments showed that, by varying the admixture composition and concentration, it is possible to control the intensity of combustion (Fig. 4).

Our measurements demonstrated that admixtures containing >5% olefin + 20% $CO_2$ prevent the ignition and combustion of any methane–air mixtures on attempted initiation (Fig. 5).

Since the rate of the chain process depends exponentially on the reactant concentrations, $CO_2$ admixtures, diluting the mixture, considerably reduce the reaction rate and self-heating and are thus favorable for the chain termination rate exceeding the branching rate. This is the cause of the observed inhibition of ignition and combustion.

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