Study of cool-flame phenomena during self-ignition of methane—oxygen mixtures

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Experimental studies and kinetic simulation have shown that the formation of cool flames is as typical of oxidation of methane as of oxidation of its homologs. Phenomena peculiar to the cool-flame processes in closed systems are observed, namely, the region of a negative temperature coefficient of the reaction, single and double cool-flame flashes, two-stage ignition, and light radiation in the range of luminescence of formaldehyde.

Key words: methane, oxidation, cool flames, kinetic simulation.

During free-radical oxidation of hydrocarbons, critical phenomena are observed such as cool-flame ignition and periodical processes of various types.[1—9] The main indication of the existence of cool flame is a rapid increase in the temperature, which usually does not exceed 100—200 °C, and subsequent retardation of the process, before the chemical transformation of the reactants is completed. Two or more cool-flame flashes can occur. In those cases where the cool flame is followed by self-ignition of the mixture, the process consists of at least two stages: the cool-flame stage and hot ignition.

At present, the most common opinion is that cool-flame processes are closely connected to the existence of a region of negative temperature coefficient (NTC) of the reaction rate (or that these processes result from the presence of this region[7,9,10]). It is clear that if, in some temperature region, the reaction rate can decrease as the initial temperature increases, then during the spontaneous self-heating of the reaction mixture the rate of the process would decrease in a similar way thus leading to characteristic cool-flame phenomena.

In all cases where cool-flame processes have been observed during oxidation of hydrocarbons, the existence of an NTC region has been simultaneously detected.[7,9] Only the behavior of methane remained obscure. Until now, it has been difficult to state unambiguously that a cool flame or NTC region or, especially, both of them occur during the methane oxidation. This question is of fundamental importance. In fact, the absence of cool flames or NTC region in the oxidation of methane is easier to explain than their occurrence, because methane differs substantially in its properties from other alkanes.

Only one paper has been published in which the region of cool-flame flashes during oxidation of methane was studied experimentally.[11] This result was not confirmed or reproduced by other researchers and is almost neglected in analyses of the general picture of cool flames in the oxidation of hydrocarbons.[1—9] Some researchers have noted the specific case of methane,[4,5,8] in particular, the fact that the diagram of the ignition of methane in the pressure—temperature coordinates presented in the known paper[11] contains no peninsula of two-stage low-temperature self-ignition.[5,8] It was stated that the mechanism of the limit of two-stage ignition found[11] for methane at ~500 °C differs from the mechanism of the low-temperature ignition limit observed for higher hydrocarbons.[5,12] A description of the existence of an NTC region during the methane oxidation at pressures close to the atmospheric pressure, not supported by any experimental evidence, has also been reported.[2] In addition, periodical temperature oscillations have been observed in the oxidation of methane at pressures of 25—35 atm.[13]

The purpose of this work was to study experimentally the possibility of the existence of cool flames and of an NTC region during methane oxidation and to perform kinetic simulation of these phenomena.

Experimental

The paper[11] in which cool-flame flashes in the $2CH_4+O_2$ mixture were observed is still the only detailed experimental study dealing with this topic. The main reason why this phenomenon has not been observed in other studies is the fact that the region in which cool flames exist depends strongly on the reactor size, the state of its surface, and the composition of the reaction mixture. Therefore, first of all, it was necessary to obtain convincing experimental evidence for the validity of the results obtained in the previous paper.[11]

Oxidation of methane was carried out in a 100-mm long cylindrical quartz reactor 36 mm in diameter with external electric heating. The prepared gas mixture was injected into

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the reactor preheated to a specified temperature. The temperature of the gas mixture was measured at the center of the reactor by a 0.2-mm thick chromel to alumel thermocouple coated with sprayed quartz. In addition to the measurement of the temperature by a piezoelectric transducer, variation of pressure in the reactor and the luminescence of the mixture in the λ = 380 to 500 nm region were detected. To determine the composition of the mixture in a specified instant of time during the reaction, gas samples were withdrawn and analyzed either by chromatography (columns with 5A molecular sieves) or by IR spectroscopy (using IRS-29U and FT-IR spectrometers).

Initially the experiments were carried out with a mixture of the composition $2CH_4+O_2$ at various pressures up to atmospheric pressure in the 743—823 K temperature range. These conditions are close to those used in the known study mentioned above.[11] At pressures above 550 Torr, temperature peaks were observed, the maximum heating being more than 30 K; they were accompanied by the corresponding luminescence peaks (Fig. 1). A pressure increase results in an increase in the luminescence intensity and in an increase in the maximum temperature rise to >100 K. At pressures of >650 Torr, signs of inflection are observed at the back fronts of the curves, whereas at pressures of >700 Torr, a repeated flash, whose amplitude is approximately half that of the first flash, is clearly manifested. In the case of the luminescence curves, the signs of repeated ignition appear earlier and the peaks are better resolved (see Fig. 1).

Up to the instant corresponding to the minimum temperature between the peaks, only ~40% of the oxygen is consumed, whereas during the two flashes, less than 80% of the oxygen is converted. Less than 60% of the oxygen is consumed during a single flash, *i.e.*, the termination of the reaction is not due to the consumption of the reactants. The low values of the maximum temperature rise during the flashes, termination of the reaction before the reactants are completely consumed and its subsequent acceleration (the second peak), and the intense luminescence in the region of emission by formaldehyde make it possible to attribute confidently the flashes observed to cool-flame phenomena. Carbon monoxide is formed as the main reaction product in a yield of no less than 70—80% of the converted methane. The yield of carbon dioxide is much lower (~10%). Formation of ethane and ethylene in a 1—3% yield was also detected.

The region of existence of cool flames, which we found experimentally for the $2CH_4+O_2$ mixture and which is located between the slow reaction and the hot ignition regions, is shown in Fig. 2. Our results confirm the data[11] on the existence and position of the cool-flame region in the oxidation of methane.

Experiments with mixtures of various compositions showed that the possibility of cool-flame ignition depends largely on the methane to oxygen ratio. When the proportion of oxygen decreases as slightly as from 33%, which is well known to ensure the highest reaction rate,[1] to 28% (p = 750 Torr, T = 781 K), the repeated flashes virtually disappear. When the

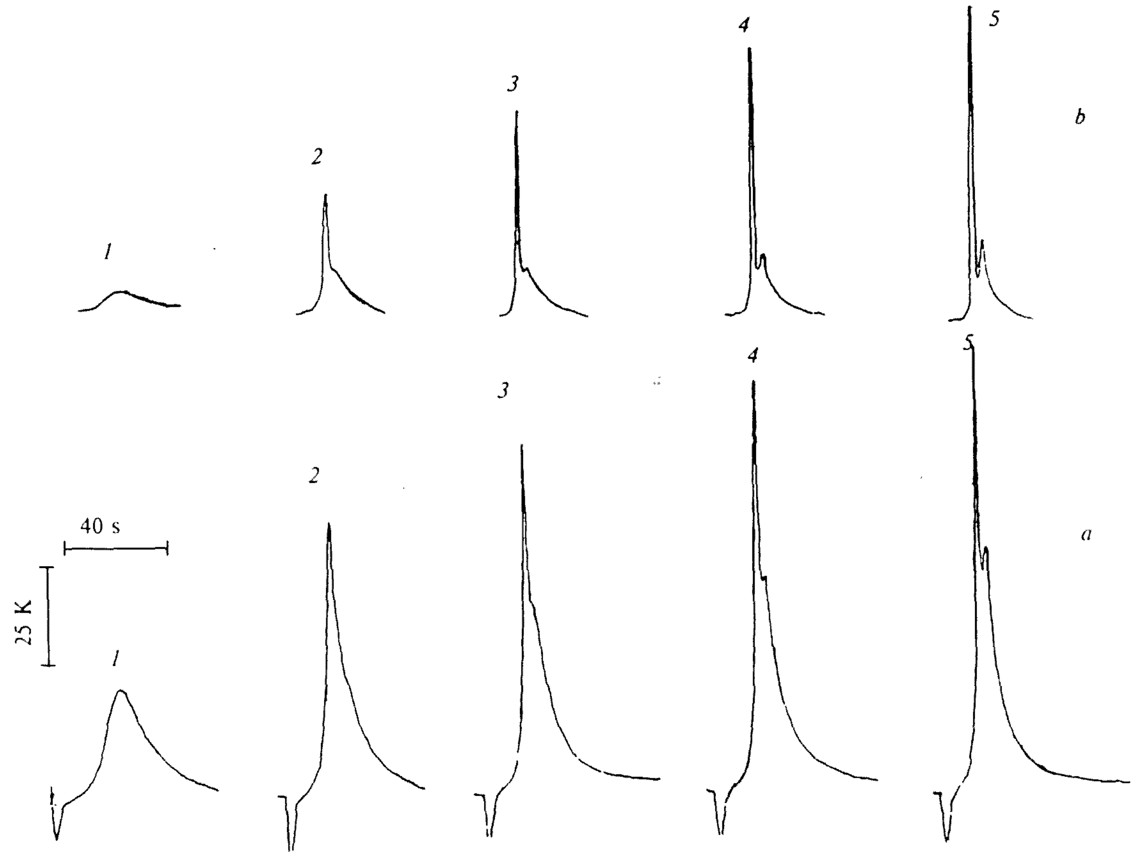

Fig. 1. Variation of the shapes of the temperature (*a*) and luminescence (*b*) curves during the oxidation of the $2CH_4+O_2$ mixture, T = 784 K and p/Torr: 585 (*1*); 650 (*2*); 683 (*3*); 709 (*4*); and 727 (*5*).

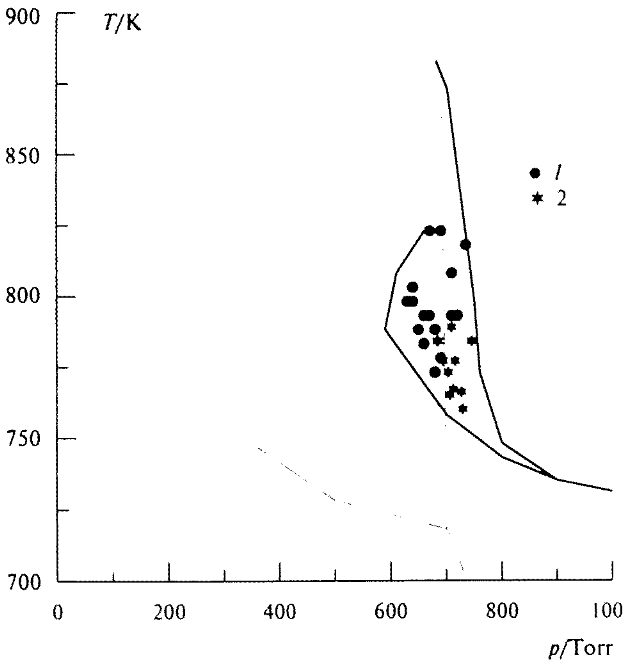

Fig. 2. The cool-flame region during the oxidation of the $2CH_4+O_2$ mixture: single (*1*) and double (*2*) cool-flame flashes. The solid line confines the region of cool-flame flashes and two-stage ignition, according to published data,[11] while the dashed line shows the calculated region of cool-flame flashes and two-stage ignition.

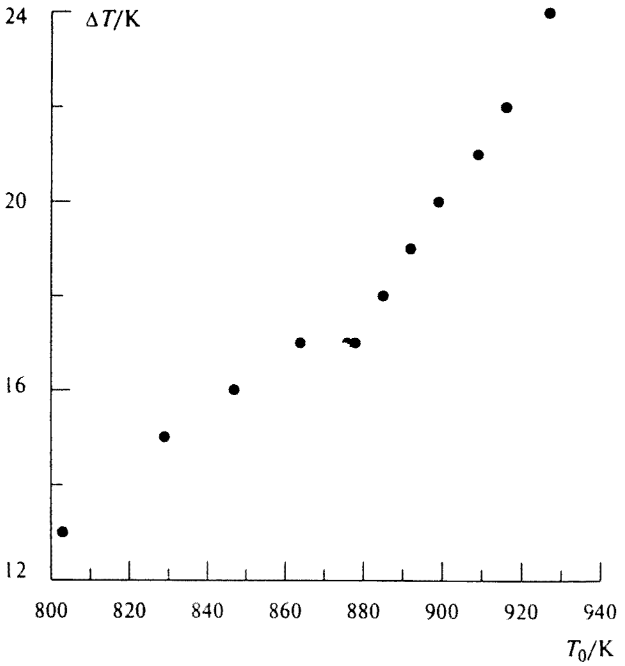

Fig. 3. Experimental dependence of the maximum temperature rise ΔT_{max} on the initial temperature during the oxidation of the $2CH_4+O_2$ mixture at p = 456 Torr.

proportion of oxygen in the mixture is lower than 25% cool-flame flashes are not detected at all at pressures down to the atmospheric pressure.

In the search for the region of the existence of NTC, the maximum value of the temperature rise in the mixture ΔT_{max} was taken as the quantitative measure of the reaction rate. The search for the NTC region was carried out with mixtures of the optimal composition $2CH_4+O_2$ at pressures of 400—500 Torr. In this region, the reaction proceeds with no signs of self-ignition at any of the initial temperatures studied. Figure 3 shows the dependence of ΔT_{max} on the initial temperature of the mixture T_0 for an initial pressure of 456 Torr. It can be seen that in the 850—880 K region, the maximum heating of the mixture and, hence, the maximum reaction rate no longer increase with an increase in the initial temperature. Thus, this temperature range is the region of negative (or zeroth for this particular pressure) temperature coefficient of the reaction rate.

A series of experiments was carried out with mixtures in which up to 10% of methane had been replaced by hydrogen. The experimental results obtained for the oxidation of methane—hydrogen mixtures are presented in Fig. 4. The addition of hydrogen results in a monotonic increase in the induction period, which is defined as the time elapsed from the instant the mixture is injected into the reaction till the maximum heating of the mixture. The magnitude of the largest heating passes through a maximum at a hydrogen concentration of 6—8% and then it rapidly decreases. In the case of double flashes, the addition of 6% hydrogen leads to a twofold increase in the temperature rise in the first peak and to a decrease in the temperature rise in the second peak; however, the peaks become better resolved (see Fig. 1). As the concentration of hydrogen is increased further, the second flash initially disappears and later ignition does not occur at all.

To find out whether or not these changes are due merely to the high heat conductivity of hydrogen, we carried out a series of experiments in which helium was added instead of hydrogen. However, even when the concentration of helium was

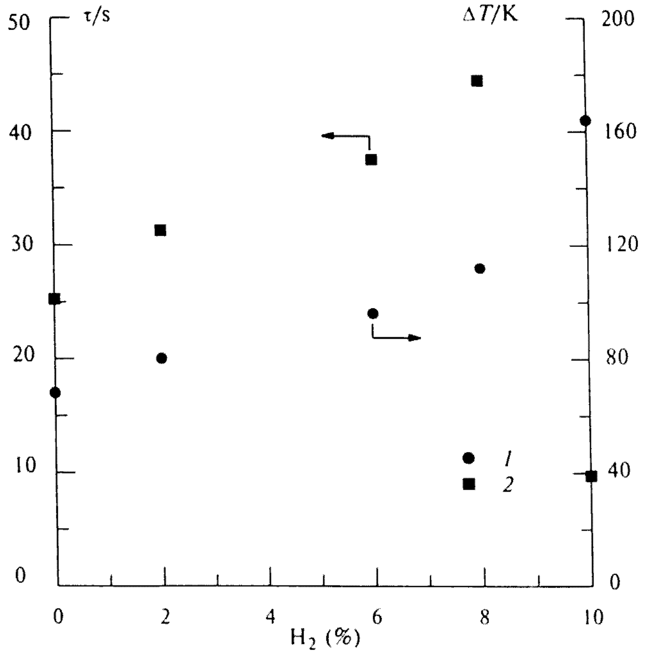

Fig. 4. The effect of the hydrogen concentration on the induction period τ_{ind} (*1*) and the maximum temperature rise ΔT_{max} (*2*).

10%, the increase in the induction period was no more than 4% of the corresponding increase following the addition of hydrogen. Upon the addition of this amount of helium, the shapes of the temperature curves and the values of the maximum temperature rise in the flashes, including the ratio between them, virtually did not change. Thus, the effect of hydrogen on the cool-flame oxidation of methane is mostly associated with its role in the chemical mechanism of the process. It is of interest that the cool flames arising during the oxidation of ethane are not affected markedly by the addition of small (up to 7%) amounts of hydrogen, whereas 40% hydrogen added inhibits the appearance of cool flames.[14]

Mathematical simulation of the process was based on the model developed previously for the oxidation of methane.[15] The coefficient of heat transfer to the reactor walls was calculated, taking into account the heat conductivity of the mixture of a given composition, the size and shape of the reactor, and the initial pressure and temperature.

The mathematical simulation of the methane oxidation in the $2CH_4+O_2$ mixture gave several main types of plots of the temperature and oxygen concentration against the reaction time. At a pressure of ~1 atm, a sharp increase in the temperature is observed, which persists until oxygen is completely consumed. This corresponds to normal ignition of the mixture. When the initial pressure p_0 decreases, two peaks of ignition similar to those observed experimentally arise on the $T(t)$ curve. Further decrease in the initial pressure leads to single ignition peaks, and then to kinetic curves corresponding to slow oxidation. A similar transformation of the shape of the curves of the heating of the reaction can be obtained by decreasing gradually the initial temperature of the reaction at a constant pressure.[16]

The results of the simulation coincide qualitatively with the experimental data; however, there are some quantitative differences. The range in which cool flames exist according to the simulation results starts at a pressure (~300 Torr), which is almost twice lower than that observed experimentally (see Fig. 2). In addition, the values of the maximum temperature rise in the mixture obtained by calculations, ΔT_{max} = 350 to 360 K, are three times larger than the experimental values (100—120 K). The observed disagreement with experimental results must be due to the fact that the effect of the reaction surface was not adequately taken into account in the calculations, because cool-flame phenomena are extremely sensitive to the state of the reactor surface.

The simulation of methane oxidation at pressures beyond the range in which cool flames exist, similarly to the experiments, led to a region of NTC. The maximum reaction rate was determined either from the ΔT_{max} value, *i.e.*, as was done in the experiments, or from the calculated maximum rate of the consumption of oxygen. Although the NTC obtained in calculations is more pronounced, is displaced to higher temperatures, and occupies a broader temperature range, the results of simulation can be considered to agree qualitatively with the experimental results.

Previously, we have shown by kinetic simulation that there is a possibility of cool-flame oxidation of methane as the first stage of the two-stage self-ignition of the mixture at pressures up to 100 atm.[16] Since the first stage lasts several microseconds, it is difficult to detect experimentally.

Results and Discussion

Since it was found that the oxidation of methane involves both cool-flame flashes and a region of NTC of the reaction, these phenomena can be explained within the framework of a general approach to the nature of cool-flame phenomena in hydrocarbons of the methane series.

The chain branching in the low-temperature region of the methane oxidation occurs *via* the formation and decomposition of methyl hydroperoxide arising in the reaction of methylperoxide radicals with methane. When the temperature increases, the concentration of MeOO• radicals decreases, in conformity with the equilibrium

$$Me^\bullet + O_2 \rightleftharpoons MeOO^\bullet \qquad (1)$$

hence, the concentration of branching molecules MeOOH also decreases. This results in the reaction rate decreasing upon an increase in the temperature in a certain temperature range, *i.e.*, in the phenomenon of NTC of the reaction. In fact, in the simulated oxidation of methane, a 10-fold increase in the rate constant k_{-1} of the corresponding reaction leads to a substantial increase in the induction period and to a decrease in the temperature rise ΔT down to the values close to those obtained experimentally.

The foregoing is valid if the displacement of equilibrium (1) to the left with an increase in the temperature is accompanied by efficient removal of the methyl radicals, since only in this case, does this displacement lead to a decrease in the concentration of MeOO• radicals in the system. A specific feature distinguishing the oxidation of methane is probably that the most efficient pathway to the removal of the alkyl radicals in this case is their recombination.

$$Me^\bullet + Me^\bullet + (M) \longrightarrow C_2H_6 + (M) \qquad (2)$$

The elimination of this reaction from the kinetic scheme of the methane oxidation leads to the disappearance of cool flames over the whole region of their existence and to "hot" ignition.

Elucidation of the detailed mechanism of the cool-flame flashes was beyond the scope of our study. The kinetic model[15] used in the calculations contains 63 homogeneous and 6 heterogeneous elementary reactions. Since the character of the cool-flame flashes and the position of the region of a NTC of the reaction depend strongly on the state of the reactor surface, quantitative analysis of the mechanism of these phenomena is complicated.

To understand the mechanism of the cool-flame ignition, it is significant to elucidate whether it begins by a purely branched chain mechanism or has a thermal chain character from the very beginning. For this purpose, isothermal and nonisothermal calculations of the kinetics of the oxidation of methane in the cool-flame ignition region were carried out. The results of these calculations are shown in Fig. 5. The curve shown in Fig. 5, *a* illustrates the typical variation of the temperature in a cool-flame flash. Figure 5, *b*, *c* show the variations in the concentrations of oxygen and methyl

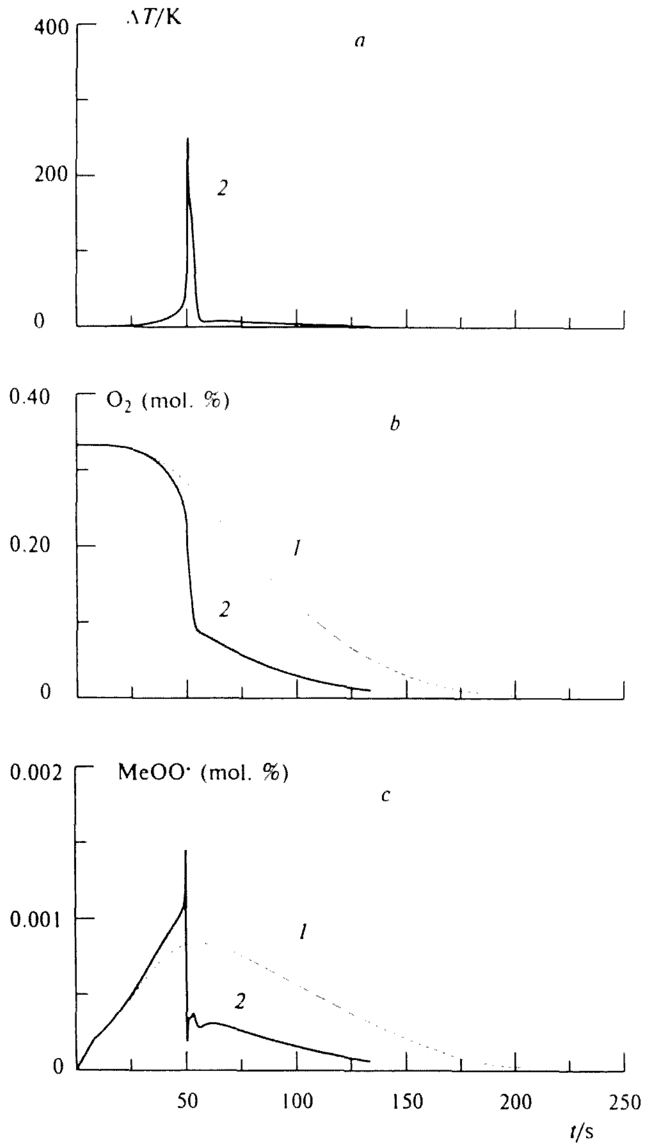

Fig. 5. Kinetics of the variation of temperature (*a*), oxygen concentration (*b*), and MeOO$^\bullet$ radicals (*c*) obtained by the isothermal (*1*) and nonisothermal (*2*) calculations (2 CH_4+O_2 = 2 : 1, p = 585 Torr, T = 748 K).

peroxide radicals calculated for isothermal (curve *1*) and nonisothermal (curve *2*) conditions.

The most important conclusion that can be drawn from the plots shown in Fig. 5 is that the cool-flame process always starts as a purely chain process capable of developing under isothermal conditions. This follows from the fact that in the initial stages of the process, the results obtained in terms of isothermal and nonisothermal models coincide. It should be noted that the double flash, which is poorly resolved in temperature, is resolved very well in the behavior of radicals.

The qualitative agreement of the calculations carried out in the present study with experimental results was achieved without any adjustment of the kinetic parameters of the model[15] except the allowance for the dependence of rate constants of some reactions on pressure. We have not attempted to obtain a closer agreement with experimental results but have only elucidated the possibility of kinetic description of reactions of this type.

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