

Kinetic Manifestations of Low-Temperature Combustion of Hydrocarbons and Hydrogen: Cool and Intermittent Flames

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Abstract: Phenomena inherent in degenerate branched and completely branched chain reactions are considered from a unified viewpoint. In the case of degenerate branched chain reactions, such phenomena include a negative temperature coefficient, cool flames, and oscillations arising in slow combustion of hydrocarbons. Another phenomenon (intermittent flames) is inherent only in completely branched chain reaction of low-temperature combustion of hydrogen at reduced pressures in the presence of SO₂ additives. These kinetic manifestations of chain branching processes are characterized by a variety of elementary reactions with participation of intermediate compounds and free radicals with different structures. A specific kinetic feature of reactions of both types is simultaneous participation of the active center responsible for chain branching in the branched reaction and in the reaction of propagation of an ordinary chain.

Keywords: slow combustion of hydrocarbons, low-temperature hydrogen flame, chain reactions, cool and intermittent flames, negative temperature coefficient.

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INTRODUCTION

The processes of slow combustion (oxidation) of hydrocarbons and also low-temperature combustion of hydrogen are branched chain reactions whose evolution is determined by proceeding of parallel and consecutive elementary reactions with participation of free radicals and atoms. The possibility of proceeding of these complicated processes at low temperatures is provided by the low activation energy of these elementary reactions. It is known that slow combustion of hydrocarbons follows a degenerate branched mechanism and is characterized by a large variety of elementary reactions with participation of free radicals having complex structures. Apparently, these specific features are responsible for kinetic manifestations of oxidation processes: slow combustion of hydrocarbons, such as a negative temperature coefficient (NTC) of the reaction rate, cool flames, and thermokinetic oscillations. Various ideas were put forward and various macrokinetic models were considered to explain the nature of these phenomena [1–7].

It should be noted that the interest to cool flames, NTCs, and oscillations is still high owing to the necessity of taking into account the influence of these factors on the dynamics, kinetics, and mechanisms of hydrocarbon oxidation and combustion in practice. Thus, for instance, the following issues have been studied: effect of gravity on cool flames [8], effect of the NTC on combustion of various hydrocarbons [9], effect of cool flames on spontaneous ignition and ignition delay time for various combustible mixtures [10, 11], on combustion of surrogate fuels [11, 12], and on combustion of hydrocarbons in various devices and rapid compression machines, including combustion in the homogeneous charge compression ignition (HCCI) mode [13–15], and effect of cool flames and oscillations on the emergence of carbon knocks in engines [16].

In almost all publications, the influence of this or that phenomenon on the examined processes was studied for each phenomenon separately. Meanwhile, all these processes occur almost under identical conditions in narrow ranges of variation of the process parameters: pressure p and temperature T .

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In contrast to degenerate branched reactions, completely branched chain reactions, in particular, the hydrogen oxidation reaction, do not manifest any kinetic deviations from theoretical predictions. Nevertheless, they are manifested in low-temperature combustion of hydrogen in the presence of SO_2 additives and also at temperatures and pressures characterizing the region of autoignition of hydrogen–oxygen mixtures with addition of SO_2 ($T = 450\text{--}510^\circ\text{C}$ and $p \leq 200$ torr) at certain flow velocities of reacting gases. Continuous combustion transforms to a sequence of alternating flashes of certain frequency and intensity, which was called an intermittent flame [17–19]. Thus, branched chain reactions proceed both in slow combustion of hydrocarbons and in low-temperature combustion of hydrogen (degenerate branched reactions in the first case and completely branched reactions in the second case).

The challenge of the present review is to summarize the results of studying NTC phenomena, cool flames, and thermokinetic oscillations by methods that allow identification of free radicals and to consider their kinetic behaviors in these processes.

Based on experimental data, a kinetic model is constructed, which demonstrates the relationship between the experimentally observed phenomena: cool flames, NTCs, and oscillations.

To study intermittent flames in the case of a completely branched chain reaction of hydrogen oxidation, a special technique was developed to register emission from consecutive flashes. This technique also allows studying the evolution of a single flash and provides information about the influence of SO_2 addition on autoignition of hydrogen–oxygen mixtures.

Results for reactions of both types are considered from a unified viewpoint and are interpreted as kinetic specific features of branched chain reactions in cases with a competition of these reactions under certain conditions, where the active center responsible for branching simultaneously enters the reaction of ordinary chain propagation.

COOL FLAMES AND NEGATIVE TEMPERATURE COEFFICIENT OF THE REACTION RATE

The concept about the nature of cool flames (CFs) and the phenomenon of a negative temperature coefficient of hydrocarbon oxidation reactions became more grounded when a kinetic method was developed for freezing out radicals with subsequent registration of these active centers by the electron paramagnetic resonance (EPR) method [20, 21]. This method allowed de-

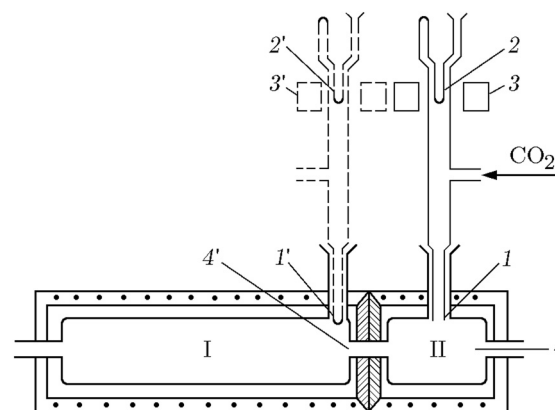


Fig. 1. Experimental setup [23]: the pre-flame region and the region of a stabilized cool flame are marked as I and II, respectively; (1, 1') diaphragm with a slot; (2, 2') finger-shaped appendix for freezing out and accumulation of radicals; (3, 3') cavity of the EPR spectrometer; (4, 4') thermocouple.

tection of free radicals in complex degenerate branched chain reactions and studying these processes and related phenomena at the level of radicals. The method was used to investigate free radical chain reactions under static and flow conditions. A small fraction of reacting gases was collected from the reactor through a narrow slot and was fed at a low pressure to the freezing system ($T = 77$ K), which was located in the cavity of the EPR spectrometer. A continuous record of the dynamics of radicals accumulated in the freezing system at the same time reflected the dynamics of formation and accumulation of these active centers in the reaction region. Such an approach allows not only detecting and recording the EPR spectra of radicals, but also tracing and studying the kinetic features of the process at the level of radicals for different conditions of the gas-phase chemical process.

CF and NTC phenomena are more clearly expressed in oxidation of hydrocarbons beginning from propane and higher. The cool flame was investigated at the level of radicals in [22–27], and the NTC phenomenon was studied in [26]. The NTC phenomenon was considered under static conditions, while a special method for flame stabilization in a two-section flow-type reactor with separately heated and thermally regulated sections made of quartz glass and shaped as cylinders connected in series through a short narrow quartz tube was developed for CF investigations. Each section was equipped with a device for collecting gas samples and freezing out of radicals further captured by the EPR

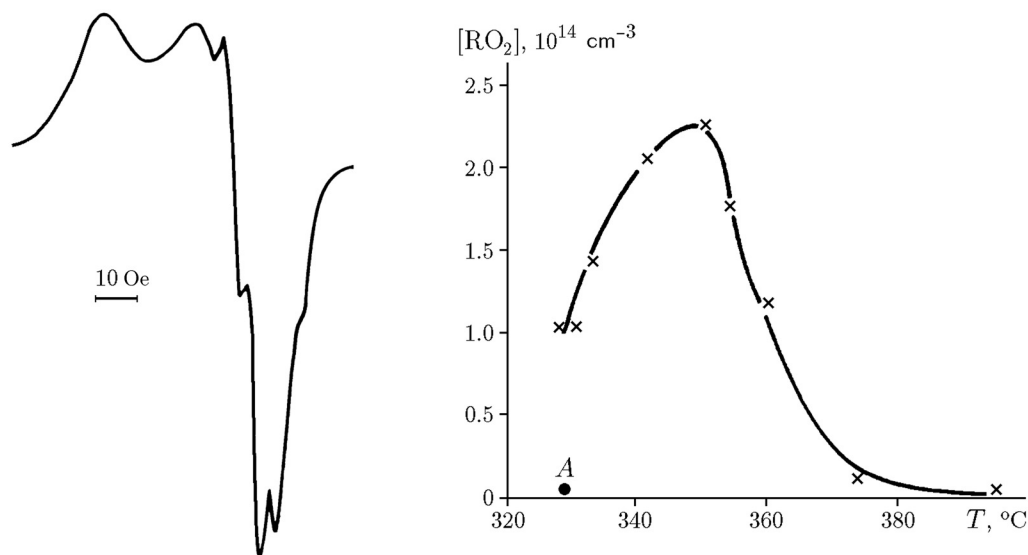


Fig. 2. Concentration of radicals in the region of a stabilized cool flame versus temperature [23]: the point marked by *A* shows the concentration of radicals in the pre-flame region; the left part of the figure shows the EPR spectrum of peroxide radicals recorded in the pre-flame region and in a stabilized cool flame.

method. The reactor is schematically shown in Fig. 1. The flow of the mixture of the reacting gases consecutively passed through the sections and was evacuated by a vacuum pump. The oxidation process at certain velocity and temperature of the gas flow in the first section proceeded in the induction period, and then the gas flow passed through the narrow tube and entered the second section, where a CF was formed and stabilized. There was no backflash of the flame into the first section, because the linear velocity of the gas flow in the tube connecting the sections was greater than the CF propagation velocity. This method allowed independent variations of the temperature in the CF region with the temperature in the first section (pre-flame region) being maintained unchanged. Thus, the effect of temperature on flame evolution was analyzed. Obviously, the temperature is expected to exert the same effect in the case of a cool-flame flash under static conditions, where the CF temperature increases due to self-heating of the system induced by heat release.

The first principal result obtained in the two-section reactor is a drastic increase in the radical concentration after the transition from the first to the second section, from the pre-flame to the cool flame region. The radical concentration in the pre-flame region at $T = 330^\circ\text{C}$ did not exceed $3 \cdot 10^{12} \text{ cm}^{-3}$; in the CF region, the radical concentration at an almost identical temperature reached $2.3 \cdot 10^{14} \text{ cm}^{-3}$ [22]. Such a drastic increase in the radical concentration after the end of

the induction period testifies to a vigorous chain reaction. At the same time, the EPR spectrum of radicals in the induction period, i.e., in the first section where the reaction proceeded comparatively slowly, is completely identical to the EPR spectrum of radicals in the CF region and refers to alkyl peroxide radicals (Fig. 2). This result shows that the chemical nature of the process remained unchanged, and it was only the chemical reaction rate that increased. The process passed to the stage of rapid evolution, which is typical for branched chain reactions. Poetically speaking, we can say that this is an explosive process: its further development can lead to fast and almost complete burnout of the reagents. However, a certain radical concentration is fixed at a certain temperature in the stabilized flame in the two-section reactor, and the process proceeds in the quasi-steady mode.

It was important to find how the radical concentration in a stabilized CF changes with an increase in the temperature in the second section, i.e., as the temperature changes directly in the course of the developing CF reaction. In other words, we had to simulate a situation in a CF flash, which is observed under static conditions of the oxidation process. The radical concentrations measured at different temperatures in the stabilized CF region are shown in Fig. 2. As the temperature increases, the radical concentration also increases and reaches a peak value at $T = 350^\circ\text{C}$. With a further increase in temperature, the radical concen-

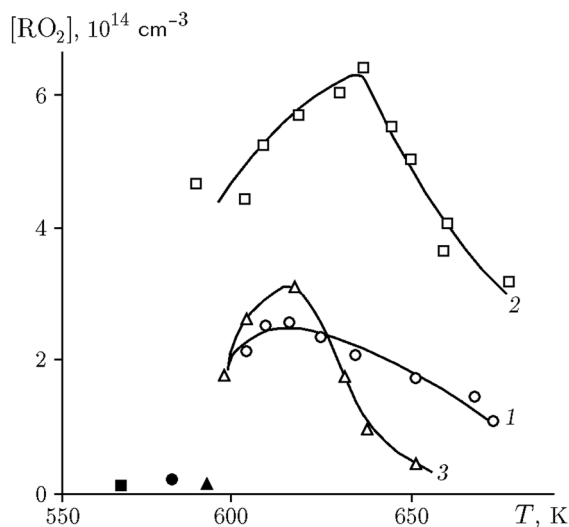


Fig. 3. Radical concentration versus temperature in stabilized cool flames [27]: (1) *iso*-C₄H₁₀ + O₂ at $p = 280$ torr; (2) *n*-C₄H₁₀ + O₂ at $p = 216$ torr; (3) C₃H₈ + O₂ at $p = 300$ torr.

tration decreases and the Arrhenius dependence is violated: instead of increasing, the reaction rate starts to decrease as the temperature increases in the interval $T = 350$ – 380°C ; as a consequence, the radical concentration decreases.

A similar dependence is observed in stabilized cool flames of other hydrocarbons. Figure 3 shows the radical concentrations as functions of temperature in a butane CF and in a stabilized propane CF. Thus, an increase in temperature in the CF mode during hydrocarbon combustion within a certain range leads to deceleration of CF oxidation in all cases. The process passes to the region of the negative influence of temperature on the chemical conversion process, where it is decelerated and the CF decays. The process returns to its usual path and goes on further in the slow oxidation mode.

It is known that this phenomenon (NTC of the reaction rate) is also observed in slow oxidation of propane and other hydrocarbons. This phenomenon was captured and proved by many researchers [6, 7]. In his famous monograph [28], Semenov wrote: Generally speaking, it should be noted that the kinetics of oxidation of all gaseous hydrocarbons is far from being clear. We think we would not be able to understand the mechanism of these reactions until we clearly understand the phenomenon of the negative temperature coefficient of the oxidation reaction, which is inherent in the majority of hydrocarbons (except for methane and benzene).

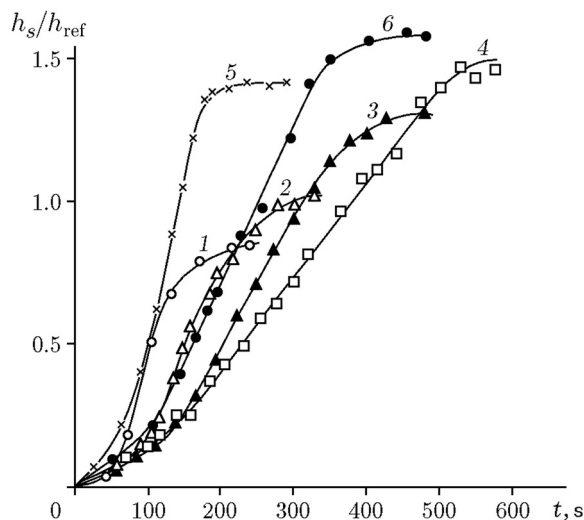


Fig. 4. Kinetics of accumulation of radicals frozen out from the propane oxidation reaction (C₃H₈ + O₂) at $p = 250$ torr [29]: $T = 348$ (1), 364 (2), 375 (3), 392 (4), 480 (5), and 436°C (6); the radical concentration is given in normalized units h_s/h_{ref} (the ratio of the radical signal amplitude to the reference signal amplitude).

Investigations of the NTC by the kinetic approach of freezing out of radicals made it possible to better elucidate the concept about the nature of this phenomenon [29]. Kinetic curves of radical accumulation were obtained (Fig. 4). The process becomes decelerated as the temperature increases from 348 to 392°C (kinetic curves 1–4). With a further increase in temperature, the process is accelerated again in the interval $T = 436$ – 480°C . In accordance with these data, the maximum concentration of radicals and the maximum rate of the oxidation process change in a symbate manner. The maximum concentration is reached at the point of inflection of the kinetic curve of radical accumulation on the cooled surface and it determined as a derivative with respect to time. Its dependence on temperature constructed on the basis of these data and coupled with the data on the maximum reaction rate measured on the basis of the pressure in the reactor is shown in Fig. 5. It is seen that these variables do behave in a symbate manner, reflecting the NTC phenomenon. At the same time, the radical concentration on the initial segments of the kinetic curves (see Fig. 4) in the entire temperature range, including the NTC region, behaves in accordance with the Arrhenius law, i.e., it increases with increasing temperature (see Fig. 5). As the radical concentration decreases with increasing temperature in the already developed process rather than at

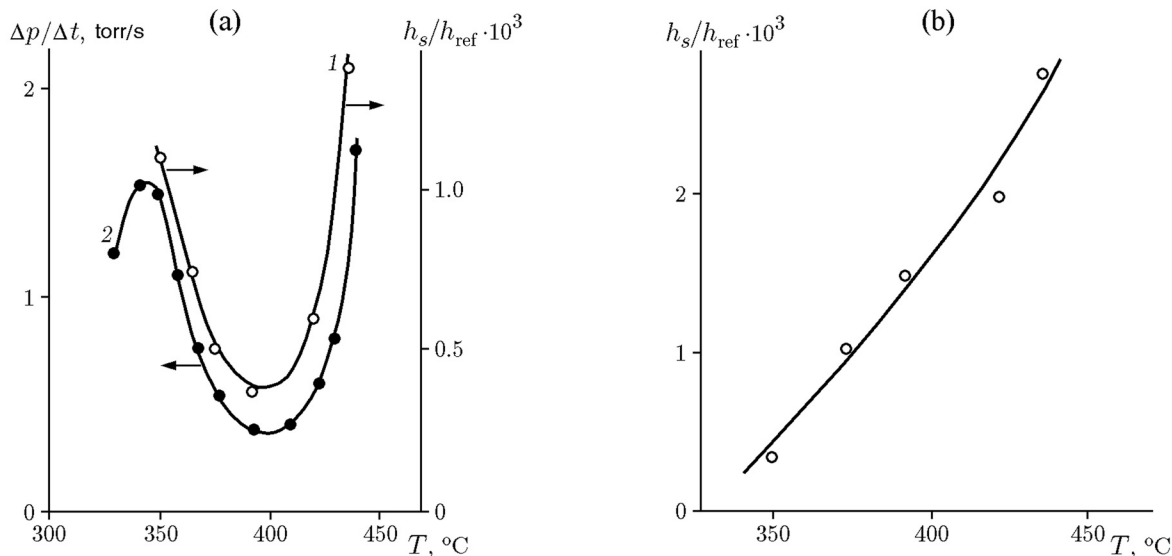
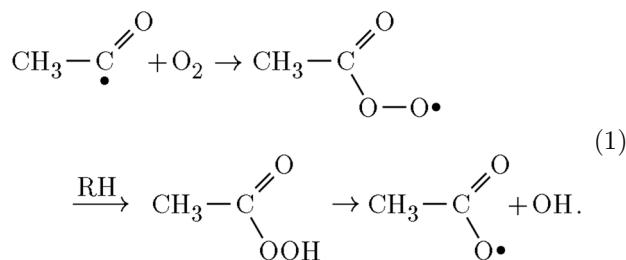


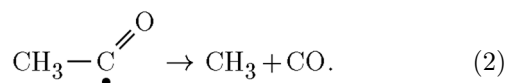
Fig. 5. Region of the negative temperature coefficient [20, 29]: (a) maximum concentration of radicals (curve 1) and maximum reaction rate (curve 2) versus temperature; (b) radical concentration versus temperature, based on the initial segments of the kinetic curves of radical accumulation.

the initial stage of the reaction, it is obviously caused by a decrease in the velocity of chain branching induced by the increase in temperature.

It is commonly believed that chain branching in degenerate branched reactions is associated with conversion of the most active stable intermediate products of the reaction accompanied by the formation of free radicals, which provide further multiplication of active centers in the course of the process. Such active intermediate products in hydrocarbon oxidation reactions are aldehydes, in particular, acetaldehyde formed during oxidation of many hydrocarbons in addition to propane. CH_3CO radicals formed from acetaldehyde can further ensure chain branching in the following way:



As a result, two active radicals (CH_3COO and OH) are formed from one active center CH_3CO , and chain branching is provided. Such a model was considered in many publications [7, 25, 28]. At the same time, CH_3CO radicals can decompose in accordance with the reaction



When the mechanism of hydrocarbon oxidation was discussed in [24, 25], this variant was also considered as a path leading to the NTC. The CH_3 radical formed in reaction (2) can only continue the propagation of ordinary chains, but it cannot branch new chains. The competition of the conversion paths (1) will be obviously enhanced due to increasing temperature because reaction (2) has a higher activation energy [29, 30]. Owing to the competition of reactions (1) and (2), the branching efficiency will become attenuated in a certain region of increasing temperature, and the process passes to the NTC region. With a further increase in temperature, the chain branching intensity will increase again, now with participation of another branching reaction. This may be the reaction of decomposition of hydrogen peroxide, which is also formed in the oxidation process:



The formation of H_2O_2 proceeds more effectively at higher temperatures; therefore, reaction (3) is the main source providing chain branching in the regions of higher temperatures. Thus, as the temperature increases, the process of conversion of the hydrocarbon-oxygen mixture leaves the NTC region and again follows the Arrhenius law.

There is a lack of data on CF oxidation for cyclic (aromatic) hydrocarbons. The phenomenological char-

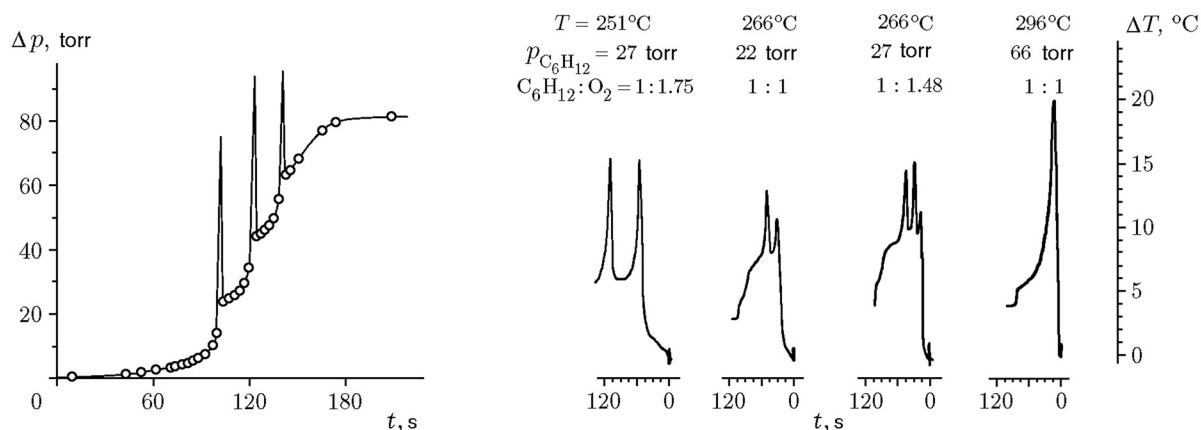


Fig. 6. Types of CF flashes of cyclohexane at different temperatures, compositions, and pressures of the reacting mixture [33, 34]: the left part of the figure shows the data [7] on CF oxidation of propane, RH : O₂ = 1 : 2, $p = 250$ torr, and $T_{in} = 350^\circ\text{C}$.

acteristics of CF oxidation of cyclohexane were studied in [31]. The cool flame of cyclohexane was considered in more detail in [32–36] under static conditions for cyclohexane pressures in the reacting mixture being lower than the vapor resilience at room temperature ($p \leq 70$ torr). A typical feature of these flames is their emergence at lower temperatures ($T \approx 220^\circ\text{C}$) than cool flames of alkanes and alkenes. Cool flames of cyclohexane are also characterized by a comparatively short delay of flame emergence [32–35]. The intensity of CF flashes (“warming”— ΔT), the frequency of consecutive flashes, and their delay period have different values depending on the composition of the reacting mixture, pressure, and initial temperature in the reactor.

Figure 6 shows various types of cyclohexane CF flashes detected at different temperatures. The temperature dependence of the limit pressure of CF flashes in the $C_6H_{12} : O_2 = 1 : 1$ mixture is illustrated in Fig. 7. The logarithmic anamorphosis constructed on the basis of these data corresponds to two straight lines with different slopes. The transition is observed in the interval $T \approx 500$ – 530 K. The activation energy is $E = 37$ kcal/mol in the low-temperature region and $E = 3$ kcal/mol in the high-temperature region [34]. It should be noted that the intensity of CF flashes also increases with increasing temperature and then decreases approximately in the same temperature region. The data on the maximum heating ΔT of the $C_6H_{12} : O_2 = 1 : 1$ mixture at the total pressure $p = 70$ torr under conditions of individual CF flashes are summarized in Fig. 8 [32]. These dependences testify to the NTC phenomenon, which accompanies cyclohexane oxidation in the CF region, as in the case of non-cyclic

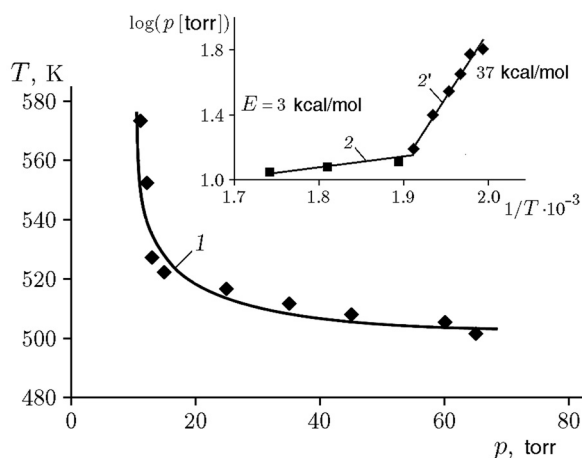


Fig. 7. Limit pressure of the emergence of CF flashes in the $C_6H_{12} : O_2 = 1 : 1$ mixture [34] versus temperature (curve 1) and logarithmic anamorphosis (curves 2 and 2').

hydrocarbons. The CF emergence delay in the cyclohexane flame, as well as the oxidation induction period of propane (aliphatic hydrocarbon), is described by the Arrhenius law in the entire interval of temperatures. This fact is illustrated in Fig. 9. According to [36], more active (than acetaldehyde) compounds are responsible for chain branching in the cyclohexane oxidation reaction. Therefore, CF oxidation of cyclohexane occurs at lower temperatures. Obviously, the NTC also occurs in this case as a result of the competition of two types of radical reactions: chain branching and decomposition of this radical with the formation of a new, less active radical capable only of chain supporting rather

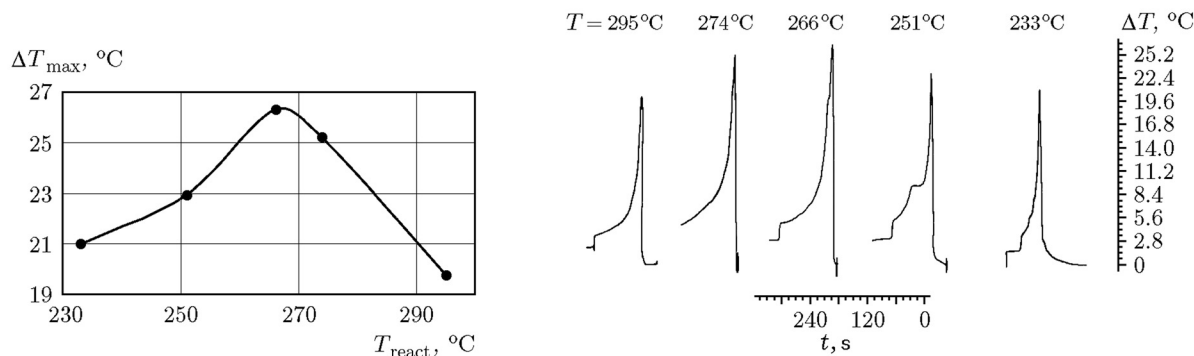


Fig. 8. Maximum heating of CF flashes for different initial temperatures in the reactor [32].

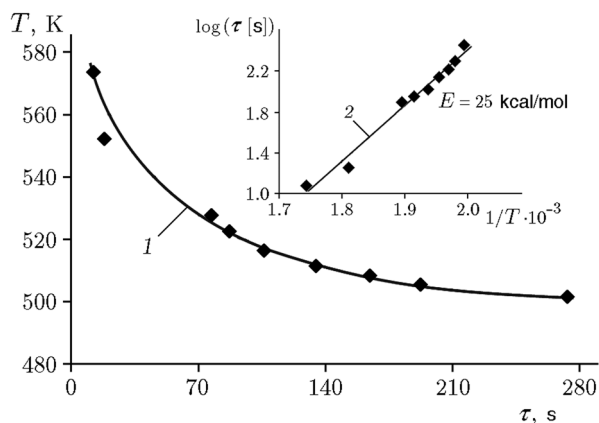


Fig. 9. Delay of the CF flash in the $C_6H_{12} : O_2 = 1 : 1$ mixture ($p = 26$ torr) [34] versus temperature (curve 1) and logarithmic anamorphosis (curve 2).

than chain branching. In the case of cyclohexane, such a compound can be propionic aldehyde or some other compound, which is more active than acetaldehyde [36]. If the radical formed from this compound has to ensure further propagation of the chain branching process and is more active than the acetyl radical (in the case of propane oxidation), the CF and NTC phenomena may occur in the course of cyclohexane oxidation at lower temperatures. The results of studying CF oxidation of cyclohexane show that cyclohexane conversion under these conditions proceeds with ring opening [35], and compounds with elevated activity may be present in reaction products.

Thus, the CF and NTC phenomena are inherent in oxidation of not only alkanes and alkenes, but also of cyclic hydrocarbons. They can be considered from a unified viewpoint as phenomena reflecting the kinetics of these complex radical-chain processes.

Speaking about the CF and NTC phenomena, we cannot avoid mentioning another phenomenon, namely, thermokinetic oscillations observed during oxidation of hydrocarbons in the same ranges of parameters (p , T , and composition of the reacting mixture). In studying stabilized flames of hydrocarbons in the two-section reactor, it was noted that temperature oscillations are observed at the beginning of CF stabilization; these oscillations gradually decay as the flame reaches a stabilized state. Systematic investigations showed that the process can proceed in a stable oscillatory mode if there are minor variations of the parameters (p , T , and contact time) [37, 38]. Stable oscillations can be harmonic, sinusoidal, and relaxing (anharmonic) [38]. In all cases, the frequency and amplitude of oscillations depend on the process parameters, such as the temperature and the contact time τ . These parameters determine both the rate and depth of chemical conversion of the reacting mixture and the kinetic characteristics of the process.

The types of oscillations and the regions of proceeding of different regimes of oxidation processes are shown in Fig. 10. As the temperature changes, the process passes from the slow reaction region to the regions of stable and damping oscillations and then to the stabilized CF region.

The specific features and the region of parameters where oscillations are observed allow us to conclude that they are related to the CF phenomenon, with the NTC playing the governing role in these regimes. The latter is responsible for deceleration of the chain reaction developing with acceleration. As a whole, all these phenomena are related to the chemical aspect of the oxidation process and reflect the kinetics of the complex degenerate branched chain reaction. The degenerate branched chain reactions of hydrocarbon oxidation considered above involve a large variety of stable intermediate products and free radicals with different

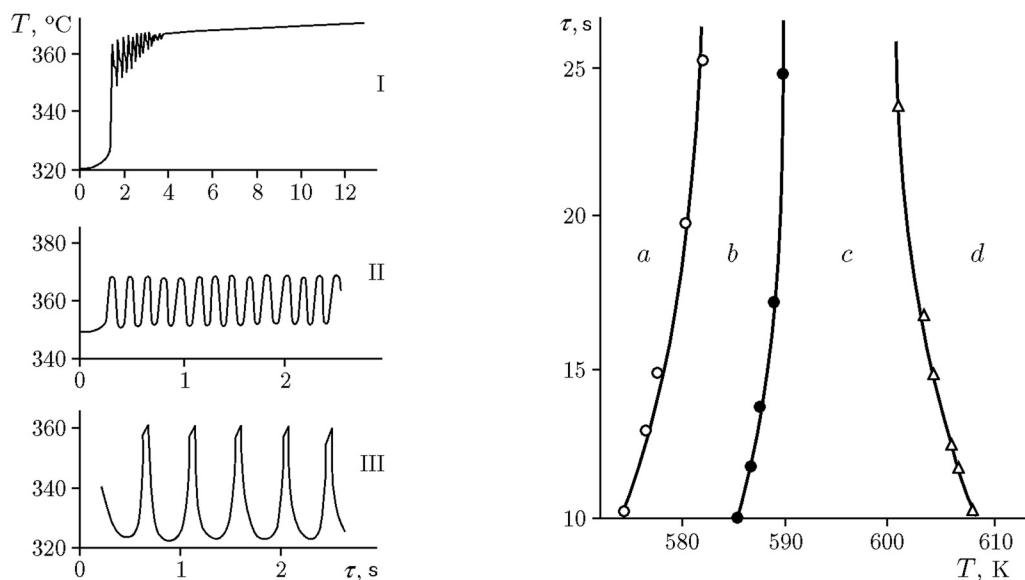


Fig. 10. Various types of oscillations in the course of C_3H_8 oxidation [38]: damping (I), harmonic (II), and relaxing (III) oscillations; $T = 581\text{--}586^\circ\text{C}$ and $\tau = 12$ s; (a) slow reaction; (b) stable oscillations; (c) damping oscillations; (d) stabilized cool flame; $p = 320$ torr; $C_3H_8 : O_2 = 1 : 1$.

structures. Such phenomena are absent in completely branched chain reactions, in particular, in the branched reaction of hydrogen oxidation, where, in contrast to degenerate branched reactions of hydrocarbon oxidation, the process evolution and chain branching occur with participation of active centers with simpler structures: H, O, and OH atoms and radicals.

INTERMITTENT FLAMES

As was noted above, a new phenomenon was observed in the case of a completely branched chain reaction of hydrogen oxidation in the low-temperature combustion mode ($T = 450\text{--}510^\circ\text{C}$ and $p < 200$ torr) in the presence of SO_2 additives; this phenomenon was called an “intermittent flame” [17–19]. It is important to note that the process proceeds with formation of elemental sulphur, i.e., sulphur dioxide becomes a participant of the chain process; in the oxidizing hydrogen medium, it serves as an oxidizer and reduces to elemental sulphur. Naturally, the mechanism of the general chain process becomes more complicated in this case. Now elementary reactions of SO_2 interaction with atoms and radicals of this chain reaction have to play a certain role. As a result, we obtain a combination of the chain reaction of hydrogen oxidation with the process of sulphur reduction from its oxidized form [39]. The phenomenological

characteristics of intermittent flames were described in [18, 19]. As an illustration, Fig. 11 shows the alternating light flashes, i.e., intermittent flames [18, 19] for different pressures of the hydrogen-enriched reacting mixture with addition of SO_2 ($H_2 : O_2 : SO_2 : N_2 = 10 : 1 : 1 : 0.5$ at $T = 470^\circ\text{C}$). An unfolded image of an individual light flash is also shown in Fig. 11. The light flashes for different temperatures [19] are shown in Fig. 12. The data of [17–19] give a general idea about the phenomenological features of these flames. It should be noted that the method of computer detection of light flashes developed in [18, 19], which is based on the analysis of an unfolded image of an individual flash, allows the analysis of autoignition of hydrogen–oxygen mixtures with and without addition of SO_2 . The time interval from the beginning of emission to the instant when the peak intensity of emission is reached ($\Delta\tau$) can be taken as the time of evolution of the hydrogen–oxygen mixture autoignition process. Experiments performed under static conditions of filling an evacuated reactor by the hydrogen–oxygen mixture with and without SO_2 additives ($H_2 : O_2 : N_2 = 10 : 1 : 1.5$ and $H_2 : O_2 : SO_2 : N_2 = 10 : 1 : 1 : 0.5$) showed that the presence of SO_2 in a reacting mixture does not exert any noticeable effect on autoignition. The process evolution time in these two cases is identical within the accuracy of determining the time interval from the beginning of emission to the instant of reaching the peak value on the emission signal curve.

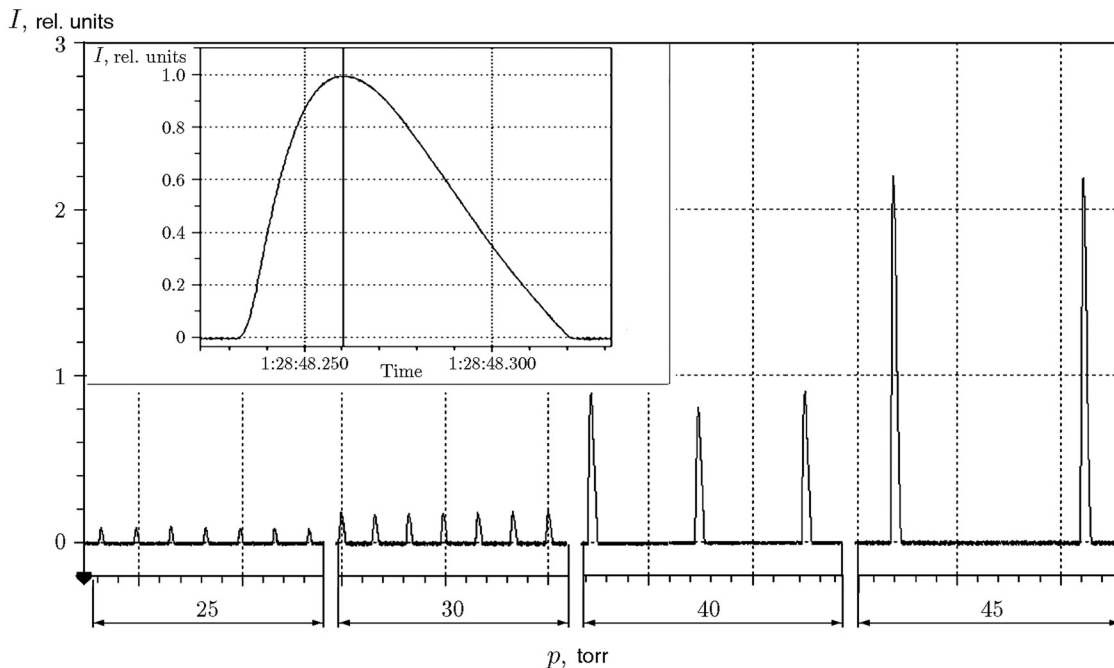
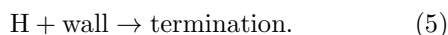
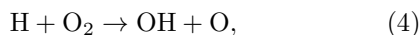
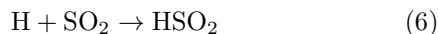


Fig. 11. Computer detection of light flashes (intermittent flames) at different pressures [18]: the inset shows an unfolded image for an individual flash; the time of its evolution is from the beginning to the peak value of emission $\Delta\tau = 0.03$ s; $\text{H}_2 : \text{O}_2 : \text{SO}_2 : \text{N}_2 = 10 : 1 : 1 : 0.5$; $T = 470^\circ\text{C}$.

According to the theory of completely branched chain reactions, this time at the lowest pressure near the first limit of autoignition, as well as the limiting branching itself, is caused by the difference in the rates of chain branching and termination on the reactor surface. In this case, these are the reactions



It is known that the rate of the chain termination reaction (5) can vary within certain limits from one experiment to another because of changes in the reactor wall state, which slightly (within the limit of reproducibility) affects the process evolution time. However, if SO_2 inhibits the process, it means that the reaction of hydrogen interaction with sulphur dioxide



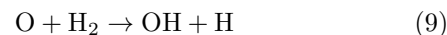
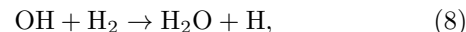
as well as reaction (5), is the chain termination reaction, because it leads to formation of the HSO_2 radical whose activity is rather low.

Another possible way of hydrogen interaction with sulphur dioxide,



is actually a chain propagation reaction rather than a chain termination reaction; therefore, as was demonstrated in [18], it should not affect the duration of this reaction.

The mathematical analysis of the kinetics of autoignition of the hydrogen–oxygen mixture with allowance for the basic reactions of chain propagation



as well as reaction (7) and the presumed reaction of chain propagation



leads to the same conclusion [18, 19].

Indeed, solving the system of differential equations over active centers in the quasi-steady approximation in both cases leads to the same differential equation over the main active center: hydrogen atoms responsible for chain branching. The time of evolution of the chain reaction of autoignition is also determined by the same variable $\varphi = 2K_1(\text{O}_2) - K_2$, which, according to the theory of branched chain reactions, defines exponential evolution of the process: $W = N \exp(\varphi t)$. Here K_1 and K_2 are the rate constants of the chain branching reaction (4) and chain termination reaction (5), respectively, and $N = (W_0/\varphi)\Delta\tau$, where W_0 is the chain nucleation rate and $\Delta\tau$ is the time of an elementary act responsible for chain propagation.

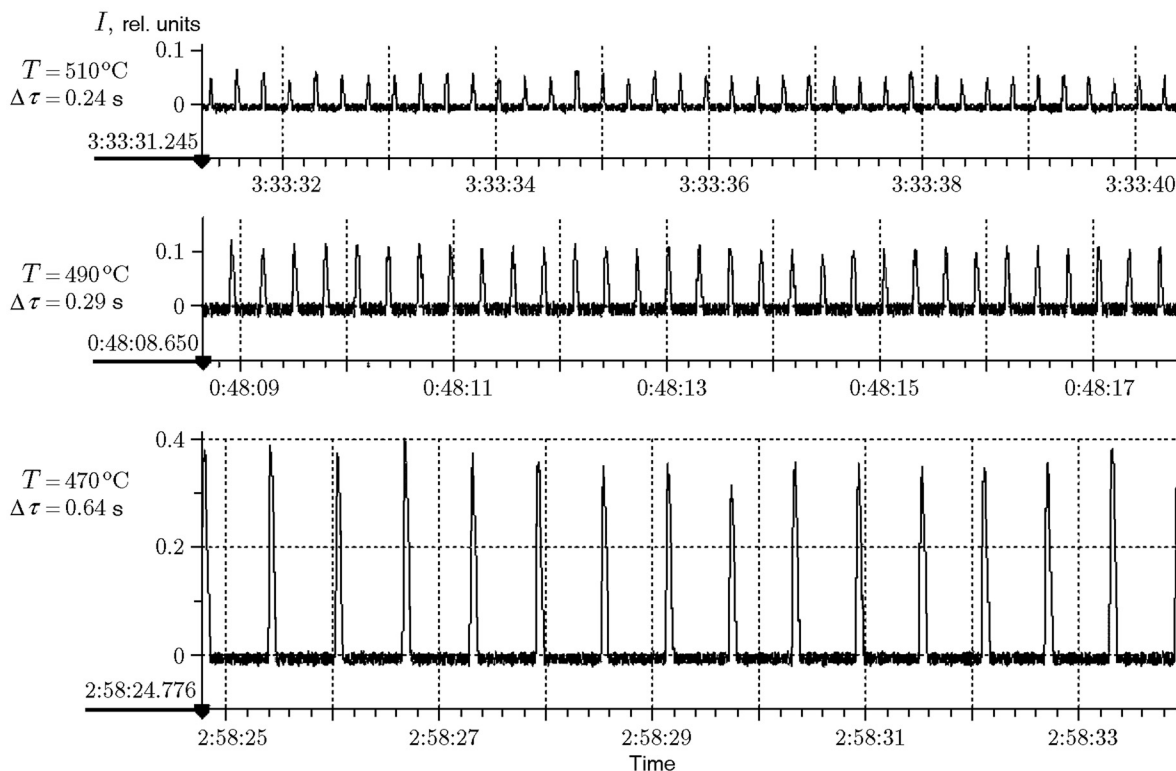


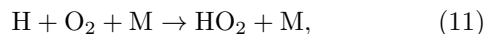
Fig. 12. Consecutive (with an interval $\Delta\tau$) light flashes in the intermittent flame regime at different temperatures ($p = 30$ torr; $\text{H}_2 : \text{O}_2 : \text{SO}_2 : \text{N}_2 = 10 : 1 : 1 : 0.5$) [19].

Concerning the presumed reactions (7) and (10), we can say, based on thermodynamic data, that their proceeding should be associated with overcoming significant energy barriers. Both reactions are essentially endothermic. Unfortunately, there are no reliable kinetic data for these reactions. At the same time, the fact of formation of elemental sulphur testifies to the presence of hydrogen because sulphur cannot reduce from its oxides without participation of hydrogen. As was found in [17–19], elemental sulphur is not formed in mixtures of H_2 with SO_2 that do not contain oxygen, which pass through a reactor heated to 470–510°C. Therefore, sulphur reduces from SO_2 in reactions that involve atomic hydrogen generated in the chain reaction of hydrogen oxidation.

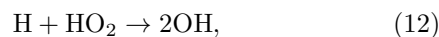
A specific feature in the kinetic aspect of the considered model of ignition of hydrogen–oxygen mixtures with participation of reactions (7) and (10) is the fact that the main active center (hydrogen atom) responsible for chain branching participates in the chain propagation reactions (7) and (10) in parallel with reaction (4). Such an unusual situation can lead to new kinetic manifestations. There elementary acts compete with each other; if reactions (7) and (10) are less vigorous than the

chain branching reaction (4), then the reacting system (i.e., the processes of autoignition and low-temperature combustion) cannot experience any significant changes, which is obvious. In this case, the situation with comparable rates of these elementary acts can be of interest for the kinetic analysis.

It should be noted that hydrogen atoms can actually react only with oxygen in the course of chain oxidation of hydrogen–oxygen mixtures that do not contain SO_2 at low pressures in the range of parameters between the upper and lower flammability limits; this reaction results in chain branching. It is only near the upper limit in terms of pressure, where the trimolecular chain termination reaction

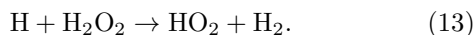


resulting in the formation of the HO_2 radical whose activity is rather low, starts to proceed with a noticeable rate and with an increase in the concentration of HO_2 radicals, that hydrogen atoms can also react with these radicals:

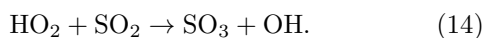


which leads to the formation of more active OH radicals. Such interaction of radicals, which is called positive in-

teraction of chains, intensifies the process and affects the upper limit position [28], thus, expanding the autoignition range. Near the upper limit, hydrogen atoms can also react with hydrogen peroxide, which is formed in reactions of interaction of HO₂ radicals with each other and with molecular hydrogen. However, this reaction again leads to the formation of the HO₂ radical with low activity:



Above the upper limit in terms of pressure, reaction (11) plays a dominating role. In this case, the reactions of HO₂ radicals, which require a high activation energy, become the basic reactions of the chain process evolution; therefore, the oxidation process becomes slower. It can be noted that the reaction of slow oxidation of hydrogen in this range of the parameters p and T becomes accelerated if SO₂ is added to the reacting mixture [30]. HO₂ radicals simultaneously react with SO₂ oxidizing it to SO₃ with the formation of the active radical OH:



As a result, the process of slow oxidation of hydrogen becomes slightly more active. The same activation effect of SO₂ is also observed in reactions of slow oxidation of hydrocarbons [39].

In the region of low-temperature combustion of hydrogen, SO₂ additives exert neither an accelerating nor a decelerating effect. This fact testifies that the active center reacting with SO₂ forms a new active center; as a result, chain branching continues. In this case, the process duration remains unchanged and is still determined by the chain branching reaction (4). At the same time, SO₂ conversion to elemental sulphur means that some part of hydrogen is oxidized by oxygen stored in a bound form in SO₂. In this case, the process should proceed with participation of the same radicals and atoms as hydrogen oxidation without addition of SO₂. Therefore, SO₂ conversion in the oxidizing hydrogen medium (main reaction of hydrogen oxidation) is related to additional consumption of not only hydrogen, but also oxygen, i.e., initial reagents of the main chain process. As a result, SO₂ conversion in a coupled chain process may affect the ignition conditions.

In [18, 19], the nature of intermittent flames is explained by the above-discussed considerations with due allowance for dynamic parameters of the process: the velocities of incoming of the reacting mixture and its passing through the heated reactor (contact time). Additional consumption of oxygen can reduce its concentration in the reacting mixture to a value below the minimum level necessary for autoignition.

As the reacted gas mixture is squeezed away from the reactor and the latter is filled by the fresh mixture, the oxygen concentration in the reactor increases, and another explosion occurs when the critical concentration is reached. Naturally, the time interval between the explosions (flashes) should be determined by the velocity of supply of the reacting mixture into the reactor. In other words, the frequency of flashes is determined by the velocities of incoming of the reacting gas flow and its passing through the reactor, i.e., by the contact time. This interpretation of intermittent flames is supported by the data of [17–19]. Figure 12 shows the results illustrating the effect of temperature on the frequency of flashes.

In general, the frequency of flashes increases for all values of p and T as the contact time τ decreases, i.e., as the velocity of the gas flow passing through the reactor increases. As the flow velocity is decelerated below a certain value ($\tau = 3\text{--}4$ s depending on p and T), the oxygen concentration in the reactor can decrease due to oxygen consumption below the limiting value, and the process will proceed without periodic flashes [17–19].

Thus, investigations of the kinetics of the conversion reaction of hydrogen-rich mixtures with addition of SO₂ revealed a new phenomenon that accompanies the completely branched chain reaction. This phenomenon is observed under conditions where a coupled process of radical-chain conversion of SO₂ in the medium with a completely branched reaction occurs. In this case, the specific kinetic feature of the chain process is the fact that, according to the above-made assumptions, the active center responsible for chain branching can simultaneously enter the reaction of chain propagation.

This issue was not considered within the framework of the formalized model of branched chain reactions. The phenomena accompanying the branched chain reactions discussed here could not be predicted by the general theory of chain reactions. The basic features and peculiarities of these self-accelerating processes of chemical conversion were obtained on the basis of a formalized principal model, which takes into account only the basic stages of the process: generation, branching, and termination of active centers. Integration of the differential equation reflecting the dynamics of these processes yields the known exponential dependence of the reaction rate on time: $W = N \exp(\varphi t)$. Naturally, this principally important characteristic of the process, which is obtained on the basis of a formalized model, cannot reflect and predict kinetic manifestations induced by the variety of possible elementary reactions with participation of intermediate products and free radicals with different structures.

CONCLUSIONS

The observed kinetic manifestations of degenerate branched chain reactions may be caused by a large variety of elementary reactions, which involve compounds and radicals with different structures. By definition, degenerate branching in the theory of chain reactions is associated with the formation of free radicals resulting from conversion of stable intermediate compounds (reaction products), which are still more active than the original reagents. It is commonly believed that the intermediate product, e.g., aldehyde, reacts with initially present oxygen with the formation of two radicals; each of these radicals, in turn, reacts with initially present reagents, forming the reaction product and a new radical. Thus, chain branching and propagation are supported. At the same time, it was found that degenerate branching can be also a complicated process with a competition of elementary reactions finally resulting in branching. As it follows from the above-discussed example of propane oxidation, chain branching in this case can be a result of a number of elementary acts of the acetyl radical, which is formed from the intermediate reaction product (acetaldehyde). The acetyl radical, which is responsible for further evolution of branching, can participate in two parallel reactions: with formation of acetyl hydroperoxide, which further decomposes into two radicals (chain branching) and with formation of a less active radical, which cannot support chain branching and ensures only propagation of ordinary chains.

Thus, if the radical responsible for chain branching can simultaneously participate in two reactions:

$$R \rightarrow \text{chain branching,}$$

$$R \rightarrow \text{chain propagation,}$$

then the competition of these reactions under certain conditions will lead to branching suppression, i.e., to overall deceleration of the chain process. In particular, such a situation may occur due to an increase in temperature if the activation energy of the second reaction is higher than the activation energy of the first reaction. Such a particular case resulting in the negative temperature coefficient is considered above by examples of slow combustion of hydrocarbons.

The experimentally observed kinetic manifestations are induced by the fact that, in degenerate branched chain reactions, the free radical with a complex structure, which is responsible for branching, can simultaneously enter another reaction that does not lead to branching. The completely branched chain reaction of hydrogen oxidation at low pressures near the lower flammability limit does not display any deviations be-

cause it proceeds with participation of active centers that have a simple structure: hydrogen and oxygen atoms and OH radicals. In this case, naturally, the main active center (hydrogen atom), which is not a free radical with a complex structure, cannot decompose and, thus, compete with the main branching reaction. In the CF regime at low pressures, the reacting hydrogen-oxygen mixture contains no intermediate compounds, which would be able to react with hydrogen atoms. Such a possibility appears if SO₂ is added to the reacting mixture. In this case, hydrogen atoms interact with SO₂ both in chain propagation and chain branching reactions. The result of the competition of these reactions is the formation of intermittent flames. Probably, addition of other compounds can lead to similar kinetic manifestations.

In the case of both degenerate branched and completely branched chain reactions, a common feature is the fact that the active center responsible for chain branching can simultaneously participate in the reaction of simple propagation of the ordinary chain.

The phenomena accompanying degenerate branched chain reactions were discovered as the methods of experimental investigations of the kinetics and mechanisms of these complex processes were developed and improved. The study of the nature of these phenomena is of interest not only from the viewpoint of the theory of chemical conversion, but also for practical purposes, namely, stimulation and control of combustion of various fuels.

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