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Non-isothermal regimes and chemical control of branching-chain processes

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Abstract. Non-isothermal modes of branching-chain reactions are analysed. Characteristic features of these reactions caused by the simultaneous action of the reaction chain avalanche and self-heating are considered in terms of concepts of the modern theory. New data are presented indicating that chain branching is the predominant factor in gas combustion processes not only at very low pressures, as it was assumed earlier, but also at atmospheric and higher pressures. The specific character of the temperature dependence of the rate of chain reactions and data dealing with the discovery of a special chain combustion mode, chain thermal explosion, are considered. The efficiency of chemical control of chain combustion in any mode including explosion, flame propagation and its transition to detonation by virtue of highly efficient non-corrosive inhibitors is demonstrated. The bibliography includes 135 references.

I. Introduction

The significance of the discovery of branching-chain processes (BCP) and chain combustion [1–3] for the development of chemistry is well known. A special place in the variety of the kinetic features of this frequently encountered class of reaction belongs to the combustion mode, which differs fundamentally from the 'purely thermal' combustion both in phenomenological features and the factors determining this mode. In recent years, it was shown that the branching-chain mechanism (BCM) predominates in most gas combustion processes not only at very low pressures, as had been considered until recently, but also at atmospheric pressure and at higher pressures. Combustion in air of virtually any hydrogen-containing compound (including hydrocarbon fuel), inorganic gaseous hydrides, and many pyrophoric compounds containing no hydrogen follows a BCM. Branching-chain decomposition of, for example, nitrogen trichloride is known.[3]

Until recently, the theory of BCP has considered only isothermal chain combustion processes which take place at pressures factors of tens or hundreds lower than atmospheric pressure, mainly in the vicinity of the first ignition limit (P_1) (Fig. 1). Under isothermal conditions, no self-heating or convection is involved; therefore, chemical mechanisms play the crucial role. Thus, this approach proved fruitful in identification of the chemical factors and elucidation of their role in chain combustion. However, chain combustion processes at pressures markedly higher than P_1 are exothermic and proceed at high rates; hence, they are accompanied by a substantial increase in the temperature of the reaction mixture. The combined influence of two fundamentally different factors, the avalanche multiplication of the intermediate active species and self-heating, both accelerating the process, determines the specific character of virtually all features of branching-chain combustion, which differ fundamentally from those of 'purely thermal' combustion caused by self-heating and heat transfer. Unlike the theory of BCP, the scope of combustion

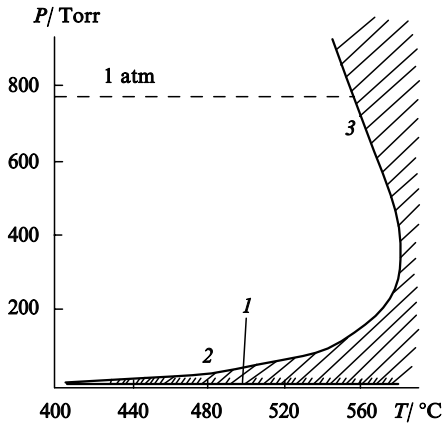


Figure 1. Region of self-ignition of a stoichiometric mixture of H_2 with O_2 in a reactor 7.4 cm in diameter with the surface coated with KCl.[3,6] (*1*), (*2*) and (*3*) are the first, second and third ignition limits, respectively.

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theory has actually been limited until recently to the latter type of combustion, this chemical process being represented as a simple one-step or, rarely, two-step reaction. Only quite recently was systematic investigation into the specific features of non-isothermal BCP started.

This review covers the regularities of BCP under non-isothermal conditions, brought about by self-heating of the reacting gas, and the role of chain mechanism over a wide range of pressures including the pressure region important for practical purposes. The data presented bring to light the governing role of chain mechanism under atmospheric and higher pressures in any mode of gas combustion; they demonstrate the specific pattern of the temperature variation of the BCP rate, disclose the chain thermal explosion mode and reveal the important role of BCM in the origination of detonation. Efficient methods and means for the chemical control of ignition, developed combustion, explosion and deflagration-to-detonation transition are described. New aspects of the relevant sections of the combustion theory and chemical kinetics are considered.

II. The main differences between thermal and chain ignition

Ignition and developing combustion are progressively self-accelerated chemical reactions. The kinetics of these reactions are characterised by not only increasing rates but also increasing accelerations (see, for example, Refs 3–5):

$$\frac{dW}{dt} > 0, \quad \frac{d^2W}{dt^2} > 0, \tag{1}$$

where W is the reaction rate and t is time.

Among other factors, ignition and combustion are governed by the positive feedback between the reaction rate and self-heating. Thermal ignition, caused by this factor alone, occurs if the rate of heat evolution (q_+) prevails over the rate of heat removal (q_-) and if the increase in the heat evolution rate upon rise of the temperature is more pronounced than the increase in the heat removal rate, *i.e.* the following conditions should be satisfied simultaneously:[3–5]

$$q_+ \geqslant q-, \tag{2}$$

$$\frac{dq_+}{dT} \geqslant \frac{dq_-}{dT}, \tag{3}$$

where

$$q_+ = WQ, \tag{4}$$

Q is the heat of the reaction,

$$q- = \frac{\alpha S(T - T_0)}{V}, \tag{5}$$

α is the heat removal coefficient, S and V are the surface area and the volume of the reaction chamber, respectively, and $(T-T_0)$ is the difference between the temperatures of the reaction mixture and the reactor walls.[3–6] The equality signs in relations (2) and (3) refer to the critical condition of thermal ignition.

In the theory of combustion, a chemical process is usually represented as a simple reaction, the rate of which depends on the temperature according to the Arrhenius law. Since the reaction rate (and hence, the rate of heat evolution), unlike the rate of heat removal, increase non-linearly with temperature, inequality (3) starts to be fulfilled, in addition to relation (2), after a definite temperature has been attained during heating. Therefore, accumulation of thermal energy in the reaction system becomes progressive, which results in an accelerated rise in temperature. Correspondingly, the chemical process becomes progressively self-accelerated, *i.e.* thermal ignition takes place.

Branching-chain ignition, unlike the thermal one, is caused by avalanche-like multiplication of active intermediate products — free atoms, radicals and, in some cases, excited species — upon fast reactions with the starting reactants and with one another.[1–8] This type of multiplication takes place if the rate of generation of active species, chain carriers (CC), is greater than the rate of their decay. The rate of BCP is

$$W = -\frac{d[B]}{dt} = w_0 + k_b n[B], \tag{6}$$

where [B] and n are the concentrations of the starting reactant and the CC, respectively, w_0 is the rate of chain initiation, *i.e.* the rate of appearance of CC in reactions involving only the starting molecules, and k_b is the effective rate constant for chain branching (the rate-determining step of the process).[1,3,8]

The change in the CC concentration is described by the equation

$$\frac{dn}{dt} = w_0 + (f - g)n, \tag{7}$$

where f and g are the branching and chain termination rates for unit concentration of CC (specific rates with respect to CC), equal to

$$f = 2k_b[B], \tag{8}$$

$$g = k_{het} + k_{hom}[B][M] \tag{9}$$

(k_{het} and k_{hom} are the effective rate constants for the heterogeneous and termolecular termination, respectively, and [M] is the concentration of the gas mixture).[1–3] The difference $(f-g)$ is often denoted by φ.

It follows from Eqn (6) that at initial stages of the process, when the decrease in the concentration of the starting compounds is still insignificant but the w_0 value can already be neglected, the following relations hold:

$$W \sim n, \quad \frac{dW}{dt} \sim \frac{dn}{dt}, \quad \frac{d^2W}{dt^2} \sim \frac{d^2n}{dt^2} \tag{10}$$

because the relative change in the concentration [B] is much smaller than the relative change in n.

It is obvious that for $f > g$, the concentration of CC increases with time with progressive self-acceleration, *i.e.*

$$\frac{d^2n}{dt^2} > 0. \tag{11}$$

The same follows from Eqn (7). Correspondingly, the rate of variation of the concentrations of the starting compounds in their reactions with active intermediate species, *i.e.* the rate of the process as a whole, increases progressively. This is indicated by relation (10) provided that inequality (11) holds. The attainment of a high reaction rate over a short period of time as a result of progressive self-acceleration is ignition. Thus, chain self-acceleration is caused by the positive feedback between the reaction rate and the CC concentration [see Eqns (6) and (7)]. Self-acceleration passes to the chain ignition mode in the case where multiplication of active intermediate species becomes avalanche-like because the multiplication rate exceeds the decay rate. Self-heating is not necessary for chain ignition. During progressive self-acceleration, high reaction rates can be attained; being exothermic, the reaction is accompanied by substantial light and heat evolution when the reactant concentrations are sizeable. This is a consequence of chain ignition alone.

It can be seen from Eqn (7) that, when $f < g$, the process occurs from the very beginning in a qualitatively different kinetic mode in which the increase in n (and, hence, in W) is retarded

$$\frac{d^2n}{dt^2} < 0.$$

In this mode, as the concentration of CC approaches the steady state value

$$n_{st} = \frac{w_0}{g-f},$$

the right-hand side of Eqn (7) and, correspondingly, dn/dt diminish and approach zero, which implies a complete cessation of increase in n and W. Since the rate of reaction between valence-saturated compounds w_0 is very low, it follows from the last-mentioned expression that under conditions where chain termination substantially prevails over chain branching (*i.e.* the g value noticeably exceeds f), the steady-state values of n and W are also extremely low.

Thus, the relation

$$f \geqslant g \tag{12}$$

is the condition for chain ignition. The equality sign determines the critical condition for transition from the steady-state mode, in which the reaction rate is extremely low, to the chain ignition and combustion mode.

For initial stages, when the variation of the f and g values during an isothermal reaction can yet be neglected, integration of Eqn (7) gives [1,3,7]

$$W = \frac{w_0}{f-g}\{[\exp(f-g)t] - 1\}. \tag{13}$$

It can be seen from this expression [see also Eqn (7)] that at $f > g$, the rate of the process increases with progressive self-acceleration, whereas at $f < g$, the increase in the reaction rate becomes less pronounced until a steady-state rate is attained.

It is noteworthy that, to consider the f and g values invariant with time, it is not enough to assume the process to be isothermal and neglect only the consumption of the initial compounds, as has been done until recently (see below). Heterogeneous propagation of reaction chains is not taken into account in Eqn (13) either.[9]

Since f and g depend on the initial reactant concentrations, temperature and the reactor geometry in different ways, the ratio of these parameters is governed by the reaction conditions. It has been found [1–3,6] that the specific patterns of the dependence of f and g on [B] and [M] and on the temperature stipulate the existence of two limiting pressures of ignition, which are both much lower than atmospheric pressure. For most combustible gases, these limiting values coalesce as the temperature diminishes, thus forming an ignition peninsula [1–3,6–9] (see Fig. 1).

If the chains branch upon reactions of CC not only with the initial molecules but also with one another (non-linear branching), the ignition condition can be written as follows:

$$f \geqslant g - 2(w_0 k_+)^{1/2}, \tag{14}$$

where k_+ is the effective rate constant for non-linear branching.[3] When there is no external source of atoms or radicals, the second term in the right-hand part of the equation is much smaller than the first one and the ignition is actually determined by relation (12). Therefore, expression (12) is used in this paper, although the discussion equally refers to expression (14).

If the quadratic chain termination (*e.g.*, recombination of the CC) is taken into account in addition to the linear chain termination, characterised by the parameter g, the rate of variation of n in the one-center consideration can be written as

$$\frac{dn}{dt} = w_0 + (f-g)n - k_- n^2, \tag{15}$$

where k_- is the rate constant for the quadratic termination.

The solutions of Eqn (7) at $f > g$ are unstable (Lyapunov instability), while the solutions of non-linear equation (15) are stable at any ratio of f to g (when $f > g$, the stability is non-asymptotic). Proceeding from this fact, some researchers (see, for example Refs 10–15) who, unlike some other authors,[1–9] define ignition as a kinetic mode described by only unstable solutions of equations, concluded that chain self-ignition requires self-heating, allowing for which accounts for the instability of the solutions. Thus they disclaimed one of the most important statements of the BCP theory, *viz*. the assumption that self-heating is not obligatory for chain self-ignition to occur. According to this view, it was proposed to elucidate the ignition conditions resorting to analysis of the character of solutions of the set of kinetic equations together with the heat balance equation and regarding the ignition limit as the condition of coalescence of stable and unstable singular points (bifurcation) on the concentration–temperature phase plane. However, this definition of ignition and this approach to the determination of its limit do not correspond to the essence of this phenomenon and, therefore, contradict experimental data. Experiments show that chain ignition is possible even when the reaction system is monotonically cooled provided that inequality (12) holds. This can be illustrated in relation to a model BCP — combustion of H_2 with O_2 above the first ignition limit.[16] When the pressure is low ($\sim$0.1 Torr) and only slightly exceeds P_1 (by 5%–8%), burning lasts for 10–15 s after an induction period. In addition to the monotonic decrease in the pressure, caused by the reduction of the number of gas moles in the reaction, the specially arranged monotonic decrease in the temperature immediately after admission of the mixture in the reactor can also be observed during this period. Ignition was detected as the appearance of chemiluminescence after the induction period and the progressive acceleration of the consumption of the reactants.

It has been shown [17–19] that equations such as (15) (or, in a more general case, a set of equations with negative quadratic terms corresponding to the concentrations of CC), although all of their solutions are stable, describe two qualitatively different isothermal modes of BCP: progressive self-acceleration ($d^2W/dt^2 > 0$) up to high rates, *i.e.* ignition, and the extremely slow reaction with establishment of a steady-state rate ($d^2W/dt^2 < 0$). It was also demonstrated that transition from one isothermal mode to the other following variation of the initial conditions has a critical character and is determined by the equality

$$f = g \tag{16}$$

both with and without allowance for the quadratic termination. If the rate constants appearing in f and g are known, the critical conditions of ignition, for example, the first and second limits calculated from expression (16) taking account of (8) and (9), coincide with the experimental values (*e.g.*, see Refs 3, 8, 20–23). This confirms once again the statement that self-heating is not a necessary condition for chain ignition.

Thus, when the notion of ignition is defined correctly, kinetic equations permit one to describe its origin without self-heating. Strict mathematical analysis of differential equations of ignition and combustion in terms of the above definition of this phenomenon as a kinetic mode characterised by progressive self-acceleration has been carried out.[24,25] The quantitative theory of the first and second ignition limits underlie precision methods for determination of rate constants.[20,23,26–32] When reactions (most of all, bimolecular) of CC with one another and heterogeneous development of reaction chains are taken into account, the theory also describes quantitatively the kinetics of isothermal chain combustion near the first limit, isothermal critical phenomena within the ignition region, and hystereses of various kinetic characteristics over a broad pressure region.[9,33–36]

Azatyan [37] has considered the difference between thermal and chain self-acceleration from the molecular-kinetic viewpoint, *i.e.* in terms of the mechanism assuming an increase in the number of species able to overcome the energy barrier to the reaction during the process (Fig. 2). The values marked on the abscissa axis are activation energies for the reactions of the initial molecules with each other (E_1) and with active intermediate species (E_2). The areas under the Boltzmann curves of the distribution of species over energy, to the right of E_1 and E_2 correspond to the number of the initial molecules whose energy exceeds the energy needed for them to enter into the reactions. As the temperature increases, the distribution curve shifts to the right (see Fig. 2); thus, the number

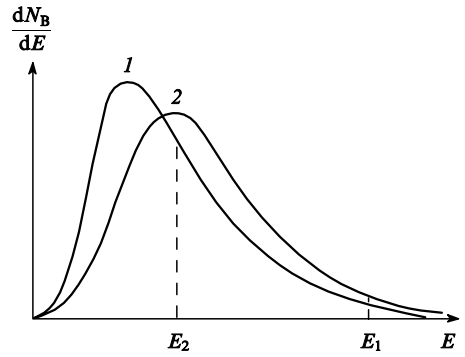


Figure 2. Equilibrium energy distribution of the initial molecules at temperatures T_1 (*1*) and T_2 (*2*) ($T_1 < T_2$);
E_1 and E_2 are the activation energies of reactions of the initial molecules with one another and with chain carriers, respectively.

of molecules of the initial compound able to overcome the energy barriers E_1 and E_2 increases. In the case of BCP, the number of species able to overcome the energy barrier and enter into the reaction increases even if no rise in temperature occurs in the reaction mixture (the distribution function does not shift towards higher energies). This is due to multiplication of free atoms and radicals in their reactions with the starting compounds, which require overcoming the barrier E_2, which is much lower than E_1. The area under the distribution curve on the right of E_2 (the fraction of initial molecules capable of reacting with free atoms and radicals) is quite large even at relatively low temperatures. Since reactions of atoms and radicals with the initial molecules not only give final products but also result in regeneration and multiplication of these atoms and molecules, the process self-accelerates even without self-heating. If $f > g$, progressive self-acceleration is observed, *i.e.* ignition takes place. Thus, chain ignition and combustion are due to chemical factors; they differ fundamentally from the self-heating factors and can alone ensure the progress of the reaction in this mode.

In the chain combustion accompanied by self-heating, the distribution curve also shifts towards higher temperatures; therefore, the number of species capable of reacting increases due not only to the chain avalanche but also to an additional increase in the number of reactive substances (both intermediate and initial), caused by the rise in temperature. This enhances additionally the chain avalanche. The specific features of combustion caused by the joint effect of the chain avalanche and self-heating are considered in Sections V and VIII. When the initial concentrations of reactants increase above the region of the first limit, self-heating which accompanies chain combustion becomes more and more pronounced, its influence on chain combustion being largely determined by the specific character of energy liberation during these processes.

Thus, the phenomena of chain and thermal ignition are caused by fundamentally different factors; the processes determining the critical conditions for their origination and the mechanisms of self-acceleration are also dissimilar. Self-heating is not a necessary condition for chain ignition.

III. Specific features of the energetics of branching-chain processes

In simple exothermic reactions, the energy equal to the difference between the chemical energies of the initial and final components is converted only to the kinetic energy of particles, *i.e.* it is liberated as heat. On the contrary, the greater part of the energy evolved during the developing BCP combustion is converted into chemical energy of active intermediates. This is a crucial factor determining the kinetic features of BCP.

Table 1. Energy characteristics of the elementary reactions of a chain cycle.

Number of step	Reaction	ΔH /kJ mol^{-1}	E /kJ mol^{-1}
I	$H + O_2 = OH + O$	66.9	69.9
II	$OH + H_2 = H_2O + H$	−60.7	21.5
III	$O + H_2 = OH + H$	8.4	43.5
II	$OH + H_2 = H_2O + H$	−60.7	21.5
A	$2H_2 + O_2 + H_2 = 2H_2O + 2H$	−46.1	

Let us consider the liberation of energy in a developing chain combustion over one chain cycle † for the model reaction of H_2 with O_2 using a procedure similar to that used in a previous study. [3] In this particular case, a chain cycle consists of the elementary reactions presented in Table 1; the Table also presents the respective changes in the enthalpy (ΔH) and the activation energies (E). The ΔH values were calculated from thermochemical data; [38] the E values correspond to the recommendations given in the literature.[39,40]

It can be seen that each chain cycle yields two additional chain carriers, free hydrogen atoms, in addition to two molecules of the final product. If the overall reaction

$$2H_2 + O_2 = 2H_2O \qquad (B)$$

followed a molecular pathway, it would give off 477.8 kJ mol^{-1} of heat. Meanwhile, the real process *A*, which follows a BCM, affords only 46.1 kJ mol^{-1} per branching-chain cycle, *i.e.* less than 10% of the heat of the overall process *B*.

As noted above, in conventional exothermic reactions, the difference between the chemical energies of the starting compounds and the reaction products is converted almost entirely into heat (to within a very small fraction of energy dissipated as radiation). Conversely, in a developing branching-chain combustion process, a substantial portion of the difference between the energies of the initial and final components is spent for the formation of free atoms and radicals, *i.e.* it is accumulated in the system as chemical energy of unpaired spins. This type of energy is the most rational for self-acceleration of the process not only due to the very high chemical reactivity of species with a free valence but also because they can be regenerated in reactions with the initial valence-saturated reagents. Indeed, the fraction of heat evolved during combustion and used to increase the number of the initial molecules able to overcome the energy barrier to a molecular reaction is extremely low bacause the activation energy is high. The rest of the thermal energy is dissipated or wasted in heating the final products. Meanwhile, the reactions of CC characterised by low energy barriers involve a much greater percentage of the initial molecules; in addition the free-valence energy (in the form of high reactivity) is actually transferred as a baton to the newly formed atoms and radicals and even provides for their multiplication. Only when the content of the initial reactants in the gas mixture decreases and the final stage of combustion, in which recombination becomes more significant, is approached, does energy evolve as heat. Of course, at the initial stages of the process when the content of reactants is still high, chain carriers also recombine partially, simultaneously with their participation in chain propagation (see Table 1, steps I – III). The role of chain termination by the route representing back reaction with respect to step I is especially significant in the combustion of hydrogen-containing compounds even at low pressures.[9]

The percentage of energy evolved in the chain termination, which ensures self-heating of the reaction mixture, depends on the rate of heterogeneous recombination, the heat of which is

† A chain cycle is the repeating set of several elementary reactions of CC including the CC regeneration.[3,8,31]

extracted by the reactor walls. For example, at very low pressures (near the first limit), chain termination is heterogeneous, the energy evolved being almost entirely absorbed by the reactor walls. In the above example of energy evolution in a chain cycle, only the indicated $\sim 10\%$ of the energy of overall process B is evolved in the bulk of the gas phase. At low pressures, virtually all the heat evolved is extracted by the reactor walls through conductive heat transfer, because the duration of combustion is hundreds or thousands times longer than the characteristic time of heat removal. This accounts for the fact that virtually no self-heating is observed near the first limit.

The numbers of free atoms and radicals diminish upon recombination; nevertheless, the concentrations of these species in the area of branching-chain combustion are many orders of magnitudes higher than the thermodynamically equilibrium values and even than those concentrations which would exist without chain branching. This is confirmed by direct measurements of concentrations of atoms and radicals during chain combustion processes of various types (see, for example, Refs 41–47).

The overall reaction A of a chain cycle shows that only one third of the consumed dihydrogen is converted into atomic hydrogen. The rest of dihydrogen is used in the formation of H_2O. It is due to this fact that the free energy (G) decreases to a degree which permits accumulation of atomic hydrogen (and other CC), bringing about a local increase in G. The overall change in the free energy G is negative; therefore, combustion proceeds spontaneously. In view of the foregoing, it becomes clear that the statements that half the dihydrogen in an oxygen–hydrogen flame is converted into atomic hydrogen, which can be found in the literature (see, for example, Ref. 48), are at variance with the thermodynamic prohibition; indeed, realisation of this process would require absorption of a large amount of heat ($\Delta H \simeq 200$ kJ per mole of O_2) and a nearly equal increase in the free energy (the entropy change is insignificant in this case). This means that such a process cannot occur spontaneously. It is also obvious that the number of free hydrogen atoms cannot exceed the number of H_2O molecules formed, even if they did not recombine at all (this can also be seen from the final stoichiometry of the chain cycle). Therefore, concentrations of hydrogen atoms (such as those presented in Fig. 136 in a monograph [41]) much greater than the total concentration of H_2O in the flames of stoichiometric (or enriched in the combustible component) H_2–O_2 mixtures are impracticable.

Since the concentrations of excited species in branching-chain combustion are much higher than the equilibrium values, the radiation of such flame is much more intense than that in a non-chain combustion. In some processes, chain branching involves species in not only vibrationally [49–55] but also electronically [53, 54] excited states. The inverted population of energy levels corresponding to a branching-chain mechanism is used in chemical lasers.[56–58]

Thus, high concentrations and high reactivity of reactive intermediate species as well as their ability to be regenerated and multiplied in reactions with the initial compounds determine the advantage of the BCM over a non-chain mechanism. This advantage is realised not only at low pressures.

It has been noted in studies,[59, 60] devoted to the elucidation of the mutual influence of chain branching and self-heating, that, when $f > g$, the W, dn/dt and dW/dt values are related to n through positive feedback [see also Eqns (7) and (10)]. The branching rate constant (k_b), which is related to the kinetic coefficient f [see Eqn (8)], increases with temperature according to the Arrhenius law. The temperature dependence of g is much weaker than that for f. Moreover, as noted above, in the case of termolecular chain termination, g decreases with increase in temperature. Therefore, an increase in temperature sharply increases the difference $f-g$, which appears in Eqn (7) as a positive factor in n; thus, the positive feedback of n with dn/dt, W, and dW/dt values is enhanced. The progressive growth of W and dW/dt brings about a similar progressive increase in the rate of heat evolution (q_+) and a rise in temperature. Thus, self-heating intensifies the chain avalanche and the process acceleration, and the enhancing chain avalanche, in turn, accelerates self-heating. This non-additive combined action of chain branching and self-heating accounts for the specific character of non-isothermal BCP including the specific temperature dependence of the chain combustion rate.

IV. Temperature dependence of the specific rate of branching-chain processes

The kinetic features of a BCP have been considered in substantially fewer studies than the first and second ignition limits. The temperature dependence of the BCP rate has received even less attention. On the basis of experimental data referring to very low pressures, it has been found [41] that the rates of combustion of H_2 and CO in oxygen are proportional to the rates of the steps

$$OH + H_2 = H_2O + H,$$

$$OH + CO = CO_2 + H.$$

Relying on this fact, it was claimed that temperature variations of these and some other branching-chain processes 'should evidently obey the Arrhenius law'. In another study,[55] this statement has been extended and it has been suggested that the rates of the rate-determining step and the chain process as a whole follow identical patterns of temperature variation. The fact that the chain propagation reactions (including the rate-determining step) constitute a branching chain is, however, ignored. This means that the temperature dependence of the reaction rate is determined not only by the temperature dependences of the rate constants of these steps themselves but, to a larger extent, by the temperature variation of the concentrations of chain carriers. Therefore, attempts to describe the temperature variation of the BCP rate by an Arrhenius function give different activation energies for the same chain process (depending on the process conditions);[61–66] in addition, the resulting values are usually very high (in some cases, $> 600-700$ kJ mol^{-1}). This is not only much greater than the activation energy values typical of reactions involving free atoms or radicals but also exceeds the activation energies of reactions of the initial valence-saturated molecules with one another and even the energies needed to cleave the bonds in these molecules. Obviously, these 'activation energies' do not correspond to the real energy barriers to the reactions and only point to the fact that the temperature variation of the specific rate of a BCP deviates crucially from the Arrhenius law. This also follows from the unnaturally great magnitudes of 'pre-exponential factors' for the rate constants (see, for example, Refs 61, 65).

Vedeneev *et al.*,[15] who considered the role of self-heating in the ignition of H_2 and O_2, transformed the exponential quantity of the Arrhenius function for the rate constant using the known [5] 'exponential quantity expansion' technique. Subsequently, the resulting new function was expanded into the Taylor series with respect to the temperature, the series being restricted to the linear term. Meanwhile, the nonlinear character of the temperature dependence of the reaction rate is the most important feature of combustion; when it is neglected, the notion of combustion itself loses its meaning (see, for example, Ref. 5).

The temperature dependence of the BCP rate has been presented [1, 7, 41] by the following expression:

$$W = \frac{A\exp(-E/RT)}{1 - B\exp(-E_1/RT)}, \qquad (17)$$

where A and B are temperature-independent factors and E and E_1 are effective activation energies. However, this formula is inapplicable to a real process. Indeed, if $B\exp(-E_1/RT) > 1$, then $W < 0$, which has no physical meaning. In addition, at a particular finite temperature corresponding to the equality

$$B\exp\left(-\frac{E_1}{RT}\right)=1,$$

the rate of the process becomes infinitely great, even at the beginning of the reaction, which has no physical meaning either.

The drawbacks of Eqn (17) are due to the fact that it has been derived using the following formula for the length of branching reaction chains (ν_b):[1,3,7]

$$\nu_b=\frac{\alpha}{\beta-\delta}, \tag{18}$$

where α, β and δ are the probabilities of chain propagation, termination and branching, equal to the ratio of the effective rate of the corresponding step to the sum of the rates of all these steps.

When deriving Eqn (17), Semenov [1,7] substituted the ν_b value expressed by Eqn (18) into the known relation

$$W=w_0\nu, \tag{19}$$

where ν is the chain length, and also took into account the temperature dependence of the rate constants included in the α, β and δ values.

However, we have shown [59] that Eqn (18), which has been used also in other studies,[41,65,67] does not correspond to the real process. For example, for $\delta > \beta$, *i.e.* under conditions corresponding to ignition and combustion, it gives inevitably a negative value for the chain length. The $\beta-\delta$ difference, appearing in the expression for the flame propagation rate, has resulted (when $\delta > \beta$) in imaginary values for this rate.[67]

In our study, [59] a fundamentally different expression for ν_b was proposed

$$\nu_b=\frac{(\alpha/\beta)[(\alpha\delta h/\beta)^m-1]}{\alpha\delta h/\beta-1}. \tag{20}$$

Here h is the average number of new branches for one branching step,

$$m=k_b[B]\alpha_1\delta t, \tag{21}$$

where α_1 is the probability that at least two of the active sites formed in the multiplication step enter into chain continuation reactions.

Unlike expression (18), Eqn (20) affords real, positive values of the chain length for any ratio of the branching and termination probabilities. This equation also shows that ν_b (the length of the growing chain) increases with time, the kinetics of this increase being dependent on the ratio of probabilities of the reaction chain branching and termination, which is consistent with the essence of this phenomenon. Under conditions where the inequality $\alpha\delta h > \beta$ holds, the increase in ν_b and, according to Eqn (19), also the increase in W proceed with progressive acceleration up to fairly high values. However, when $\alpha\delta h < \beta$, the increase in the ν_b and W values slows down until steady-state values are attained. The critical point for the transition from one kinetic mode to the other is determined by the equality:

$$h\alpha\delta = \beta. \tag{22}$$

It can be seen from Eqn (21) that the exponential quantity m includes the k_b value, which is an Arrhenius function of temperature. Therefore, in the combustion mode, *i.e.* for $\alpha\delta h > \beta$, the temperature dependences of ν_b and W_b contain a positive Boltzmann factor in the exponential quantity (the double exponent law) and, thus, they differ fundamentally from the Arrhenius law.

When deriving the analytical expression for the variation of the BCP rate as a function of temperature,[59] we took into account the fact that the contribution of w_0 to the rate of variation of CC concentrations in a propagating combustion process is insignificant, except for the very early steps of the process. This provides grounds for neglecting the w_0 value in Eqns (6) and (7) for the time $t > t_0 \simeq 2.5/\varphi$. Integration of the equation obtained in this way from Eqn (7)

$$\frac{dn}{dt}=(f-g)n, \tag{23}$$

with allowance for the f value [see Eqn (8)] and for the temperature dependence of k_b, gave the following expression for the temperature variation of the concentration of chain carriers:[59]

$$n=n_0\exp\left\{\int_{t_0}^{t}\left[f_0\exp\left(-\frac{E_b}{RT}\right)-g\right]dt\right\}. \tag{24}$$

Here n_0 is the concentration of chain carriers at t_0, E_b is the activation energy of branching, $f_0 = 2k_b^0[B]_0$, where k_b^0 is the pre-exponential factor for the constant k_b, $[B]_0$ is the initial concentration of the reactant B participating in the chain branching step.

By substituting this expression into the rate equation

$$W=k_b n[B], \tag{25}$$

we obtain the temperature dependence of the specific rate [59]

$$\frac{W}{[B]_0}=k_b n_0\left\{\exp\int_{t_0}^{t}\left[f_0\exp\left(-\frac{E_b}{RT}\right)-g\right]dt\right\}. \tag{26}$$

The rate constants for chain termination vary with temperature to an appreciably lesser extent than the rate constant for branching; therefore, the temperature dependence of the rate of the process is mainly determined by the first term in the square brackets.

Thus, when the difference $\varphi = f-g$ is positive, *i.e.* in the chain combustion mode, the increase in the specific rate of BCP with temperature is due not only to the increase in k_b but also (to a greater extent) to the substantial increase in the n value, the temperature dependence of which [see Eqns (24) and (26)] contains this rate constant and its Boltzmann factor in the positive exponential quantity.

This type of dependence was verified experimentally in relation to a model BCP, namely combustion of H_2 with O_2 near the first ignition limit.[60] The reaction was carried out at several temperatures, which were maintained in each experiment using a thermostat. The high-speed recording of pressure, chemiluminescence and temperature were carried out. Due to the low pressures of the mixture, exceeding only slightly the pressure of the first ignition limit P_1, to heterogeneous chain termination, which ensured removal of the energy of recombination, and to the high rate of conductive heat removal, the process was virtually isothermal at each specified temperature. The time taken to reach the maximum reaction rate counted from the end of the induction period was 0.36–0.5 s, which is thousands of times longer than the time of heat removal. The degrees of conversion considered were relatively low; hence, the consumption of O_2 could be neglected without substantial error, *i.e.* the subintegral function in expression (26) could be considered to be constant. Thus, as applied to the given reaction, Eqn (26) can be represented in the form

$$\frac{W}{[O_2]_0}=k_1[H]_0\exp\left\{\left[2k_1^0[O_2]_0\exp\left(-\frac{E_1}{RT}\right)-k_{het}\right](t-t_0)\right\}. \tag{27}$$

In this expression, E_1 is the activation energy of the rate-determining step (branching), equal to 69.9 kJ mol^{-1}, and k_{het} is the rate constant for heterogeneous decay of H atoms, which is known [3,8] to be equal to $2k_1[O_2]_1$, where $[O_2]_1$ is the O_2 concentration at the first ignition limit. This expression was used to determine the ratios of the rates of the virtually isothermal chain combustion at various temperatures. Table 2 presents the results obtained experimentally and by calculations using Eqn (27). The third column contains the value for the increase in the reaction rate calculated in accordance with the Arrhenius law using the same activation energy for the branching step.

Table 2. Ratios of the reaction rates at the temperatures 773 and 768 K.

$t-t_0$ / s	Experiment	Calculation by formula (27)	Calculation by the Arrhenius law
0.06	1.60	1.45	–
0.08	1.70	1.62	1.07
0.10	1.62	1.75	–

Since self-heating of the mixture in these experiments is rather weak and remains almost constant, it can be neglected when considering the ratio of the rates with an even smaller error. It can be seen from Table 2 that the experimental reaction rate increment caused by the rise in temperature is in agreement with that calculated from Eqn (27) and exceeds substantially the value expected relying on the Arrhenius law. Slight increase with time of the value presented in the third column is due to the fact that consumption of O_2 was not taken into account.

The unusually sharp temperature dependence of the branching-chain combustion rate ('the double exponent law') is brought about by the positive feedback relationship between the n value and dn/dt, W and dW/dt, considered above, which results in a non-additive combined effect of the chain avalanche and self-heating on the process rate. The double exponential law determines the enhanced sensitivity of the rate of a chain reaction to temperature variations; in particular, this facilitates fulfillment of condition (3). Yet another important feature of the temperature dependence of the BCP rate is that it varies exponentially as a function of the difference between the branching and chain termination specific rates ($f-g$). Therefore, both the reaction rate itself and its temperature dependence are highly sensitive to reactant concentrations and other parameters of the reaction system.

Equation (20) also indicates that, when the inequality $\alpha\delta h < \beta$ holds, the chain length reaches the steady-state value

$$\nu_b = \frac{\alpha}{\beta(1 - h\alpha\delta/\beta)}.$$

In accordance with equality (16), the process rate also reaches a steady-state value under these conditions, the self-acceleration of the reaction diminishing from the very beginning. Substitution of the ν_b value from the last equality into Eqn (19), with allowance for the temperature dependences of the rates of the steps determining the α, β and δ values, gives an expression similar to (17), which refers only to a very slow steady-state reaction without ignition.

Thus, the BCP rate follows different temperature variation patterns, depending on whether the reaction occurs in the combustion mode or in the very slow mode without progressive self-acceleration.

The pattern of the temperature variation of the BCP rate identified in the study of Azatyan [59] provides an interpretation for the unusually high effective activation energies, different for the same reaction depending on the experimental conditions, found in the studies noted above. In fact, any continuous function, including that for the temperature dependence of the reaction rate, can be represented approximately, in some narrow range of the argument, in the form

$$W(T) = b\exp\left(-\frac{a}{RT}\right),$$

where a and b are coefficients which are constant over the temperature range considered and play the roles of activation energy and preexponential factor, respectively.

By taking the logarithm of both parts of this expression with allowance for the condition of contact between the specified and approximated functions and by differentiation with respect to T, we obtain

$$a = RT_0^2\left[\frac{d\ln W(T)}{dT}\right]_{T_0}, \quad (28)$$

$$b = W(T_0)\exp\left\{T_0\left[\frac{d\ln W(T)}{dT}\right]_{T_0}\right\}, \quad (29)$$

where T_0 is the center of the temperature range considered. The rate of BCP depends sharply on the temperature [see expression (26)]; therefore, if this dependence is represented by the Arrhenius form, the derivative appearing in square brackets in expression (28), and, hence, the effective activation energy prove to be abnormally high. Since f and g, present under the first exponent in relation (26), depend on the process conditions in different manners [see Eqns (8) and (9)], the effective activation energy of this BCP should change appreciably upon variation of the reaction conditions. This is confirmed by all the experimental data. When the temperature variation of the BCP rate is described using an Arrhenius function, the 'pre-exponential factor' b found from Eqn (29) becomes too great and has no physical meaning.

V. The governing role of the branching-chain mechanism in the ignition and combustion of gases under atmospheric and higher pressures

The theory of BCP was based only on experimental data obtained under isothermal conditions because virtually all experimental studies on the kinetics of chain combustion have been performed at very low pressures in the absence of self-heating. It is clear that characteristic features of an isothermal process cannot be extended to non-isothermal conditions; therefore, the theory developed resorting to experimental data which refers only to isothermal regimes should be actually regarded as a theory of isothermal chain processes. Elucidation of the role of chain branching and avalanche multiplication of active intermediate species in the phenomenology of the process over a broad range of pressures (including atmospheric and higher pressures) presents considerable interest both for the theory of chemical kinetics and combustion and for the solution of applied problems related to the control of combustion modes.

It has been considered until recently that the BCM plays a crucial role only in combustion at very low pressures, tens or hundreds times lower than atmospheric pressure (see, for example, a number of publications [3–7, 41, 55, 68–76]). Interpretation of the nature of the third combustion limit is an important point in the formation of these views. The pressure of this limit (P_3) for, for example, H_2-O_2 mixtures, lies in the range of >40 kPa (which includes atmospheric pressure) and increases with a decrease in the temperature [3, 6] (see also Fig. 1). According to the generally accepted views, ignition in the region of P_3 is a non-chain process brought about only by self-heating, which accompanies the reaction (see, for example, several publications [3–7, 13, 41, 48, 55, 69–82]). An important role of a chain mechanism has been recognised only for very low pressures located in the ignition peninsula, closer to the first ignition limit (region *1* in Fig. 1).

The statement that the reaction in the region of P_3 is a thermally induced non-chain process has been substantiated by the facts that ignition at this (and higher) pressures is accompanied by great self-heating of the reaction mixture and by explosion and that the P_3 values for a hydrogen – air mixture calculated from the critical condition of thermal explosion [5, 82] are in good agreement with the results of experimental measurements reported in other publications.[83, 84] For instance, it has been stated in a monograph [3] (p. 436) that 'the excellent agreement between the calculations and experiments indicates unambiguously that the third limit for mixtures of hydrogen with oxygen has a thermal nature.' Similar statements can be found in some other studies.[4, 5, 41, 55]

The interpretation of the third ignition limit as a non-chain phenomenon is equivalent to the assertion that ignition and combustion of gases under atmospheric and higher pressures are induced only by self-heating. Indeed, since the third limit includes these pressures, the factors determining ignition and combustion play a crucial role at any pressure in the region of P_3 and above. In addition, since propagation of, for example, a laminar flame occurs as layer-by-layer ignition following the heat transfer from the burning area to a neighbouring layer of the mixture which has not yet reacted, the view of non-chain 'purely thermal' character of ignition at pressures near P_3 is equivalent to the statement that the flame propagates through a non-chain process.

Oxidation of hydrogen is usually regarded as a model BCP, because the main steps of its mechanism and a number of kinetic features are common to processes of this type. Many regularities of other branching-chain reactions and combustion processes are interpreted by proceeding from the views on the H_2 oxidation. This also refers to the view that the role of BCM at atmospheric and higher pressures and at high temperatures is insignificant. For instance, it is claimed in a monograph [70] (p. 52) that 'Branching-chain reactions are not so frequently encountered; moreover, for combustion temperatures above 1000°C, which exist even in the flames of dilute hydrogen–oxygen mixtures, thermal self-acceleration exceeds markedly the acceleration related to the branching-chain propagation. The latter is apparently the only mechanism of acceleration in some cool flames, for example, in CS_2-O_2 cool flames. This self-acceleration mechanism seems to predominate also in the cool flames of hydrocarbons and other organic compounds. However, self-acceleration in so-called hot flames, *i.e.* those normally dealt with in practice, occurs by a thermal rather than chain mechanism.' Below it is also written that 'an increase in the temperature in a reacting system induces thermal explosion at pressures below those for which the condition of chain explosion is met ...' (p. 182).

Actually, this has been the generally accepted opinion. Even nowadays, only the two lower limits are usually considered to be the limits of chain ignition; plots for only these limits are usually included in the graphical depiction of chain combustion regions.[3–7,48,58,74–81,85,86] Branching-chain chemical processes are considered as a class of reactions, which although interesting, occur only in the exotic region of very low pressures and relatively low temperatures.

Characteristic features of combustion at higher pressures have been interpreted taking self-heating as the only reason for self-acceleration of the process (see, for example, studies[3–7,68–82,87,88]). Meanwhile, some specific features of combustion at atmospheric pressure point to a very important role of a chain mechanism. One of these features is the effect of small admixtures of propane on the ignition of carbon monoxide in air under atmospheric pressure; these admixtures can either promote or inhibit the reaction depending on the amount added (Fig. 3).[89] The important role of BCM in the combustion of gases is also indicated by the results of studies on the mutual effect of chain avalanche and self-heating and on the temperature dependence of the BCP rate, which refer not only to low but also to atmospheric and higher pressures.[37,59,60] The contribution of a chain mechanism has been taken into account in the interpretation of ignition delay at near-atmospheric pressures [90] and in the numerical solution of equations related to combustion.[91–93] However, as has been correctly noted,[92,94] combustion has been usually represented as a one- or two-step reaction, the temperature dependence of the reaction rate being written as an Arrhenius function (see, for example, Refs 95–98). Even when the steps that can compose reaction chains were taken into account in the numerical modelling of combustion, they were still inserted in the reaction mechanism together with a large number of other (including insignificant) steps. The relative roles of the chain and thermal factors either have not been considered at all or, in those cases where pressure exceeded the second ignition limit, ignition and combustion have been considered to be non-chain processes.[72–76,99–102] Although Zel'dovich *et al.*[4] admits that most combustion processes follow chain mechanisms, he still considers these processes, as other researchers, only from the viewpoint of thermal combustion and uses the corresponding equations.

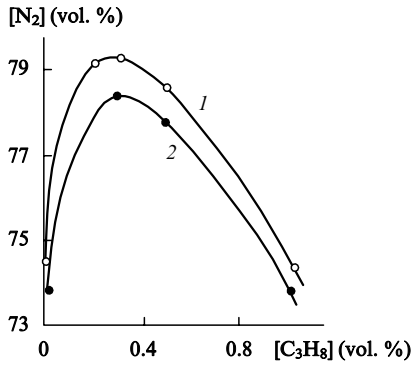


Figure 3. Ignitability of a $CO + O_2$ mixture in N_2 *vs.* the content of propane at 0.1 MPa and 293 K;
(*1*) in the presence of 0.11% of water vapour, (*2*) the mixture was dried with dry ice.

Our analysis [103,104] shows that the views according to which the BCM is restricted to the region of very low pressures are faulty. The substantial increase in the temperature and the appearance of thermal explosion are often regarded as evidence supporting the 'purely thermal' character of the third ignition and combustion limit under these conditions. However, any process, irrespective of its type and chemical mechanism, is able to switch to the thermal explosion mode provided that the conditions expressed by Eqns (2) and (3) are fulfilled.[103] This is equally true for chain processes. A specific feature of BCP is the fact that, owing to chain avalanche, reactions can proceed in the combustion mode even in those cases where conditions (2) and (3) do not hold. When these conditions are fulfilled, chain combustion passes into a mode in which the chain avalanche is accompanied by thermal avalanche. Moreover, in the case of BCM, transition to the thermal avalanche mode should occur in broader ranges of initial conditions and kinetic parameters than in the case of non-chain reactions. Indeed, if condition (12) holds and the reaction proceeds in the chain combustion mode, the rate of heat evolution reaches great values even at relatively low temperatures and low concentrations of the reactants. This facilitates fulfillment of the self-heating condition [see relation (2)]. In addition, the exceptionally sharp, non-Arrhenius temperature variation of the rate of chain combustion [see function (26)] makes easier the fulfillment of the second necessary condition for the generation of chain avalanche, relation (3). Therefore, as indicated by experimental data reported in the literature,[105] branching-chain combustion can readily switch to a mode involving a thermal avalanche (chain-thermal explosion) even when the reactant concentrations and temperatures are so low that thermal explosion is impossible and, hence, it is not observed in non-chain processes (see below).

Thus, substantial self-heating and thermal explosion do not give occasion for rejecting the important role of chain mechanism in ignition and combustion at atmospheric and higher pressures: these phenomena are also peculiar to branching-chain reactions. The agreement between the calculated and experimental temperatures of the third ignition limit is not a convincing argument either. These calculations were performed [82] using the expression obtained for the critical condition of thermal explosion

$$\frac{QEr^2W}{RT_0^2\lambda} = \delta_{cr}, \qquad (30)$$

where r is the radius of the reactor, λ is the heat conduction coefficient of the gas mixture, δ_{cr} is a dimensionless critical parameter; for example, for a cylindrical reactor it is equal to two.[106] The empirical formula for the rate constant for H_2 oxidation, obtained previously[61] using the data related to pressures approaching P_3,

$$w = kP_{H_2}^2 P_{H_2O}, \quad (31)$$

(where P_{H_2} and P_{H_2O} are the partial pressures of hydrogen and the water vapour formed, respectively, and k is an empirical rate constant) was substituted into the above expression.

The temperatures of the ignition limit at atmospheric pressure found from expression (30) were consistent with the results of measurements[83,84] carried out in reactors with various diameters. This provided grounds to conclude that BCM does not play any role in the ignition at the third limit and that combustion at these or higher pressures is brought about only by accelerating self-heating.[3–5,41,55] In other publications,[3–5] it has been assumed that a chain process is possible at the third limit over a KCl surface but only as an exception.

In our study,[103] we attracted attention to the fact that, since expression (30) was derived without any restrictions regarding the type of reaction or its chemical mechanism, it is also applicable to BCM. Therefore, the agreement between the results of calculations by Eqn (30) and experimental results can be considered equally reasonably to be an indication of a branching-chain reaction mechanism. It was also noted that Eqn (31) used in these calculations is empirical; it has been selected in accordance with the observed kinetics of the overall process. Therefore, the fact that Eqn (31) holds cannot serve as evidence supporting a molecular (rather than chain) mechanism either. Thus, the consistency of experimental data with the results of calculations according to Eqn (30), valid for reactions of any type, does not provide grounds for rejecting an important role of chain avalanche in combustion in the region of high pressures.

It is also noteworthy that, in addition to the experimental data mentioned above,[83,84] which agree with the calculations,[82] some other data which differ markedly from the calculated results are also known (see, for example, Refs 62, 63, 65). Since Eqn (30) was derived for reactions of any type, discrepancy between the data found from this equation and those obtained experimentally may point to inconsistency of some calculation variables with the experimental conditions; however, in some cases, this discrepancy can imply an inadequate description of the phenomenon by kinetic equations. For example, it is stated in a study[101] devoted to the numerical simulation of hydrogen combustion that the calculation carried out with the assumption of a constant temperature does not attest to the possibility of sharp transition from the slow process mode to the ignition mode in the vicinity of the third ignition limit. According to this calculation, the reaction rate only increases smoothly following an increase in the initial pressure of the mixture, *i.e.*, the process does not proceed by a chain mechanism. This result, however, cannot be regarded as evidence for the 'purely thermal' character of the real ignition limit because the calculations were based on kinetic equations the order of which does not correspond to the real reaction course. More precisely, the equations in the study cited were set up under the assumption that the rate constants for the heterogeneous decay of active intermediate species (including HO_2 radicals) were proportional to the heterogeneous recombination coefficients, *i.e.*, it was assumed that the rate of heterogeneous chain termination is limited by the probability of adsorption of CC upon collisions with the surface (the kinetic control of heterogeneous chain termination) even at pressures of the third ignition limit. Meanwhile, by using known coefficients of the heterogeneous decay of the H and O atoms and OH and HO_2 radicals even on inert surfaces and the diffusion coefficients for these species and by comparing the rates of their decay in the kinetic and diffusion regimes, one can easily make certain that heterogeneous chain termination reactions at high pressures are mainly limited by the diffusion rate rather than by the probability of adsorption upon collision with the surface. For example, the coefficients for the heterogeneous decay of CC reported in the study in question[101] are matched by chain termination rate constants that are several times greater than those observed with the rate-determining role of diffusion and calculated by the known formula[3]

$$k_D = \frac{39D}{d^2}, \quad (32)$$

where D is the diffusion coefficient of an active intermediate species, d is the reactor diameter, and the numerical factor with D allows for the spherical shape of the reactor.

Thus, the slowest (rate-determining) step in the capture of active species by the surface under conditions used in the study cited[101] is diffusion rather than the attachment of the species to the surface. Since the diffusion coefficient (and, hence, the rate 'constant' k_D) is inversely proportional to pressure, the order of kinetic equations with respect to the gas concentration should be three rather than two. Therefore, if the rate-determining role of diffusion is taken into account even when self-heating is neglected, solution of the set of kinetic equations in a particular temperature range indicates that, in addition to the two critical pressures (P_1, P_2), there exists the third critical pressure (P_3) of chain self-ignition, which is much higher than P_1 and P_2. When the initial pressure reaches each of these limits, the slow, steady-state reaction mode sharply switches to fast, progressive self-acceleration, *i.e.* ignition. When self-heating is not taken into account, the pressure P_3 becomes somewhat overestimated compared to the experimental value. This is due to the fact that at these high pressures, slight self-heating which accompanies the reaction in the slow mode facilitates somewhat the fulfillment of the condition of chain ignition; due to the slight increase in the temperature, chain branching starts to prevail over chain termination at lower pressures than it would occur without self-heating. An analytical expression indicating the presence of three self-ignition limits without self-heating has been obtained and verified by numerical solution of a set of equations.[107]

In order to find whether ignition, combustion and explosion at high pressures are brought about by the avalanche-like progressive self-heating alone or they are due, most of all, to chain branching, one should consider a feature of the process peculiar to only one of these two accelerating factors, either self-heating or chain avalanche. As specific features exhibited near atmospheric pressure or at higher pressures, we have chosen[103] the dependence of the process kinetics and the P_3 value on the chemical properties of the reactor surface and the influence of minor admixtures on the ignition and flame propagation including its transition to detonation.

Experimental data demonstrating the dependence of the P_3 value and the process kinetics on the material of the reactor surface are known. For example, it has been shown[4,29] that P_3 above a KCl surface is markedly higher than those above quartz and glass surfaces. Numerous data (see, for example several studies[6,29,62,63]) indicate that the process kinetics at the third-limit pressures depend on the chemical properties of the reactor walls. Hysteresis phenomenon is known, which means, for example, that the kinetic behaviour of the reaction system in a particular experiment depends on what reaction has been carried out in the preceding experiment prior to evacuation of the reactor.[6,62,108–111] However, these data have not been taken into account in considering the role of chain mechanism in the ignition and combustion near atmospheric pressure. Meanwhile, if the process were 'purely thermal', neither the reaction kinetics nor P_3 would depend on the material or, particularly, on the 'previous history' of the surface. This dependence is exactly a characteristic of radical and chain reactions. It is an integral feature of the third ignition limit and of the reaction kinetics observed when the reactants contact with a solid surface. It is also noteworthy that the results of calculations without allowance for heterogeneous chain propagation and chemical modification of

the surface cannot correspond to the process characteristics observed experimentally even though a large number of reactions are included in the process scheme and self-heating is taken into account. For example, the results of the calculation of the temperature dependence of the first ignition limit reported in a study [101] do not correspond to the experimental data presented in the same publication because heterogeneous chain propagation is not taken into account. In some studies devoted to the numerical solution of sets of equations for the third limit, heterogeneous reactions are completely neglected (see, for example, Refs 112, 113).

The chain mechanism of the process at atmospheric pressure is also indicated unambiguously by the data on the influence of admixtures of some compounds on the ignition of various combustible gases; in some cases, the dependence of the efficiency of an admixture on its amount has an extremum (see Fig. 3).[89] Yet another example is the decrease in the upper concentration limit of hydrogen ignition in air at atmospheric pressure from 75% to 55% in the presence of 1.5% of dibromotetrafluoroethane.[103]

Until recently, the influence of additives on ignition has been explained in applied studies either by dilution of the mixture and by the change in its thermal characteristics (increase in the heat capacity, acceleration of heat removal) or regarded as being equivalent to ionisation or chain termination without giving preference to either of these reasons (see, for example, Refs 114–117). However, small amounts of additives (0.3%–1.5%) cannot dilute a mixture, change heat capacity or decrease self-heating to a noticeable extent.

It is obvious that a theory in which self-heating is considered to be the only reason for the generation and progress of combustion cannot account for the pronounced influence of small admixtures of chemical substances on these processes at near atmospheric and higher pressures. It does not explain either the dependence of the efficiency of an admixture on its chemical properties or the above-mentioned extremum character of the effect of propane in concentrations of about tenths of percent. It is notable that the substantial effect of small admixtures on ignition and combustion, which, as can be seen from the given examples, is manifested, in particular, at atmospheric pressure, is actually ignored in the studies on the theory of combustion, in which various aspects of combustion, ignition and explosion are considered in detail. In some recent publications, the dissimilar influence of various admixtures on combustion has been taken into account by introducing empirical coefficients.[116] However, the use of only empirical parameters to describe the features observed does not allow one to explain the essence of the phenomenon. In addition, when extrapolations or even interpolations are made, this can distort the results because empirical 'constants' usually vary as functions of concentrations, temperature, *etc*. Meanwhile, the influence of very small amounts of inhibitors on the ignition and combustion over the whole range of pressures (including atmospheric and higher) indicates that they affect the competition between the chain branching and chain termination processes. The effect of inhibitors is due to the fact that they react with atoms and radicals to give radicals of a different type unable to regenerate active species.[31]

Some investigators claim (see, for example, Refs 6, 117) that the inhibitory effect can be explained by assuming that the role of chain branching is substantial only up to the instant of ignition and that the inhibitor suppresses only this pre-flame mode, thus preventing heat evolution. However, one can easily make certain that a chain reaction can proceed at a noticeable rate outside the ignition region only in the case where the chain branching rate is a shade lower than the chain termination rate, *i.e*. if f is slightly smaller than g. On heating, the f value increases exponentially together with the rate constant for branching [see expression (8)], whereas the g value, which relates at these pressures to termolecular termination, decreases. Therefore, even when the self-heating is slight and is much smaller than that needed for thermal ignition, f becomes greater than g, *i.e*. condition (12) is met. Thus, the mixture enters the region of chain ignition and ignites as a result of generation of a chain avalanche. For example, simple calculations carried out using Eqn (13) demonstrate that heating by only several degrees is enough for the ratio of branching to termination rates (f/g) in the $2H_2 + O_2$ mixture at 1 atm and 830 K to change from 0.95 (at which the reaction occurs in a steady-state mode and is virtually unnoticeable) to 1.05 and for chain ignition to occur. Note that under this conditions, substantial self-heating prior to ignition is impossible anyway, because the heat has time to dissipate due to the extremely low reaction rate ($f < g$).

Experimental data and the calculation using Eqn (13) demonstrate that, even when a mixture is located only 5% below the ignition region, the increase in the reaction rate becomes extremely low and soon ceases. Self-heating becomes substantial only under conditions of developed chain combustion and enhances the chain avalanche. However, as noted above, for self-heating to become a heat avalanche, fulfillment of condition (3) is also required. This requirement, however, can be not realised until the end of chain combustion (see below).

Analysis of the equation for the length of a branching chain and of the temperature dependences of the chain branching and termination rates has shown [59, 103] that at any pressure, self-heating in a branching-chain process results first in the fulfillment of condition (12) and, only after that, does chain ignition occur.

The conclusions made in several studies [59, 103, 104] concerning the predominant role of the BCM in the combustion at atmospheric and higher pressures and the simultaneous action of chain avalanche and self-heating have been verified experimentally.[89, 105, 118–121] The governing role of the branching-chain mechanism in the combustion of carbon monoxide in air at atmospheric pressure was demonstrated in a study,[89] in which the main reactions responsible for the promotory and inhibitory influence of admixtures are also presented. As an example, below we consider the results [118] dealing with the influence of various additives, inert diluents and chemically active compounds (inhibitors), on the ignition and on the intensity of combustion in the model hydrogen oxidation process. The reactions were carried out in a metallic evacuated closed reactor with a height of 25 cm and a diameter of 8.5 cm. Gas mixtures were prepared in the reactor according to partial pressures of the components with an accuracy of 0.6%. Within some period after the preparation, necessary for intermixing, the mixtures were conflagrated by pulse heating of a nichrome coil. The setup permitted the duration and power of the conflagrating pulse to be controlled. The chemiluminescence and pressure variations accompanying the ignition were detected using a FEU-39 photomultiplier (wavelength range 300–600 nm) and a quick-response pressure sensor, respectively. The signals from the sensors were recorded using a two-channel digital memory oscilloscope. After combustion had been completed, chromatographic analysis was carried out. The initial pressure of the mixture was 1 and 5 atm in various series of experiments.

The results of the measurements showed that the minimum concentration of argon needed to prevent the hydrogen–air mixtures of any composition from ignition, *i.e*., the so-called peak concentration of the diluent, is higher than 85 mol. %. The peak concentrations of inhibitors are much lower: for dibromotetrafluoroethane [chladone (Halon) 114B2] and a complex inhibitor of the AKAM series they do not exceed 16% and 9.5% (Fig. 4). The addition of, for example, 2.5% of the AKAM inhibitor decreases the upper concentration ignition limit (UCIL) from 75% to 45%. Meanwhile, the same amount of argon decreases the UCIL only to 73%. The much higher efficiency of inhibitors compared to that or argon and the dependence of the effect of inhibitors on their chemical properties indicate that small admixtures of inhibitors (unlike argon) influence ignitability through chemical reactions with the chain carriers. Thus, ignition of H_2, like that of CO, in the presence of hydrogen-containing compounds at the atmospheric pressure (see Fig. 3) follows a chain rather than a 'purely thermal' mechanism.

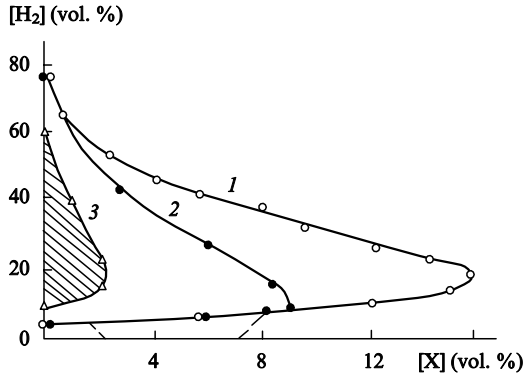


Figure 4. Concentration limits of ignition (*1*, *2*) and boundaries of the chain-thermal explosion region (*3*) for hydrogen – air mixtures containing various amounts of inhibitors X: halon 114B2 (*1*) and AKAM-3 (*2*, *3*); dashed lines correspond to ignition with a very high conflagration power in a small reactor.

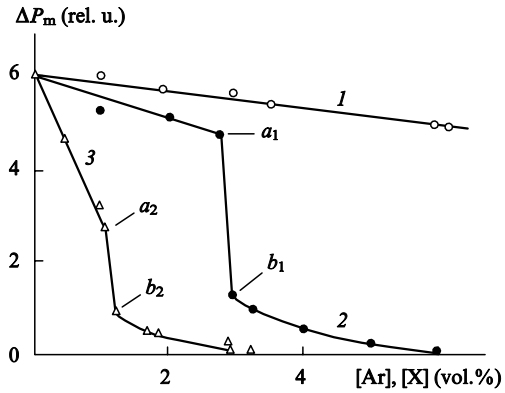


Figure 5. Dependence of ΔP_m on the initial content of admixtures X: argon (*1*), halon (*2*), AKAM-3 inhibitor in a mixture of 40% of H_2 with air (*3*).

The inhibitory action is due to fast reactions of the inhibitor with CC. In particular, the effect of the halon 114B2 is mainly determined by the reaction

$$H + C_2F_4Br_2 = HBr + C_2F_4Br,$$

resulting in the replacement of atomic hydrogen by a haloalkyl radical unable to regenerate chain carriers.

Experimental data obtained in a study [118] made it possible to elucidate the role of a chain mechanism in a developed combustion process. Since hydrogen oxidation is accompanied by monotonic decrease in the number of moles of the gas mixture, the increase in the pressure observed during the reaction carried out in a confined space can be due only to rise in the temperature of the reacting gas, *i.e.* its self-heating. Correspondingly, the rate of the pressure increase and the maximum pressure surge characterise the intensity of combustion. The kinetics of the reaction can also be judged from the rate of the growth and the maximum value of the chemiluminescence intensity.

The experiment with variation of the mixture composition made it possible to identify two kinetic modes of combustion. In the absence of inhibitors, the combustion of mixtures of hydrogen with air containing more than 16 vol. % and less than 60 vol. % of H_2 proceeds in a mode characterised by a very sharp pressure increase — to 6 – 7 atm (the initial pressure being 1 atm). This pressure surge points to an increase in the temperature to at least 2000 K. The process is accompanied by a characteristic bang. The time it takes to reach the maximum pressure and chemiluminescence intensity in these mode is 1 – 2 ms, *i.e.* it does not exceed the characteristic time of the heat removal from the reactor. This is the explosion mode, the kinetics of which differ substantially from the kinetics of ignition occurring in mixtures with compositions close to the concentration limits, *i.e.*, those containing more than 60 vol.% or less than 16 vol.% of H_2. The maximum pressures and chemiluminescence intensities and the rates of their growth attained in the ignition of these 'near-limit' mixtures are substantially lower. The temperature increases to 1300 – 1600 K. On smooth variation of the initial composition of the mixture, the transition of the process from one kinetic mode to the other is discontinuous, *i.e.* has a critical nature. Thus, ignition and combustion of hydrogen – air mixtures at atmospheric pressure can occur in two different kinetic modes depending on the initial composition; one mode does not involve thermal explosion, although it is accompanied by substantial self-heating, while the other one occurs as a thermal explosion. The parameters of the reactor used (calibre 3.1) precluded detonation. It is known that thermal combustion (unlike chain combustion) does not involve two different kinetic modes.

To elucidate the role of chain mechanism in the kinetics of developed combustion, argon and inhibitors were admixed (in various amounts) to the initial mixture. The plots for the maximum pressure gain (ΔP_m) *vs.* the contents of various admixtures — argon and inhibitors (halon and AKAM) — in a mixture of 40% of hydrogen with air, based in the results of several series of experiments, are presented in Fig. 5. The dependence of ΔP_m on the amount of an admixture characterises the efficiency of the influence of this compound on the process. In the absence of additives, ignition and combustion of this mixture switch to the explosion mode described above. It can be seen from the Figure that the inert gas decreases the ΔP_m value only slightly. The explosive character of the process does not change. This influence of argon is due merely to the dilution of the mixture. The dependence of the efficiency of the action of halon and AKAM on the amount added (curves *2* and *3*), when this amount is insufficient to dilute the mixture noticeably or to change substantially its heat capacity or heat conductivity, differs qualitatively from that observed for mixtures with an inert diluent. Curve *1* has no turns over the whole range of argon concentrations employed. Conversely, curves *2* and *3* exhibit sharp inflections at points a_1, b_1 and a_2, b_2, respectively. When the concentrations of the admixtures correspond to points b_1 and b_2, the maximum chemiluminescence intensity (not shown in the Figure) also changes abruptly. In addition, the efficiency of the influence of inhibitors on the combustion intensity is much greater than the efficiency of the influence of argon and depends on their chemical properties (*cf.* curves *1*, *2* and *3*). When the content of AKAM is greater than 3.4 vol. %, this hydrogen – air mixture does not ignite (no pressure and chemiluminescence growth are observed). At these inhibitor concentrations, the reactants are barely consumed after the source of conflagration has been switched on. The mixture can be ignited only when the content of halon is less than 6% and that of AKAM is less than 3.4%. Thus, a mixture containing 40% of H_2 and 3.4% of the inhibitor AKAM corresponds to the concentration limit of ignition. The same is true for a mixture with 6% of halon.

The smaller the amount of an inhibitor, the more intense the ignition: as the content of an inhibitor in the initial mixture decreases, ΔP_m increases (see Fig. 5). When the reactant mixture contains 3.2% of halon, the final degree of conversion of O_2 during combustion is 40% – 50%. When the concentration of AKAM is higher than 1.2% or that of halon is higher than 3.05%, the combustion does not pass to explosion, although the increase in pressure, which accompanies the ignition, points to substantial self-heating. The intensity of combustion increases with a decrease in the concentration of the inhibitor. These facts indicate directly that in this mode, developing combustion is substantially depressed by the inhibitor; hence, the process follows a BCM and its kinetics are mainly determined by the competition between chain branching and chain termination. Thus, chain mechanism

determines the kinetic features of the process not only before ignition and during the induction period, as has been assumed in the consideration of the influence of admixtures on the delay of ignition, but also under conditions of developing combustion after ignition has started.

The absence of signs of explosion in this combustion mode implies that the chain avalanche developing due to fulfillment of condition (12) and accompanied by self-heating owing to fulfillment of relation (2) is the only factor which accounts for the progressive self-acceleration of the reaction. The condition for thermal explosion [inequality (3)] is not met for these mixtures and self-heating only enhances the chain avalanche. This implies that the combustion of mixtures with compositions close to the concentration limits, which occurs without explosion in the absence of inhibitors, is also due only to chain avalanche enhanced by self-heating.

The comparison of the action of inert gas and inhibitor admixtures in the experiment in question [118] made it possible to establish the governing role of the branching-chain mechanism in the transition of combustion to explosion and in the explosion itself. When the initial content of the inhibitors decreases, the maximum combustion intensity and the ΔP_m value increase discontinuously (see Fig. 5, regions to the left of points b_1 and b_2). The time it takes to reach these maximum values decreases sharply and the process is accompanied by a click typical of an explosion. Judging by the ΔP_m value, the temperature in this case exceeds 2000°C.

Thus, there are two critical concentrations for each inhibitor, one of them corresponding to the ignition condition and the other (lower) corresponding to the transition of combustion into a chain-thermal explosion (see Fig. 4, curves *2* and *3*, respectively).

The fact that the slopes of curves *2* and *3* on the left of points a_1 and a_2 in Fig. 5 are much greater than the slope of curve *1* means that in the explosion mode, too, halon and AKAM have a much stronger effect on the combustion than the inert gas. The difference between the slopes of curves *2* and *3* reflects the dissimilar efficiency of the inhibitors, which depends on their chemical properties. Hence, the effect of halon and AKAM on the explosion intensity, unlike that of argon, is due to chemical reactions (inhibition) rather than to dilution. The fact that the slope of curve *3* is greater than that of curve *2* is consistent with the greater inhibiting activity of AKAM compared to that of halon. These data indicate unambiguously that a chain mechanism predominates in the mode of combustion which is realised when conditions (3), (13) and (2) are fulfilled and which has been named [119] chain-thermal explosion (CTE).

Experiments in which the initial pressure of the mixtures was 5 atm have given similar results.[118]

VI. Specific features of heterogeneous reactions determining the dependence of combustion characteristics on the surface properties at high pressures

Dependence of the kinetic parameters and critical conditions on the properties of the surface is an essential feature of BCP at any pressure. In particular, ignition limits include not only critical pressures or concentrations, as has been considered until recently, but also the dependence of these characteristics on the composition and properties of the surface adsorption layer and the ability of adsorbed species to enter into not only recombination reactions but also reactions leading to regeneration of CC. Therefore, to interpret correctly the characteristic features of the process, the reasons for this dependence should be identified and taken into account. In our studies, [9, 36, 121] we interpreted the dependences of the process kinetics and the P_3 value on the properties of the reactor surface over a broad range of pressures (from a very low to atmospheric pressure), both found experimentally in the same studies and reported in the literature,[6, 62, 63, 65, 110] within the framework of the concept of the chain mechanism of ignition and combustion near atmospheric pressure and heterogeneous propagation of the reaction chains.[9, 54, 122] The hysteresis phenomena mentioned above were also interpreted.‡ The dependence of the BCP characteristics on the surface properties points unequivocally to an important role of heterogeneous reactions involving CC in the competition between the reaction chain branching and termination. Since the same amounts of reactants are admitted into the reactor in each experiment, the influence of a preceding experiment on the process characteristics is due only to reactions involving the adsorbed intermediate species, which have been formed in the previous experiment and have not been removed completely during evacuation. The atoms and radicals adsorbed on the surface can participate in the propagation of reaction chains. It has been established [9, 33–36, 54, 122] that in the combustion of, for example, H_2, heterogeneous chain propagation involves the HO_2 radicals formed in the reactions of adsorbed H atoms with O_2 and also in the gas phase. In this review, we consider those heterogeneous reactions which are significant at high pressures. It has been noted [9, 122] that, due to high pressures, adsorption of HO_2 from the gas phase is limited by diffusion. Therefore, if each adsorbed HO_2 radical participated in chain termination, no dependence of, for example, P_3 on the properties of the surface would be observed. The presence of this dependence indicates that reactions of some of the adsorbed HO_2 radicals result ultimately in the regeneration of chain carriers, *i.e.*, active species that pass in the gas phase. The following reactions can be cited as examples of regeneration of CC with participation of adsorbed radicals:[9, 36, 122]

$$ZO_2H + O_2 = Z + O_2 + HO_2\uparrow,$$

$$ZR + O_2 = Z + RO_2\uparrow,$$

$$ZO + RH = ZOH + R\uparrow,$$

where Z is an adsorption site, R is a radical, the arrow marks the departure of a species into the gas phase. In the first reaction, the H atom passes from an adsorbed HO_2 radical to an O_2 molecule which attacks it from the gas phase.

Since the rates of reactions of adsorbed species depend on the properties of the surface, these properties also influence the fraction of the surface HO_2 species that regenerate the CC. When this fraction (θ) is taken into account, the effective rate constant for the heterogeneous chain termination is

$$k_{het} = k^0_{het}(1-\theta), \tag{33}$$

where k^0_{het} is the rate constant for the capture of CC by the surface. Unlike k^0_{het}, which is determined by the rate of diffusion, the θ value depends on the type of bonding between HO_2 and the surface, *i.e.* on the properties of the surface adsorption layer.[36] Therefore, despite high pressures, k_{het} depends on the state of the surface. The surface is subject to the action of the chain reaction products. During evacuation of the reactor, the chemisorbed radicals are removed incompletely, and, after a new portion of the mixture has been admitted, they react with the gas-phase components of the fresh mixture; it is in this way that the 'surface memory' is manifested. The hysteresis phenomenon is also observed in many catalysed oxidation and pyrolysis processes.[108–111, 123]

It has been shown [9, 36] that regeneration of atoms and radicals with participation of the CC adsorbed from the gas phase (heterogeneous chain propagation) differs fundamentally from the heterogeneous formation of active species in the reactions involving only initial molecules (heterogeneous initiation). This difference is due to the much higher rates of heterogeneous chain

‡ It is noteworthy that until recently, the majority of researchers have not taken into account heterogeneous chain propagation (see, for example, Refs 92–95, 98).

propagation reactions and to their more important and diversified functional role in BCP. It is this type of reaction rather than chain initiation (which is significant in catalytic reactions according to the generally accepted view) that accounts for the dependence of the process kinetics on the properties of the surface (including hysteresis). Under certain conditions, heterogeneous chain propagation also influences the critical conditions for flame propagation [121] and CTE.[105]

VII. The role of chain mechanism in the transition from deflagration combustion to detonation

The branching-chain mechanism plays the governing role in the ignition and combustion at atmospheric pressure; therefore, competition between chain branching and termination also has a crucial influence on the propagation of, for example, a laminar flame, *i.e.* layer-by-layer ignition of a combustible gas. This conclusion was verified experimentally in a study of the influence of inhibitors on the rate of flame propagation [118] and in a study dealing with the dependence of the concentration limits of flame propagation on the composition of the adsorption layer on a contacting surface.[121]

The influence of inhibitors on the flame propagation velocity was studied in 2-m long horizontal tubes with diameters of 2.4 and 5.4 cm. The ignition was carried out at the end face of the tube and the track of the flame was recorded based on chemiluminescence, the signal of which entered a photoelectric multiplier through three quartz windows, located along the reaction tube, and a branched optical waveguide. It was shown that inhibitors not only narrow down the concentration range of ignition but, at concentrations lower than the first critical concentration (*i.e.* corresponding to the regions confined by curves *1* and *2* in Fig. 4), they also decrease the flame propagation velocity. In addition, if the flame is not stationary and accelerates, inhibitors decrease the acceleration rate. Thus, chain branching also plays the governing role in flame propagation, and this enables one to control both its concentration limits and velocity by using inhibitors. When the inhibitor concentration exceeds a certain value, the flame becomes diminishing.

A correlation between the critical conditions for flame propagation and the chemical properties of the surface contacting with the gas has been elucidated.[121] The study was based on the hysteresis of the upper concentration limit of flame propagation discovered and studied for the combustion of hydrogen in air in a reactor characterised by an especially great surface area-to-volume ratio. When the initial content of H_2 in the mixture was successively increased in each experiment (*i.e.* when the limit was approached from the side of the ignition region), higher values were attained than in the case where the concentration of H_2 decreased and the limit was approached from the side of non-ignitable mixtures. The reactor was evacuated after each experiment; therefore, the dependence of the critical condition of ignition on whether or not combustion had occurred in the previous run was due only to the change in the chemical properties and functions of the adsorption layer of the reactor surface under the influence of intermediate products of combustion, namely, adsorbed CC (see the previous Section). These results are directly related to the filtration and catalytic combustion.

Transition from deflagration to detonation is known to occur as a result of progressive self-acceleration of a flame to velocities higher than the sound velocity (and generation of a shock wave thereupon) at the cost of the energy of a chemical reaction.[4, 6] The fact that inhibitors retard the flame propagation and switch it to a damped regime permitted us to conclude that transition of deflagration to detonation can be prevented by using inhibitors. This was accomplished in another study [124] for various conditions of combustion at atmospheric pressure. The results of bench testing of an air-feed jet engine are presented in Fig. 6. Suppression of detonation in a hydrogen–air mixture containing 40% of H_2 was also attained in a plexiglass reaction tube of length 600 cm

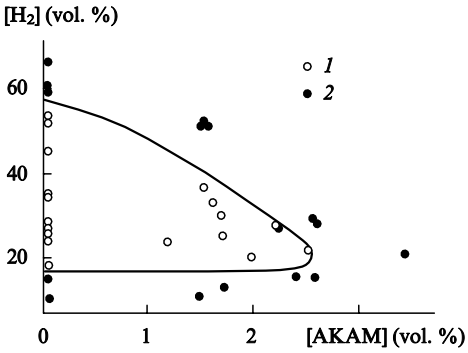


Figure 6. Regions of normal and detonation combustion of hydrogen–air mixtures for the operation of a bench of an air-feed jet engine in the presence of various amounts of the AKAM inhibitor; (*1*) detonation, (*2*) normal combustion.

by introducing 2.5% of an inhibitor of the AKAM series.[103] High-speed filming made it possible to determine exactly the site where detonation arose. It was shown that addition of 0.5% and 1.0% of an inhibitor extends substantially the induction period of detonation and, when the amount is $> 2\%$, detonation does not occur.§

It has been shown [21] that heterogeneous propagation of reaction chains influences the reaction kinetics not only under conditions of developed combustion but also during the induction period (τ). This manifests itself as a decrease in the time τ and as a hysteresis similar to the hysteresis of the upper concentration limit of flame propagation in hydrogen–air mixtures described above.[121] In both cases, the phenomenon is due to the heterogeneous chain propagation reactions involving adsorbed atoms and radicals left on the surface after the previous experiment, because evacuation of the reactor between the experiments does not remove completely the adsorbed species. Heterogeneous chain propagation might influence in a similar way the induction period of detonation in the transition of deflagration combustion to detonation, for example, in shock tubes. This should show as shortening of the pre-detonation period under the influence of detonation of a stoichiometric mixture or a mixture enriched in the combustible component performed in the preceding experiment. Under these conditions, despite the high pressures, the access of gas species to the surface is facilitated by turbulence.

The temperatures typical of a hydrogen detonation wave in air are 2100–2800 K depending on the composition of the mixture.[4] In addition to the experimental data presented above, the determining role of a chain mechanism at these temperatures and atmospheric pressure is confirmed by comparison of the rate of consumption of dioxygen in the reaction with H_2 [103]

$$H_2 + O_2 \xrightarrow{k} \text{products},$$

which is the rate-determining step of the process occurring by a molecular mechanism, with the rate of dioxygen consumption in the chain pathway, *i.e.* in the reaction with atomic hydrogen

$$H + O_2 \overset{k'}{=} OH + O.$$

This step determining the rate of the reaction chain is followed by chain continuation steps

$$OH + H_2 = H_2O + H,$$

$$O + H_2 = OH + H.$$

The ratio of the rate constants for these reactions, k and k' found using concentrations of atomic hydrogen in H_2 flames at 2500 K recommended in reference literature [39, 40] and those measured experimentally or calculated [125, 126] is less than

§ The study on the inhibition of detonation was partly performed together with H Gg Wagner.

5×10^{-2}. Thus, more than 95% of O_2 is consumed in the chain process even without allowance for the fact that the primary reaction products are atoms and radicals able to start reaction chains.

At high pressures and temperatures, in addition to the above step, an important channel of branching is provided by the following sequence of reactions (see, for example, Ref. 107):

$$H + O_2 + M = HO_2 + M,$$

$$HO_2 + H_2 = H_2O_2 + H,$$

$$H_2O_2 = 2\,OH.$$

The above data pointing to the predominant role of the chain mechanism even at about 2500 K also indicate that under conditions where detonation has already occurred, inhibitors are still able to influence the process substantially up to destruction of the detonation wave.

Thus, despite the fact that chain combustion at high pressures is accompanied by intense self-heating of the reaction mixture, which enhances the chain avalanche and, under particular conditions, switches the process to the CTE mode, it is sufficient to weaken the chain avalanche, for example, by adding a small amount of an inhibitor, to diminish appreciably the rate of any mode of the process down to complete suppression of the combustion.[16, 103, 105, 118, 121, 124] The high sensitivity of the process to the influence of inhibitors is due to the fact that the BCP rate, the temperature dependence of the BCP rate and other important characteristics of the process are largely determined by the difference between the chain branching and termination rates [$f-g$, see Eqns (7) and (20)] rather than by the absolute magnitudes of these rates. Therefore, to suppress combustion, the inhibition rate should not necessarily be close to the branching or termination rates taken separately. It is only required that the inhibition rate be commensurate with the difference between these rates. Note that the difference $f-g$ appears in the exponent of power in the function for the temperature dependence of the BCP rate.

The concentration limits of ignition of hydrocarbons in air are markedly narrower than those for ignition of hydrogen–air mixtures (see, for example Ref. 6), although heats of combustion of hydrocarbons are much greater. This is due to the fact that the combustion is inhibited; the hydrocarbon itself acts as the inhibitor because the chain carriers H, O and OH react with its molecules and are thus replaced by less reactive intermediate species.[31]

To conclude this section, we shall list briefly the characteristic features of gas-phase combustion near atmospheric pressure that cannot be interpreted without taking account of the governing role of the branching-chain mechanism of the process and competition of the reaction chain branching and termination.

1. The substantial influence of inhibitors and promoters on all modes of combustion including ignition, developed combustion, explosion, deflagration flame propagation and transition to detonation.

2. The presence of two different kinetic and, correspondingly, thermal modes of chain combustion; the critical character of transition of the process from one mode to the other.

3. Dependence of the critical ignition conditions, the chain-thermal explosion, flame propagation and the process kinetics on the properties of the contacting surface and on the composition of the adsorption layer even if the access of CC to the surface is limited by diffusion.

4. The unusually strong temperature dependence of the specific rate of the process, which differs fundamentally from the Arrhenius law.

5. The much narrower concentration limits of ignition for hydrocarbons in air compared to those for hydrogen in air, although the molar heats of combustion of hydrocarbons are substantially higher.

Unlike the traditional, 'purely thermal' approach, the theory of non-isothermal chain processes developed in a number of studies,[59, 103, 104, 119, 121] which takes into account not only linear but also non-linear heterogeneous and homogeneous reactions of CC and heterogeneous chain propagation, accounts for all the above-listed and some other features observed. Previously these characteristic features of combustion have not been considered.

VIII. Thermal modes of chain combustion in the low-pressure region

When conditions of chain combustion ensuring self-heating of the system are met and the rate of chain combustion obeys a very strong, non-Arrhenius temperature dependence, which facilitates the fulfillment of condition (13), chain combustion is able to switch to the CTE even at low pressures and temperatures, where processes not occurring by a branching-chain mechanism cannot pass to the chain explosion mode. This has been demonstrated [16, 105, 125] for the oxidation of H_2, SiH_4 and GeH_4. It was shown in these experiments that existence of two different kinetic (and, correspondingly, thermal) modes is peculiar to branching-chain combustion irrespective of whether or not heat and mass transfer, convection, or concentration and temperature gradients are present in the system.

Combustion was performed in temperature-controlled heated quartz reactors, the walls of which had been treated preliminarily with hydrofluoric acid, which ensured small coefficients for the decay of CC on the surface, kinetic control of the heterogeneous chain termination and very low P_1 values. This virtually excluded the presence of CC concentration, process rate, or temperature gradients in the reactor; thus, combustion was uniform throughout the whole bulk. The use of mixtures prepared beforehand ruled out the possibility that the process would be controlled by diffusion. High-speed recording of chemiluminescence in the wavelength range of 200–600 nm and at the pressures of the mixture was carried out from the instant the reaction mixture was admitted into the evacuated reactor until the combustion was over. In experiments with SiH_4 and GeH_4 actual concentrations of these compounds were also recorded based on the intensity of the corresponding absorption bands in the IR spectra. Prior to the measurements, the mixture under study was ignited repeatedly until quantitative reproducibility of the state and properties of the surface was attained.

The ratio of chain branching to termination rates was varied by changing the initial pressure of the mixture, and, hence, the reactant concentrations inside the ignition region. When the pressures P_0 exceeded the first ignition limit, the branching rate for unit concentration of CC, *i.e.* the f value, increased proportionally [see also expression (8)]. Since the role of termolecular reactions near the first ignition limit is insignificant, the g value [see expression (9)] is virtually equal to k_{het}. Upon an increase in P_0, this constant does not change or even decreases if the rate of capture of chain carriers by the surface is limited by diffusion to the surface. In both cases, in the low-pressure region, an increase in P_0 results in higher f/g ratios and, what is more important, the difference $f-g$ also increases. Correspondingly, the growth of n and W is enhanced [see Eqns (7) and (10)] and heat evolution accelerates. As a consequence, under conditions of developed combustion, self-heating is significant even at pressures slightly exceeding P_1; it sharply increases on further increase in P_0. This pressure dependence of the process characteristics permitted the researchers to vary the kinetics of combustion and, correspondingly, the intensity of heat evolution.

To record correctly self-ignition from its very beginning and to transfer combustion to explosion, a special technique was used which ensured that the delay time of self-ignition was longer than the time it took for the gas mixture to enter a heated reactor and for a stationary pressure to be established. The essence of the method is introduction into the reaction mixture of tenths of percent of ethane as an inhibitor, which delays the ignition, being

partially consumed. The ignition occurs only after the diminishing concentration of the inhibitor reaches a critical value. The remainder of the inhibitor burns during the ignition, and combustion proceeds in the presence of the inhibitor, which is rapidly spent.

As an example, Fig. 7 presents the pressure oscillograms for the combustion of a stoichiometric mixture of H_2 with O_2 in a reactor with a diameter of 5.5 cm.[16] Point *A* corresponds to the beginning of the admission of the combustible mixture to the reactor and point *B* marks the onset of self-ignition. Since the number of moles of the gas mixture steadily decreases during the hydrogen oxidation, the observed increase in pressure during the propagating combustion can be due only to self-heating of the mixture, as in the experiments at high pressures described above. The initial pressures in runs *1* and *2* differed by 2.25%, those in runs *2* and *3* differed by less than 0.5%. Nevertheless, as can be seen from oscillograms, the combustion kinetics in runs *2* and *3* were much more different than those in runs *1* and *2*. The maximum self-heating in runs *1* and *2* was 200–250°C (measurements were carried out using a quick-response gas thermometer — a high-sensitivity quartz membrane manometer). Meanwhile, self-heating in runs *3* and *4* was almost an order of magnitude greater. It can be seen that variation of P_0 in the vicinity of a particular value (in this case, 26.7 Torr) resulted in a discontinuous change in the maximum temperature (see Fig. 7 *b*). The ignition in runs *3* and *4* and at higher initial pressures was accompanied by a sonic effect — a click. These findings indicate that in runs *3* and *4*, condition (3) holds in addition to relation (2). Thus, runs *1* and *2* correspond to non-isothermal chain combustion without explosion, whereas runs *3* and *4* correspond to a CTE realised at very low pressures. Attention is attracted to the low activation energy of the rate-determining step of the process, namely reaction I (< 70 kJ mol^{-1}).

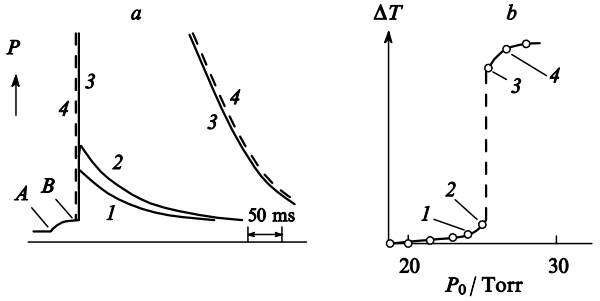


Figure 7. Pressure oscillograms for combustion of a stoichiometric mixture of H_2 with O_2 in a reactor of diameter 5.5 cm at an initial temperature of 728 K (*a*) and change in temperature *vs.* initial pressure of the reaction mixture in the same experiments (*b*).
P_0/ Torr: (*1*) 26.1, (*2*) 26.7, (*3*) 26.8, (*4*) 27.2.

Figure 8 shows the temperature dependences of P_1 and P_2 (curves *I* and *IV*) measured in the same series of experiments as the data of Fig. 7. The region between curves *I*, *II* and *IV* in Fig. 8 is the region of self-ignition and chain combustion without explosion. Oscillograms *1* and *2* in Fig 7 correspond exactly to this region near curve *II*. The region above curve *II* to the right of curve *I* is the region of CTE. The point marked by the arrow is the limit of CTE found from the data of Fig. 7. It can be seen that the CTE region is confined on the low-temperature side by the second ignition limit at any composition of the mixture; as the region of chain ignition narrows down due to an increase in the content of the inhibitor, the CTE region narrows down in a similar way. Thus, CTE can arise only in the developing chain combustion. The CTE limit (curve *II* in Fig. 8) is higher than the first chain ignition limit because origination of a CTE requires that the chain combustion rate and the temperature be sufficiently high for the second condition for thermal explosion, relation (3), also to hold.

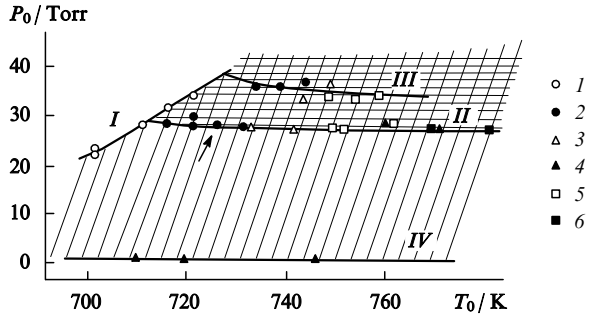


Figure 8. Regions of chain ignition and CTE in a stoichiometric mixture of H_2 and O_2;
(*I*, *IV*) the second and first limits without an inhibitor; (*II*, *III*) the CTE limit in reactors of diameters 5.5 and 3.3 cm, respectively. The content of the inihibitor in the initial mixture (mol. %): (*1*, *2*) 0, (*3*) 0.2, (*4*) 0.3, (*5*) 0.4, (*6*) 0.7.

The limit itself depends only slightly on the temperature because the critical rate of the chain process at which combustion turns into explosion also depends slightly on the initial temperature.

In the experiments the results of which are presented in Figs. 7 and 8, the pressures P_1 were only 12–13 Pa, depending on the temperature, which is ~ 200 times lower than the CTE limit. Under these conditions, chain termination and the heat evolution which accompanies it in the CTE proceed in the gas phase. It has been verified [105] whether chain combustion could turn into CTE at a lower rate of heat evolution, namely, under conditions of heterogeneous chain termination ensuring virtually complete removal of the energy of recombination of atoms and radicals by the reactor walls. The rate constant for chain branching in the oxidation of monosilane, carried out for this purpose, is much greater than that for the oxidation of H_2; therefore, it should be expected that the conditions for CTE — relations (2) and (3) — would be met at even lower pressures and temperatures than in the combustion of H_2 with O_2. At low pressures, chain termination occurs on the reactor walls; hence, the recombination energy is removed almost entirely from the reaction medium and heat evolution in the reaction bulk substantially decreases. In addition, the activation energy of the rate-determining step of this chain process does not exceed 25 kJ mol^{-1} (see Ref. 129), which is much lower than the values needed for the generation of thermal explosion in non-chain processes.[3, 5]

Chain termination in this reaction system also occurred in the kinetic region. The reaction was carried out under conditions of double self-ignition of SiH_4 in a confined space. The first ignition occurred near the reactor surface, while the second one occurred over the whole bulk (this was established by the kinetic method of separate photometry [128]).

When the initial pressure exceeded a definite critical value by only a few percent, the intensity of combustion in the second outburst increased by a factor of several dozens (Fig. 9). The combustion proceeded dozens of times faster, its duration diminished and became shorter than the characteristic time of heat removal. This points to the switching of the combustion to the CTE mode. The same is indicated by the data obtained upon partial replacement of O_2 by He or Ar. The thermal conductivity of argon differs slightly from that of O_2. Therefore, replacement of 50% of O_2 by Ar does not change the CTE limit (Fig. 10). In the case where oxygen is replaced by helium, the CTE limit markedly increases, because thermal conductivity of helium is much greater. Thus, in the combustion of SiH_4, the chain-thermal explosion occurs even at pressures of about 200–300 Pa (see Figs 9, 10), which is an order of magnitude lower than the CTE pressures for the $2H_2 + O_2$ mixture. Nevertheless, the boundary of CTE remains very sharp even in dilute mixtures.

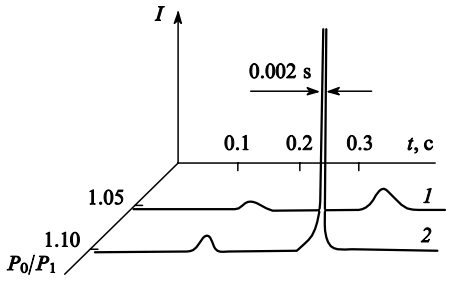


Figure 9. Chemiluminescence oscillograms obtained for ignition of the $0.05\,SiH_4 + 0.95\,O_2$ mixture at an initial temperature of 363 K and different P_0/P_1;
(*1*, *2*) are the numbers of outbursts.

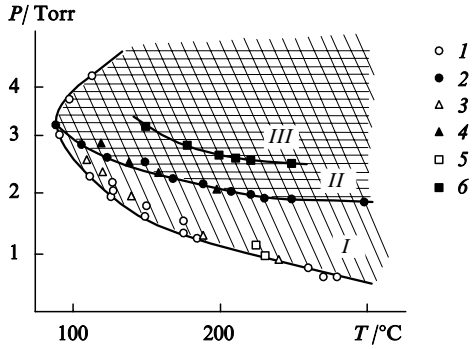


Figure 10. Self-ignition (*I*) and CTE (*II*, *III*) limits for various mixtures; (*1*, *2*) $0.05\,SiH_4 + 0.95\,O_2$; (*3*, *4*) $0.05\,SiH_4 + 0.45\,O_2 + 0.50$ Ar; (*5*, *6*) $0.05\,SiH_4 + 0.045\,O_2 + 0.50$ He.

When the initial pressure increases, combustion in the first outburst does not pass to the CTE mode because this outburst is located just near the surface, and the heat evolved is quickly removed by the walls (almost 50 times as fast as in the second outburst).

The fact that replacement of some of the O_2 by Ar or He does not change the self-ignition limit implies that the chain termination step occurs in the kinetic region (see Fig. 10, curve *I*). There are no gradients of CC concentrations or the process rate in this reaction system until combustion passes to the CTE mode; thus, the presence of two different combustion modes is inherent in the reaction kinetics itself.

At low pressures, as at the atmospheric pressure, the process passes to the CTE mode after the critical reaction rate has been attained during the chain combustion. The concentration range of the CTE is much narrower than the concentration range of ignition (similarly to Fig. 4). In the case of mixtures the composition of which does not differ much from the stoichiometric composition, chain combustion at atmospheric pressure switches to the CTE within a very short period of time after chain ignition has started; hence, the process is perceived only as an explosion.

The experimental data on the combustion of H_2 and SiH_4 at low pressures presented here demonstrate that the ignition peninsula is kinetically non-uniform; it is divided by a sharp boundary into a region of chain combustion that does not pass to the explosion mode and the region of CTE, characterised by a markedly greater self-heating and by a more vigorous behaviour of the process. These data also indicate that combustion switches to chain-thermal explosion even when the low pressure and temperature and the efficient heat removal from the reaction system make impossible a thermal explosion by a non-chain mechanism. The activation energies of the limiting steps of a BCP are much lower than the energy needed to bring about an explosion in a non-chain reaction.

A chain-thermal explosion differs from a classic explosion not only by its fundamentally different mechanism and a broader range of initial conditions under which it can occur but by very sharp critical conditions even at low pressures, which is due to the 'double exponent law'. In simple types of reactions, explosion becomes degenerate despite the very high activation energies.[130, 131] Degeneration of a BCP is possible in processes characterised by rarely branching (athough long) chains, for example, in reactions of CO with O_2 in the presence of very small amounts of hydrogen-containing compounds.[132] The difference between the CTE and a non-chain explosion also shows in the fact that, when heterogeneous reactions play an important role, the course of the CTE depends on the composition and properties of a contacting surface.

Since the kinetics of a chemical reaction determines the macrokinetic features of the process, it should be expected that different kinetic modes of the reaction would be matched by different velocities of flame propagation. Study of the two kinetic modes of chain combustion, one of which is the CTE, elucidation of the differences between these modes, manifested as specific features of the process macrokinetics, and concentration and temperature fields, and determination of the critical conditions for the transition between these modes present considerable interest both for the BCP and combustion theory and for practical purposes (for example, to ensure explosion safety).

The existence of two modes of branching-chain processes in the region of ignition peninsula is indicated by the results of the numerical solution of equations corresponding to the generalised kinetic scheme of a BCP below the second ignition limit under static conditions, together with the equation for the heat balance of the reaction system.[37, 133–135] The parameter χ, equal to the ratio of the heat evolution rate to the heat removal rate, varied in these calculations. Figure 11 presents the kinetic curves for the variation of the relative concentration of one CC (x) for various χ. As the χ value approaches 1.381, the change in the reaction kinetics becomes more and more pronounced, the transition from 1.381 just to 1.382 inducing an abrupt increase both in the maximum x value and in the rate of its growth.

It is notable that, despite a large number of studies dealing with the numerical solution of equations describing combustion of gases, the CTE phenomenon has not been recognised even after publication of works [16, 105, 118, 119, 133] in which this mode has been detected both experimentally and theoretically. This may be explained by the fact that the discovery of specific features of

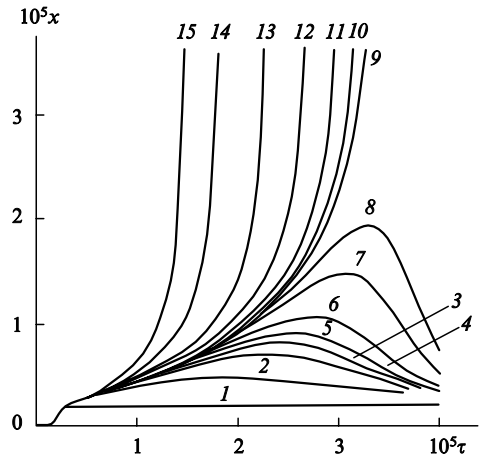


Figure 11. Kinetic curves for the CC at various ratios of the rates of heat evolution and heat removal (the parameter $\chi \times 10^3$) constructed based on a generalised kinetic scheme for a BCP.[133]
The values $10^3\chi$: (*1*) 0, (*2*) 1.00, (*3*) 1.20, (*4*) 1.30, (*5*) 1.35, (*6*) 1.37, (*7*) 1.38, (*8*) 1.381, (*9*) 1.382, (*10*) 1.383, (*11*) 1.39, (*12*) 1.41, (*13*) 1.50, (*14*) 2.00, (*15*) 2.50.

combustion inaccessible to a physical experiment has not been the aim of these calculations; they have been usually undertaken in order to describe particular observations or to compare experimental and calculated characteristics of a process (most often, the induction period) using a large number of parameters for calculations. In addition, when the pressure is relatively high, chain combustion rapidly switches to the CTE and, therefore, the whole process is identified with this mode and is regarded as being 'purely thermal'.

It should be noted that in the solution of sets of equations describing non-isothermal combustion of various gas mixtures, the temperature dependence of the heat of reaction is usually neglected. Meanwhile, since the heat capacities and the temperature dependences of the heat capacities of the reactants and products are different, the heat of a non-isothermal reaction changes as the reaction proceeds, this change being quite substantial in many cases. As a consequence, the real rate of heat evolution differs from the value calculated using an invariant heat of the reaction. Correspondingly, the calculated temperature also differs from the real one. Since the rate of a BCP follows an unusually strong temperature dependence and is inversely related to self-heating, it is obvious that errors in the calculation of the temperature result in deviations of the calculated reaction rates and other kinetic characteristics of the process from those observed experimentally. Therefore, the results of calculations of this type are reliable only for qualitative discussions.

IX. Conclusion

The results of experimental and theoretical studies carried out in recent years indicate that branching-chain mechanisms and competition between branching and termination of reaction chains are the governing factors in the gas-phase ignition and combustion of hydrogen-containing and many other compounds not only at very low pressures (tens or hundreds of times lower than the atmospheric pressure) but also at atmospheric and higher pressures. Self-heating becomes substantial only during developing chain combustion and enters a positive feedback with chain avalanche. It has been found that combustion, being a chain process over the whole pressure range studied, can be caused, depending on the initial reactant concentrations, either by the chain avalanche alone, enhanced by self-heating, or by simultaneous action of chain avalanche and avalanche-like accumulation of thermal energy in the reaction system. The second mode can occur only after chain ignition and after a particular rate of chain reaction and, correspondingly, the rate of heat evolution have been attained. The transition between these modes induced by variation of the initial conditions is a critical process. The competition of chain branching and termination throughout the whole range of pressures (both low and high) determines the kinetic features of each combustion mode including ignition, developed combustion, chain-thermal explosion (unknown until recently), flame propagation and its transition to detonation. The branching-chain mechanism also determines the dependence of characteristic features of combustion on the properties of the contacting solid surface under conditions where the access of atoms and radicals to the surface is unhindered (for example, when the ratio of the surface area to the reactor volume is great or in the case of turbulent movement of gases). This relates, for example, to fluid bed and catalytic combustion and to the transition from deflagration to detonation. Thus, the main factor governing the regularities of the gas combustion of hydrogen-containing and many other compounds was actually identified.

Elucidation of the governing role of the branching-chain mechanism in the gas-phase combustion processes at atmospheric and higher pressures and the regularities discovered open up new prospects for the theory of chemical kinetics, first of all, as regards chain processes, and for combustion theory. The data obtained recently would help in the solution of important applied problems. This is confirmed by the above-cited examples, which demonstrate that the use of proposed and tested highly efficient non-corrosive and inexpensive inhibitors can help in controlling not only ignition but also the intensity of developed combustion and explosion, the velocity of flame propagation and its transition to detonation. The predominant role of a chain mechanism at temperatures typical of detonation creates conditions for controlling also the velocity of a detonation wave, within certain limits, by using inhibitors and promoters. Development of the scientific foundations of the chemical control of all the combustion modes mentioned above by selection and application of appropriate inhibitors and promoters is a topical theoretical and practical task.

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