

Kinetic Aspects of Chemical Control over Flame Propagation in Combustible Gases

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Abstract—Kinetic aspects of controlling ignition and flame propagation parameters in the gas phase by chemical methods are considered. The efficiency of the chemical methods is due to the branched chain character of gas-phase combustion reactions and the dominant role of the competition between chain branching and chain termination in these processes.

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Ignition and developing combustion are known to be a chemical process that occurs with progressive self-acceleration and is accompanied by heat and light release (see, e.g., [1–5]). Progressive self-acceleration takes place in various combustion modes: ignition, flame propagation, explosion, and detonation.

Flame propagation in gases is one of the most important manifestations of combustion processes from both theoretical and practical standpoints. This phenomenon is considered in specialized sections of fundamental monographs and in specialized collections of works (see, e.g., [1, 2, 5–10]). Flame propagation laws are also described in numerous articles in scientific journals. The propagation of laminar flame through a fuel mixture is due to the fact that intermediate species from the combustion zone come into an adjacent layer of the fresh mixture and provide ignition conditions therein. For this reason, laminar flame propagation is viewed as layer-by-layer combustion [1, 6, 8, 9].

Until recently, the methods of regulation of combustion parameters have mainly been of nonchemical nature (flame arrestors, flame suppressors, dilution of the combustible mixture, etc.). The chemical agents were some hydrocarbon derivatives (halons, e.g., tetrafluorodibromoethane). However, the utility of most of these agents is limited by their low efficiency. The amounts of these agents required to suppress combustion are so large that their effect is viewed in some works, and with good reason, as arising primarily from the dilution of the combustible mixture and from the increase in its heat capacity [11–13]. Since a chemical process underlies combustion, a higher efficiency is expected from agents and methods that will allow the

process to be controlled via affecting its chemical mechanism and kinetics.

Here, we consider kinetic aspects of chemical control over combustion and flame propagation.

TWO MECHANISMS OF GAS IGNITION AND COMBUSTION

Ignition and combustion can occur via two fundamentally different physicochemical mechanisms. One is an exclusively positive feedback between the reaction rate and the self-heating of the reaction system. Ignition caused by this factor alone, referred to as thermal ignition, takes place when the following conditions are fulfilled simultaneously:

$$q_+ \geq q_-, \quad (1)$$

$$dq_+/dT \geq dq_-/dT. \quad (2)$$

Here, q_+ is the rate of heat evolution in the chemical reaction, which is equals to the product of the heat of the reaction and the reaction rate; q_- is the rate of heat dissipation from the system; and T is temperature [1, 2, 8].

In thermal combustion theory, a chemical process is represented as a one-step reaction in which the product results directly from the initial reactants. Usually, the reaction is assumed to be first-order. Accordingly, the reaction rate is represented as

$$-d[B]/dt = w = k^0[B] \exp(-E/RT), \quad (3)$$

where $[B]$ is the reactant concentration, t is time, E is the activation energy, and k^0 is the preexponential factor of the rate constant [2, 7, 8]. Thus, self-acceleration in thermal combustion is determined by the positive feedback between the reaction rate and the self-heating of the system.

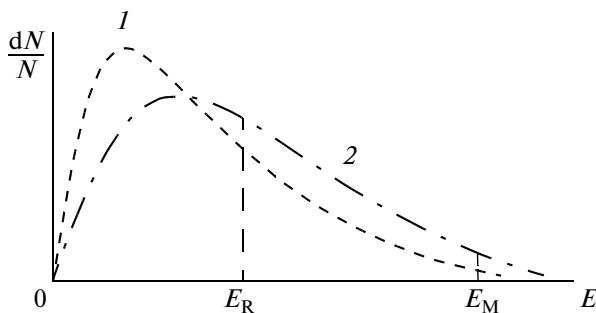


Fig. 1. Equilibrium species energy distribution at temperatures (1) T_1 and (2) T_2 .

A radically different key factor in ignition is the avalanche multiplication of active intermediate species (free atoms and radicals) in their repeated reactions that produce reaction chains:



In this scheme, x and y (free atoms and radicals, respectively) denote reaction-chain carriers; A and B stand for the initial molecular reactants; and P is the final product [1].

The rate of a branched chain process is

$$w = -d[B]/dt = \omega_0 + k_p n[B], \quad (4)$$

where t is time; n and $[B]$ are the concentrations of the chain carrier and the initial reactant, respectively; ω_0 is the chain initiation rate, i.e., the chain-carrier generation rate in reactions of initial molecules alone; and k_p is the effective rate constant of the rate-limiting step [1]. Because of the high reactivity of the chain carriers and their high concentrations, the initial reactants are consumed in developing combustion mostly via reactions with these species.

Along with being regenerated and multiplied, chain carriers are involved in loss reactions; that is, they recombine or are adsorbed. Therefore, the time variation of the chain-carrier concentration caused by a chemical reaction is described by the equation

$$dn/dt = \omega_0 + (f - g)n = \omega_0 + \varphi n, \quad (5)$$

where f and g are, respectively, the chain branching and chain termination rates for unit chain-carrier concentration, and φ is the branching factor.

When branching dominates over termination, i.e., when

$$f > g, \quad (6)$$

n increases progressively until the consumption of the initial reactants comes into play. Accordingly, the process rate increases in an avalanche manner as well, which also follows from Eq. (4). Relationship (6) defines the chain ignition condition also in case of quadratic-law chain termination [14]. The main features of a branched chain process are defined by the feedback between the process rate and the concentra-

tion of active intermediates and between n and dn/dt , expressed by Eqs. (4) and (5).

The different characters of self-acceleration in the thermal and chain mechanisms and the different physicochemical mechanisms by which the system uses the chemical energy of the reactants in thermal and chain self-acceleration are considered in terms of molecular kinetic theory with the help of Fig. 1. This figure displays the distribution of molecules over energy (Boltzmann's distribution) for two temperatures. The E_M value on the abscissa indicates the activation energy of the reaction between initial molecules. E_R is the activation energy of the reaction of the initial molecules with active species (atoms and radicals) that carry out the chain mechanism. This figure demonstrates that the amount of molecular reactants that are capable of reacting with one another at temperature T_1 is represented by the very small area enclosed between curve 1, the abscissa axis, and the vertical dashed line E_M . Upon self-heating to temperature T_2 , the distribution curve shifts to the right and the amount of initial molecules that are capable of reacting with one another is represented in this case by the slightly larger area bounded by curve 2, the abscissa axis, and the vertical dashed line E_M . This is responsible for the self-acceleration of the reaction of molecules with one another (i.e., thermal self-acceleration). Figure 1 also makes it clear that the area bounded by curve 2, the abscissa, and the same vertical dashed line is far smaller than the area enclosed between curves 1 and 2 to the right of their intersection point. This means that the self-heating-induced increase in the number of species that are capable of entering an intermolecular reaction is incomparably smaller than the number of all heated molecules; that is, the energy released as heat is largely dissipated unproductively from the standpoint of reaction self-acceleration.

The proportion of molecules that are capable of reacting with atoms and radicals, as distinct from the proportion of molecules that enter intermolecular reactions, is represented by the area bounded by the same species energy distribution curves, the abscissa axis, and the vertical dashed line E_R , not E_M (Fig. 1). One can see that, for each temperature, the probability of the initial molecules reacting upon collision with a reactive species is far greater than the probability of a reaction occurring upon collision of valence-saturated molecules with one another.

Another difference between the self-acceleration mechanisms is the fact that the chain carrier concentration increases progressively in developing chain ignition even at a constant temperature, without the species energy distribution curve being shifted. Accordingly, when the multiplication rate of chain carriers exceeds their loss rate, there is a progressive increase in the amount of molecular reactants that react with these active species; that is, there is an increasing self-acceleration of the chain process that

needs no self-heating. This means that, even though temperature is unchanged and so is the number of molecular reactants corresponding to the area between curve 1, the abscissa axis, and vertical dashed line E_R , the chain process rate increases owing to chain-carrier multiplication. Another difference is in the way self-heating affects the process rate. Figure 1 shows that, as the temperature rises from T_1 to T_2 , the increase in the amount of molecules capable of reacting with active species far exceeds the increase in the number of molecules capable of reacting with one another.

The fundamental difference between the self-acceleration factors in chain and thermal combustion implies the equally strong difference between the main regularities of these types of processes, which shows itself both as different critical ignition and flame propagation conditions and as specific features of the time evolution of developed combustion with and without admixtures.

DEVELOPMENT OF THE CONCEPTS OF GAS-PHASE COMBUSTION CHEMISTRY

It was long believed that the branched chain mechanism is the key mechanism of gas-phase combustion only at pressures hundreds of times lower than atmospheric pressure (see, e.g., [1–6, 9, 15–17]). In the formation of these views, an important role was played by the interpretation of the third self-ignition limit (P_3) of hydrogen with oxygen, which lies in a pressures range above 40 kPa and includes atmospheric and elevated pressures [1, 6, 9]. The third limit is viewed to be a consequence of the heat avalanche alone in a number of monographs [2, p. 355; 5, pp. 24, 26; 8, p. 43; 16, p. 171]. Semenov in his monograph [1] on page 545 interprets the third limit in terms of the chain mechanism. On page 436, however, he writes the following: "A perfect agreement between calculations and experiments leaves no doubt that the third limit for hydrogen–oxygen mixtures is thermal in nature." In his later works [18, 19], Semenov again considers, as chain limits, only the two lower limits, which are tens and hundreds times lower than atmospheric pressure. Encyclopedias [3, 4] and handbooks of chemical kinetics and physical chemistry also interpret ignition in the atmospheric pressure region as thermal explosion. Based on these concepts, the combustion process was regarded as a reaction in which the product results directly from the initial reactants. Accordingly, mathematical equations for a hypothetical one-step event were employed in the analysis of flame propagation [2, 5–8, 15, 16]. Obviously, one-step reactions can self-accelerate only as a result of self-heating. For this reason, ignition was regarded as a merely thermal phenomenon. In numerical simulations of combustion at atmospheric pressure with the use of kinetic schemes that comprise reactions of atoms and radicals, the role of chain branching was ignored [20]. In studies in

which this question was raised, ignition was regarded not as a result of the appearance of a chain avalanche, but as a thermal explosion (see, e.g., [16]). Thus, the recognition by some researchers of the presence of atoms and radicals in the combustion zone does not mean that they actually accept the chain character of ignition and explosion, because these phenomena are qualified by them as being thermal [2, 6, 15, 16, 21].

Some authors (see, e.g. [6, 8]) mention chain combustion under self-heating conditions. However, the same researchers in the same or later works consider the reaction as a single step and use equations applicable to one-step reactions only; that is, they ignore the chain character of combustion. Accordingly, self-heating is postulated to be the only reason for the self-acceleration of the process. The competition between chain branching and chain termination was also ignored in the consideration of the concentration limits of flame propagation for hydrogen, hydrocarbons, and may other compounds. Zel'dovich et al. [8] devote paragraph 5.3 to branched chain combustion, but the hydrogen oxidation mechanism is represented there by two steps, namely, linear-law branching and quadratic-law chain termination. With this scheme, in which linear-law chain termination is missing, the chain process rate would have increased from the very beginning without an induction period with progressive self-acceleration at all, even moderate, temperatures. The accumulation of hydrogen atoms would have ceased only at the unrealistically high concentrations of these species at which the quadratic-law recombination rate is equal to the linear-law branching rate. In addition, Zel'dovich et al. [8] assume that heat is released only upon quadratic-law recombination of H atoms. This assumption also underlies the postulates and equations reported by, e.g., Rubtsov et al. [22]. In fact, the heat release rate in this recombination reaction is much lower than the overall heat release rate in H_2 combustion. Some of the equations used by Rubtsov et al. [22] are in principle inapplicable to chain combustion and apply only to thermal combustion occurring as a hypothetical one-step reaction.

Until very recently, articles have been encountered where it was claimed that ignition in the atmospheric pressure region is not a chain process, but a thermal explosion. The possibility of inhibiting detonation was also denied. These articles are analyzed in [23–26].

Many fundamental effects remain unexplained in terms of ideas that ignore the chain character of combustion. An example is the influence of some minor admixtures on ignition, including inhibitory effects. Note that this well-known effect was regarded by those who denied or ignored the chain character of combustion. Monographs on combustion even did not consider inhibition of combustion. Other examples of the conflict between experimental data and the ideas ignoring the chain character of combustion can be found in our earlier works [27, 28].

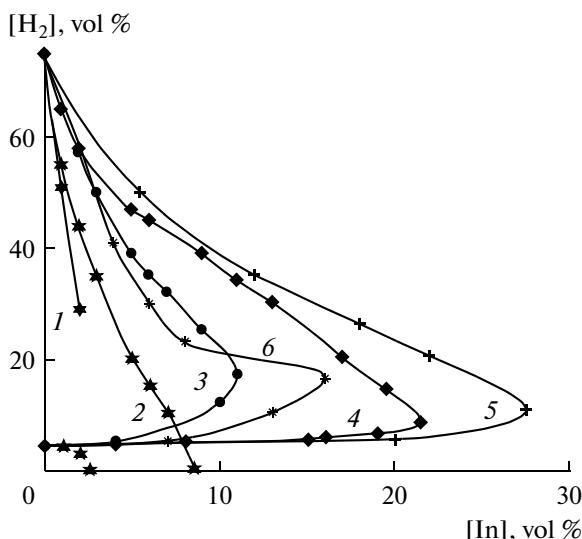


Fig. 2. Effect of inhibitors on the concentration limits of flame propagation in hydrogen–oxygen mixtures [28]: (1) octane, (2) hexane, (3) $C_2F_4Br_2$, (4) NAFS-III, (5) CF_3H , and (6) C_2F_5H .

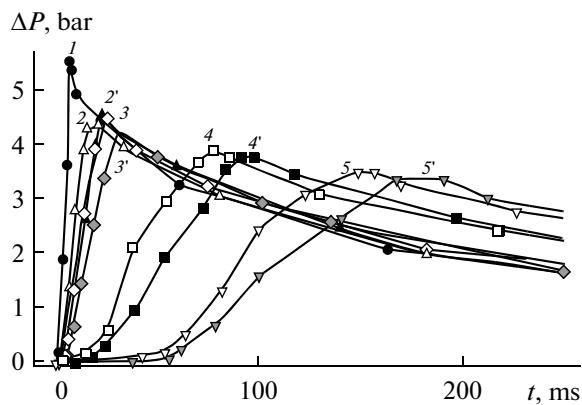


Fig. 3. Effect of (1–5) isopropanol vapor and (1'–5') propylene vapor on the combustion intensity of their mixtures with 40% H_2 . Inhibitor percentage (vol %): (1, 1') 0, (2, 2') 0.75, (3, 3') 1.0, (4, 4') 1.5, and (5, 5') 2.0 [26].

CHAIN CHARACTER OF GAS COMBUSTION AT ANY PRESSURE AND IN SELF-HEATING MODES

We revealed the role of chain branching in combustion under atmospheric pressure in a large series of experimental and computational studies. In these studies, including [23–38], we showed that, contrary to traditional ideas, all parameters of gas-phase combustion processes are primarily determined by the competition between chain branching and chain termination not only at extremely low pressures, but also at any higher pressure. Numerical simulation showed that, above 720 K, the ignition of, e.g., H_2 in air at 1 bar can occur even when there is no self-heating [31]. The starting chain combustion is additionally

accelerated by self-heating. The role of the chain mechanism in various combustion modes can be elucidated using effective inhibitors suggested by us. This provided a means to controllably vary the ratio between the chain branching and chain termination rates and thereby change the contribution from the chain avalanche to the process. Based on these studies, it was established that, for all pressures and temperatures (up to at least 1700 K), minor admixtures of the proposed inhibitors strongly affect combustion characteristics in all combustion modes, including flame propagation and detonation [32, 35, 38].

The results presented in Fig. 2, which illustrate the effects of various admixtures on the concentration limits of flame propagation for hydrogen/air mixtures, provide an unambiguous indication of the chain character of ignition and propagation of the combustion zone and are in good agreement with the inference made in our earlier [28]. Indeed, if the combustion reaction occurred directly between initial reactant molecules, an admixture in an amount of 1 or 2% could not exert any significant effect on the process kinetics and certainly could not prevent combustion. Therefore, the inhibition of ignition and flame propagation by an inhibitor shows that combustion does not occur as a direct reaction between the initial reactants, but it proceeds via a mechanism in which the initial reactants react rapidly with active intermediate species (atoms and radicals). In these reactions, active species are regenerated and multiplied to yield branching reaction chains. In the presence of an inhibitor, active species react with the inhibitor still more rapidly to form low-active products; that is, the inhibitor terminates reaction chains and thereby slows down the combustion reaction. The blocking of the chain pathway of the process by the inhibitor prevents ignition and flame propagation.

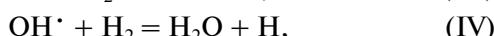
In one method of investigation of the effect of inhibitors on the combustion intensity, the reaction is carried out in a closed steel reactor. Combustion is initiated with a spark or a hot wire. Pressure and chemiluminescence are rapidly and simultaneously recorded in the course of the process. By way of example, Fig. 3 displays the results of a series of such experiments on a 40% H_2 + air mixture in a 3.2-l reactor. Inasmuch as H_2 combustion is accompanied by a monotonic decrease in the number of moles of the mixture, pressure elevation during the process is solely due to the self-heating of the reactant gas. In the propagating flame zone, where heat release takes place, temperature is obviously higher than in the unburned gas. When there is no explosion, however, the pressure is equalized over the volume of the reactor with the speed of sound. Therefore, if combustion does not turn into explosion, the pressure rise (ΔP) characterizes the average temperature rise (and, accordingly, the average temperature) over the volume of the reactor. This temperature rise is determined by the ratio of the rates of heat release accompanying the combustion reaction

and heat dissipation from the reactor. The smaller the characteristic reaction time compared to the characteristic heat dissipation time, the greater the temperature rise and the more closely does it approach the combustion zone temperature. Thus, ΔP serves as a measure of combustion intensity.

One can see in Fig. 3 that, as the inhibitor percentage increases, the rate curves progressively flatten and the induction period lengthens; that is, combustion is inhibited. The observed strong effect of admixtures on the concentration limits of flame propagation and on the flame speed unambiguously show that traditional views, which disregard the chain character of combustion, cannot explain these characteristics of combustion. Indeed, as was demonstrated above, the strong effect of the inhibitor in an amount of 0.7–2% on the concentration limits and kinetics of the process is possible only with the chain mechanism. Thus, the competition between chain branching and chain termination reactions is the decisive factor not only in the formation of the concentration limits of ignition and flame propagation, but also in the flame speed.

In the course of the development of a chain avalanche, the initial reactants are consumed, with an acceleration increasing with time, in their reactions with multiplying active species. The inhibitor blocks the chain pathway of the process, and the initial molecules have only to react with one another, overcoming a high energy barrier equal to the activation energy E_M in Fig. 1. The proportion of such molecules is extremely low, which can also be seen from Fig. 1. Ignition and flame propagation are thereby prevented, resulting in the narrowing of the concentration limits demonstrated in Fig. 2. At very low inhibitor concentrations, the chain pathway is blocked only partially. In this case, ignition is not prevented, but combustion and, accordingly, flame propagation are decelerated (Fig. 3). In expression (5), inhibition is accounted for by the additional term $g_{In} = k_{In}[In]$ as a component of g .

During H_2 combustion, the most significant reactions of the initial reactants with active intermediates are as follows [1, 9]:



The inhibiting effect of propylene (Fig. 3) is due to its rapid reactions with H , O , and OH^\cdot reactive species, primarily the addition of an H atom at the π -bond,



which occurs at atmospheric pressure and obeys a second-order rate equation. The reactions of newly formed propyl radicals lead mostly to chain termination and partial propylene regeneration [27, 39]. When propylene is added in amounts larger than 2%, the mixture does not ignite.

Unlike the reaction between the hydrogen atom and propylene, the reaction involving isopropanol

(whose molecule has no π -bonds) proceeds via the H atom abstraction pathway:



Because this reaction is slower than reaction (VI), isopropanol produces a weaker effect than propylene, which can also be seen from Fig. 3.

During the development of chain combustion, self-heating accompanying the chain avalanche is accelerated under certain condition so that the system fulfills not only the chain combustion condition, but also the condition ensuring the avalanche accumulation of thermal energy (relationship (2)), and combustion acquires the character of chain thermal explosion. The limits of the initial conditions corresponding to the transition from chain combustion to chain thermal explosion are critical in character. Inhibition offers a means to control both the critical conditions for the transition from chain combustion to chain thermal explosion and the explosion intensity [27].

The chain character of the model hydrogen ignition process at atmospheric pressure was also verified by numerical simulation [40] based on a conventional reaction network [1, 9]. The undistributed set of rate equations, combined with the heat-balance equation,

$$\begin{aligned} \sum_1^N c_i n_i \frac{dT}{dt} &= \sum_i^N \sum_1^M Q_i (\beta_{ij} - \alpha_{ij}) w_j - \frac{S}{V} \alpha (T - T_0) \\ \frac{dn_i}{dt} &= \sum_j^M (\beta_{ij} - \alpha_{ij}) w_j \end{aligned} \quad (7)$$

was solved by Newton's iterations at each temporal layer and by automatic selection of the time step, based the estimation of the approximation error of the difference scheme. In this set of equations, n_i is a component concentration; w_j is an elementary reaction rate; α_{ij} and β_{ij} are stoichiometric factors; Q_i is the heat content of the i th compound; α is the heat-transfer coefficient; C_j is the heat capacity of the i th component; S and V are the reactor surface area and volume, respectively; and M and N are the numbers of initial reactants and final products, respectively.

The heats of reactions and rate constants were borrowed from handbooks [41, 42]. The computational software allowed the rate constant of a selected process step to be changed at any preset point of time during combustion and the role of this step in combustion to be thus studied.

In simulation, ignition was defined as the rapidly progressing self-acceleration of the chemical process induced by the multiplication of active intermediates as a result of chain avalanche and/or progressively accelerating self-heating. The limiting initial temperature T_{lim} was determined as the value above which the aforementioned features of ignition are observed, but below which they are not. The critical ignition temperatures calculated with and without self-heating taken into account differ by a small value of 2–3%, which is within the error in the thermal parameters of

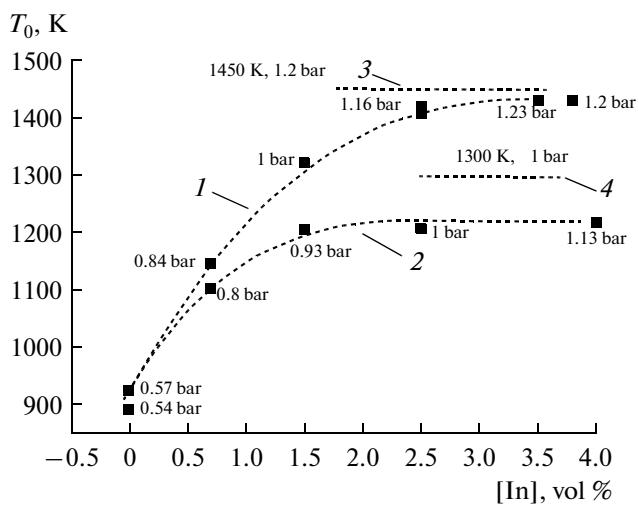


Fig. 4. Ignition temperature of $2\text{H}_2 + \text{O}_2$ mixtures versus the concentration of (1) propylene and (2) isopropanol; (3, 4) self-ignition temperatures of propylene and isopropanol, respectively [38].

the reaction system and elementary reactions. Furthermore, the critical temperature calculated for atmospheric pressure coincides with the well known measured value of 830 K [9] with the same accuracy. Thus, hydrogen self-ignition at atmospheric pressure is a result of a chain avalanche.

Self-heating outside the ignition region even in the immediate vicinity of the critical temperature does not exceed several degrees and cannot lead to ignition without a chain avalanche. The termination of chain avalanche during combustion, which is implemented in simulation by means of decreasing the chain branching rate constant, leads to the immediate cessation of combustion. This result, which is in agreement with experimental data, shows that self-heating without chain avalanche is likewise incapable of maintaining combustion.

The relative roles of self-heating and chain avalanche in producing the ignition and flame propagation critical conditions were also elucidated experiments in which the process was carried out at high initial temperatures [38]. The combustion of a stoichiometric H_2/O_2 mixture in the presence or absence of an inhibitor was initiated in a shock tube by an incident shock wave with a preset initial speed. In this way, the required initial temperatures and pressures were created in a fraction of a microsecond. The method also allows monitoring of the transition of deflagration to detonation in the presence and in the absence of an inhibitor by simultaneous recording of pressure and flame spectra. The data displayed in Fig. 4 show that, if the chain termination rate is raised by adding an inhibitor to the initial mixture, it will be required to increase the initial temperature for ignition to occur. One can see that the H_2/O_2 mixture, which ignites in the absence of an inhibitor at 900 K, is non-

ignitable in the presence of 0.75% propylene not only at this temperature, but also when the initial temperature is increased by 150 K. Flame propagation and detonation, which are detected in the absence of an inhibitor, are thereby prevented as well. These data demonstrate that high temperatures themselves, without a chain avalanche, cannot cause ignition and flame propagation. This also explains why a mixture that contains 2% propylene and does not ignite at, e.g., 1300 K is ignitable even at a 400 K lower temperature when it contains no inhibitor. Thus, the competition between chain branching and chain termination plays the key role in the establishment of critical ignition and flame propagation conditions not only when the initial temperature is equal to room temperature, but also at temperatures far above 1000 K. Earlier reported data [35, 38] show that what was said about the chain character of the critical conditions also applies to the concentration limits of detonation.

The decisive role of the chain avalanche in flame propagation is demonstrated by experiments in which flame is extinguished by very small amounts of a hot aerosol-forming inhibitor introduced the hydrocarbon combustion zone [29]. However, the same amount of the same inhibitor added to sodium vapor flame does not affect the process because the combustion of this vapor, unlike hydrocarbon combustion, occurs via a nonchain mechanism.

The cessation of combustion with the termination of the chain avalanche by means of reducing the ratio of the chain branching and chain termination rates in the burning system was also simulated by numerically solving the set of equations for ignition and combustion in a hydrogen/air mixture at 1 bar [40]. It was thereby shown that the model that takes into account the chain character of the process adequately describes not only the critical ignition conditions, but also the regularities of developed combustion.

COMBUSTION CHARACTERISTICS AS A FUNCTION OF THE INHIBITION RATE

The above data demonstrate that, for any degree of self-heating, the main regularities of branched chain combustion processes are primarily dictated by the existence of a positive feedback between the concentration of active intermediates and the rate at which this concentration changes. From Eq. (5) one can see that the character of the feedback between these quantities is, in turn, determined by the difference between the chain branching and chain termination rates. For this reason, equations for combustion should contain the difference between the rates of the competing reactions that lead to the multiplication and loss of reactive species. In particular, this is true for flame propagation. From Eq. (5) it also follows that, for each given temperature, n is an exponential function of $(f - g)t$ [1]. It was also noted that the branching rate constant, which is

included in f and thereby appears, together with its Boltzmann factor, in the exponent, leads to a very strong and specific temperature dependence of n and w [27].

In general form, the role of the aforementioned feedback is clear from the set of Eqs. (7), where the products of the concentrations of active species and molecular reactants and the rate constants of reactions are included in w on the right-hand side. The concentrations of all active species vary according to the $\exp(\Phi t)$ law [43], where Φ plays the role of the factor φ in relationship (5).

In equations that refer to flame propagation, the inclusion of terms describing diffusion and thermal conductivity does not eliminate the feedback between the concentrations of active intermediates and the rates at which these concentrations change [1, 43]. Ivanova et al. [43], based on an analytical consideration of sets of equations for the branched chain process, demonstrated that the ignition condition is determined by the existence of a positive eigenvalue of the Jacobi matrix corresponding to the set of differential equations that refer to the change in the concentrations with time. This set of equations is, in general, nonlinear. But at each point of space and at each point of time, the behavior of the solutions of this set is determined by the properties of a linearized set that comprises diffusion terms.

The products of the rate constants and reactant concentrations referring to chain branching and chain termination enter Φ with a positive sign and a negative sign, respectively. A positive value of Φ corresponds to the domination of chain branching rates over chain termination rates; a negative value of Φ corresponds to the domination of chain termination rates over chain branching rates. Obviously, the rates included in Φ and, accordingly, Φ itself change in response to temperature variations. However, the exponential dependence of the active species concentrations (and, accordingly, the rate of the chain process as a whole) on Φt and on the rate constants appearing in the exponent persists.

In view of the above, for explaining the qualitative pattern of the phenomenon, the chain process rate at a given place of the reaction space may be represented as

$$W = k_p [B] n_i^0 b \exp \int_{t_0}^t (f_1 - g_1) dt. \quad (8)$$

Here, n_i^0 is the chain-carrier concentration at the moment t_0 , when chain initiation may be already ignored; b is a factor characterizing the coordinate; and f_1 and g_1 are, respectively, the effective chain branching and chain termination rates at a unit chain carrier concentration. The term g_1 accounts for the contribution from diffusion.

Since the flame propagation rate is primarily determined by the rate of the chain reaction, an expression analogous to (8) will also define the flame propagation rate as a function of the initial reactant concentrations and temperature.

Let us now consider the cause of the strong effect of inhibitors on the rate of the combustion reaction. The specific features of the dependence of the process rate on temperature and on the initial reactant concentrations, including the inhibitor concentration, arise primarily from the fact that the difference between f_1 and g_1 (more generally, between f and g) in rate equations appears in the exponent in the functional dependence of the reaction rate on time (8). As a consequence, even a small amount of an inhibitor strongly decreases this difference and, accordingly, decreases the process rate and the heat evolution rate. The resulting temperature drop exponentially decreases the rate constants, including those in the exponent. The strongest effect is exerted on the rate constant of branching reaction (III), which has the highest activation energy. Obviously, this temperature reduction causes an additional, very strong deceleration of the reaction. When the effect of the inhibitor is such that $f_1 < g_1$, ignition and combustion are totally suppressed.

Note that inhibition also strongly weakens the temperature dependence of the reaction rate in view of the same functional dependence (8) of the rate on temperature and inhibitor concentration. This makes it difficult to satisfy the thermal explosion condition (2) for the chain mechanism. For this reason, chain thermal explosion is prevented by lower concentrations of a given inhibitor than ignition.

Taking into account the exponential dependence of the reaction rates on the difference between the specific chain branching and chain termination rates, we gave the following explanation for the synergism of the joint action of the inhibitor and a chemically inert compound on combustion [44]: the inhibitor and inert admixture concentrations enter into the expression for the chain process rate in the exponent as negative terms. Therefore, the joint action of these components on the rate is represented by the product of exponents and should be nonadditive. The synergistic effect of the admixtures points to the feasibility of enhancing the efficiency of chemical methods for controlling combustion via using a combination of admixtures.

The foregoing makes it clear that the efficiency of chemical control over gas combustion is determined by the aforementioned features of the rate of the branched chain process as a function of the initial reactant concentrations, including the inhibitor concentration, and as a function of the rate constants of the reactions of all components.

Thus, the totality of features of gas-phase combustion at atmospheric pressure points to the key role of the competition between chain branching and chain termination and the impossibility of explaining the observed combustion regularities in terms of ear-

lier ideas about the one-step mechanism, contrary to the statement of, e.g., Rubtsov [45]. At present, however, an increasing number of publications, including those dealing with the inhibition phenomenon, take into account the branched chain character of combustion in gases (see, e.g., [46, 47]).

CHANGE OF THE ENERGY RELEASE REGULARITIES UPON INHIBITION OF COMBUSTION

The above analysis shows that the occurrence of chain branching and chain termination reactions not only means the existence of additional steps in the combustion mechanism, but also determines the energetic features of the process, which differ fundamentally from the features of nonbranched chain reactions. The energetic features specific of chain combustion are as follows: in atom and radical multiplication events, the chemical energy of the starting molecular reactants converts partially into the free-valence energy of these species. This is the optimal form of chemical energy for a high rate of the process, because not only do species having free valences react more rapidly with the initial molecules, but they are also regenerated and multiplied until the consumption of the initial reactants comes into play. In chain-propagation and chain-termination reactions, the free-valence energy is actually relayed from one chain carrier to another and is additionally accumulated. For this reason, the uncoupled spin energy, which determines the reactivity of atoms and radicals, is dissipated in branched chain processes to a much lesser extent than thermal energy. These energetic features are responsible for the higher rates and some other features of chain combustion processes.

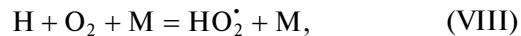
Since the inhibition events are exothermic, the deceleration and suppression of combustion by means of inhibitors are not a consequence of heat outflow from the reaction mixture; that is, they do not result from heat losses. Conversely, thermal energy is supplied to the reaction system during the chain termination event involving, e.g., an inhibitor. An example of such a heat inflow channel is the above-considered exothermic hydrogen atom addition to propylene (reaction (VI)).

Note that the starting materials are not spent at all provided that ignition has been prevented with the use of an inhibitor. Accordingly, in this case there are no heat losses in the system and there is virtually no heat inflow. Ignition is prevented in the following way: when an inhibitor is added, the chain termination rate, which is insignificant because of the very low concentrations of active species, from the very beginning is still higher than the branching rate, which is also low for the same reason. The inhibitor-induced narrowing of the concentration limits results from the violation of the chain ignition condition (5) even under some heating of the mixture (Fig. 4), but does not result from

heat losses, which are nothing more than a consequence.

Chain termination, which is responsible for the deceleration of combustion under the effect of inhibitors, occurs for the reason that low-activity radicals formed in the inhibition event to replace chain carriers eventually recombine, and the free-valence energy turns into thermal energy, which is utilized by the reaction system for accelerating the combustion reaction much less efficiently, as was demonstrated above (Fig. 1). This energy is dissipated over all species of the system. The vast majority of this species has no free valences and, for this reason, cannot react with one another. In this case, mixture cooling is a consequence, not the cause, of reaction deceleration. Evidently, inhibition is only one manifestation of the key role of the competition between chain branching and chain termination. This competition is inherent in branched chain processes irrespective of whether there is an inhibitor in the system.

During combustion of, e.g., H_2 and O_2 heat is released primarily upon the formation of the final product (H_2O) owing to the high rate of exothermic chain propagation (step (IV)) and in the reaction



in which an H atom, which is very reactive, turns into a low-activity radical HO_2^+ . The heat release rate in the quadratic-law recombination of H atoms during almost the entire process is tens of times lower than the overall heat release rate (see, e.g., [40]). In this connection, note that Rubtsov et al. in their computational study [22] believe that heat is released upon H_2 combustion only in the quadratic-law recombination reaction of H atoms, that is, only to the extent to which the initial fuel (in the case at hand, H_2) is regenerated and returned to the reaction medium. Thus, Rubtsov et al. [22] believed that the regeneration of H_2 in an amount corresponding to the total amount of released heat occurs during hydrogen combustion along with water formation. This is also in conflict with experimental data concerning, e.g., the flame structure [16, 47]. Furthermore, using known values of reaction rate constants and the heats of reactions, one can easily see that the heat release rate even in reaction (VIII) alone is far higher than in the quadratic-law recombination of H atoms. The amount of heat released from the recombination of H atoms solely is so small that, contrary to the calculations Rubtsov et al. [22], is incapable of providing a temperature necessary for chain combustion and flame propagation to occur. Contrary to their claim about taking into account the heat from recombination of H atoms solely and the equations used, Rubtsov et al. [22] carried out calculations for 1800 K, the temperature corresponding to heat release from all exothermic steps of combustion. Their statement about the chain mechanism of flame propagation and concentration limits is not an inference from their calculations; rather, this is

a mere repetition of what was said in [26–29] about the dominant role of chain branching and chain termination based on the results of targeted experiments. In addition, Rubtsov et al. [22] do not cite studies [26–29] in a proper place. Furthermore, references to [16, 41] given in [22] in the context of the proposal to take into account the heat released only from the recombination of H atoms are not real. The rate-constant handbook [41] says nothing about this, and in [16], conversely, it is proposed to take into account reactions (IV) and (VIII). V.V. Azatyan is undeservedly acknowledged in [22]: he has never discussed this article with its authors.

Let us now turn to the factors that determine the flame propagation limits. For the reason that the chain ignition conditions have a critical character, ignition does not occur if, at any fixed temperature, the concentration of any initial reactant is lower than a certain critical value. Flame does not propagate for the same reason. Furthermore, we have seen that a nonignitable mixture becomes noninflammable at this temperature and even at higher temperatures if the dominance of the termination rate over branching is ensured in one way or another. Accordingly, flame will not propagate either. Thus, the critical flame propagation condition is not determined by heat losses; rather, it is primarily determined by the critical chain ignition conditions. In a similar way, when branching dominates over chain termination in the initiation site only insignificantly because of a low fuel or oxidizer concentration, then chain combustion will be weak so as to fail to heat the adjacent layer of the fresh mixture to the critical ignition temperature, and the mixture in this layer will not ignite. Accordingly, flame will not propagate. We see that the critical flame propagation conditions are determined by the combustion initiation condition and combustion intensity, which is in turn determined by the competition between chain branching and chain termination. Taking into the chain character of the concentration limits also provides an explanation for the character of their dependence on the amount of the admixture [28].

To summarize, unless the chain character of combustion is taken into account, the view of heat losses as the reason for the existence of flame propagation limits and detonation [2, 5, 8, 15] fails to explain the existence of concentration limits of flame propagation and detonation neither in the presence nor in the absence of inhibitors. When the branched chain character of the process is taken into account, the concentration limits and their dependence on additives obtain natural interpretation. Certainly, the reaction system cools as a result of the deceleration or complete suppression of combustion. But this is a consequence, not the cause, of increasing chain termination rate and blocking chain pathway.

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