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Simulation of the Inhibition of Hydrogen–Air Flame Propagation

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Abstract—The results of simulation and experimental data presented here demonstrate that the competition between chain branching and chain termination is the key factor in hydrogen–air flame propagation, including the temperature regime of the process and the formation of concentration limits. Self-heating becomes significant in developed combustion. It enhances the chain avalanche and ensures the temperature necessary for layer-by-layer chain ignition. By varying the ratio between the chain branching and termination rates by means of an inhibitor makes it possible to control the flame propagation process.

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The competition between heat evolution in the chemical reaction and heat removal from the reaction system was long considered the only factor governing gas-phase combustion at atmospheric pressure. The role of the chain avalanche was recognized only for pressures tens of times lower than atmospheric pressure, when there is almost no self-heating (see, e.g., [1–8]). For combustion near atmospheric pressure, even if reactions of atoms and radicals were taken into account, it was believed that combustion is caused only by increasingly accelerating self-heating and that ignition is a thermal explosion (see, e.g., [2–8]). In analytically solving the flame propagation equation, the chemical process was usually represented as a single-step reaction in which the initial reactants turn directly into the final product and mathematical expressions relevant to this type of reaction were used. Obviously, single-step reactions cannot speed up solely due to self-heating. The temperature dependence of the rate of the combustion reaction was represented as an Arrhenius function involving empirical parameters derived from combustion data under the same assumption that the process consists of a single step [2–4, 9–12].

In the numerical simulations of gas-phase combustion with kinetic schemes including reaction chains, the role of branching was not investigated [13] and ignition at atmospheric pressure was viewed as a thermal explosion (see, e.g., [14–16]). Moreover, some of the authors that used reaction networks involving atoms and radicals often represented combustion as a single-step reaction in their later publications, thus denying the chain character of the process. Indeed, the statement that calculations ignoring the chain mechanism are in agreement with experimental data is equivalent to the statement the role of the chain process is insignificant. All characteristics of branched-chain processes, including the dependence of the reaction rate on time, on the concentrations of the initial reactants, and on temperature, differ radically from the same characteristics of simple reactions. Therefore, without taking into consideration the competition between chain branching and chain termination, it is possible to account only for some features of flame propagation. Furthermore, this is possible only with the use of empirical kinetic parameters derived from data obtained for the same process under the same assumption that the process is a single-step reaction. This anyway leaves serious contradictions between theory and experiments. For example, the preexponential factor of the empirical rate constant determined in this way is several orders of magnitude larger than the number of binary collisions, thus being inconsistent with its own physical meaning.

It was demonstrated by theoretical and experimental studies, including [17–22], that the chain avalanche plays the key role in the combustion of hydrogen and many other gases not only at pressured hundreds of times lower than atmospheric pressure, but also at pressures of tens of bars, and at any degree of self-heating. Under these conditions, which are of importance in practice, the main features of combustion are primarily determined by the existence of a positive feedback between the concentration of reactive intermediates and the rate of change of this concentration. In turn, the character of this feedback is determined by the difference between the chain branching and termination rates. Therefore, the equations relevant to combustion should contain the difference between the rates of the competing reactions that lead to the multiplication and loss of reactive species. Taking into account the key role of this competition,

Reactions involved in the chemical process and their rate constants [31, 32]

Reaction	k_i^{0*}	n	E, kcal/mol
$H_2 + O_2 \longrightarrow 2OH^{\bullet}$ (0)	0.60×10^{14}	0	42.0
$O_2 + H \longrightarrow OH^{\bullet} + O$ (I)	1.98×10^{14}	0	16.8
$OH^{\bullet} + O \longrightarrow O_2 + H$ (–I)	1.78×10^{13}	0	0
$H_2 + OH^{\bullet} \longrightarrow H_2O + H$ (II)	1×10^{8}	1.6	3.3
$H_2 + O \longrightarrow OH^{\bullet} + H$ (III)	0.15×10^{8}	2	7.55
$H \longrightarrow H_s$ (IV)	$D_2(T)$**	–	–
$H + O_2 + M \longrightarrow HO_2^{\bullet} + M$ (V)	2.30×10^{18}	–0.8	0
$H_2 + HO_2^{\bullet} \longrightarrow H_2O_2 + H$ (VI)	3.0×10^{13}	0	26.0
$HO_2^{\bullet} \longrightarrow H_s$ (VII)	$D_7(T)$**	–	–
$H + HO_2^{\bullet} \longrightarrow 2OH^{\bullet}$ (VIII)	2.5×10^{14}	0	1.9
$H_2O_2 + M \longrightarrow 2OH^{\bullet} + M$ (IX)	1.2×10^{17}	0	45.4
$2H + M \longrightarrow H_2 + M$ (X)	1.98×10^{18}	–1	0
$H + C_3H_6 \longrightarrow C_3H_7^{\bullet}$ (XI)	1.13×10^{13}	0	1.64

* The units of $k_i = k_i^0 T^n \exp(-E/RT)$ are $cm^3\ mol^{-1}\ s^{-1}$, $cm^6\ mol^{-2}\ s^{-1}$, and s^{-1} for bimolecular, termolecular, and heterogeneous reactions, respectively.

** $D_2(T)$ and $D_7(T)$ are the rate constants calculated from the diffusion coefficient and reactor diameter as described in [1].

we used selected effective admixtures as a means to elucidate the role of chain reactions in different combustion modes [18–22].

Note that the effects of some dopants, primarily halogenated hydrocarbons, on the hydrogen ignition limits at atmospheric pressure were known earlier. However, the authors who ignored or denied the role of the chain mechanism in combustion disregarded these effects. Moreover, there have been recent publications in which even the possibility of inhibition of flame propagation and detonation is denied [23, 24], contrary to what is suggested by experimental data. These articles were analyzed in our earlier publications [25–28].

In a serious of our works, including [18, 19, 21, 22], we suggested efficient inhibitors whose minor amounts exert a strong effect both on the critical conditions of ignition and on other characteristics of all modes of combustion, including flame propagation. It was noted that the effect of inhibitors on the combustion of hydrogen-containing compounds is unambiguous evidence in favor of the branched-chain mechanism of the process at any pressure. Indeed, the inhibition of the combustion and explosion of, e.g., hydrogen is possible only with a chain mechanism involving free atoms and radicals, including $OH^{\bullet}$ and H. The presence of H atoms in the mixture at combustion temperatures means that their reaction with O_2 proceeds at a high rate, yielding O atoms and $OH^{\bullet}$ radicals, thus causing chain branching. Owing to the high rate constant of the $H + O_2$ reaction at these temperatures, most of the oxygen is consumed in this reactive species multiplication reaction. Therefore, inhibition is unequivocal evidence of the branched-chain nature of H_2 combustion.

Here, we analyze, by numerical simulation, the role of the chain avalanche and self-heating in flame propagation, including the ability of self-heating to sustain chain propagation in the absence of a chain avalanche. We also report the role of the regeneration of reactive species via reactions of the $HO_2^{\bullet}$ radical. Calculations were carried out for the combustion of 50% hydrogen in air at 1 bar in cylindrical reactors 7.4 cm in diameter and 20 or 50 cm in length. The calculated data are discussed together with experimental data available from the literature.

METHODS OF INVESTIGATION

Based on earlier works [1, 4, 29], the reactions listed in the table were included the reaction network. For the combustion of nonlean hydrogen–air mix-

tures, this set of reactions determines the main features of the process at 1 bar and an insignificant role is played by termolecular reactions, such as [30]

$$O + O + M = O_2,$$
$$H + OH^{\cdot} + M = H_2O + M.$$

The rate constants were taken from the reference literature [31, 32]. In reactions (V), (IX), and (X), M is any species removing excess recombination energy. The subscript *s* at H and $HO_2^{\cdot}$ in reactions (IV) and (VII) indicates that these species are adsorbed. At the given reactor diameter, their role is insignificant.

We solved the following set of kinetic equations and heat balance equations taking into account heat and mass transfer:

$$\sum_1^N c_i u_i \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\lambda(T)\frac{\partial T}{\partial x} + \sum_i^N \sum_j^M Q_i(\beta_{ij} - \alpha_{ij})W_j - \frac{s}{V}\alpha(T - T_0), \quad (1)$$

$$\frac{\partial u_i}{\partial t} = \frac{\partial}{\partial x} D_i(T)\frac{\partial u_i}{\partial x} + \sum_j^M (\beta_{ij} - \alpha_{ij})W_j \quad i = 1, \ldots, N.$$

The boundary conditions were

$$\frac{\partial T}{\partial x}_{x=0} = \frac{\partial T}{\partial x}_{x=L} = 0,$$
$$\frac{\partial u_i}{\partial x}_{x=0} = \frac{\partial u_i}{\partial x}_{x=L} = 0, \quad i = 1, \ldots, N.$$

In this set of equations, u_i is the concentration of the *i*th component, W_j is the rate of the *j*th elementary reaction, α_{ij} and β_{ij} are stoichiometric coefficients, Q_i is the enthalpy of the *i*th substance, α is the heat transfer coefficient, $c_j(T)$ is the heat capacity of the *j*th component, $\lambda(T)$ is heat conductivity, and $D_i(T)$ is the diffusion coefficient of the *i*th component.

The set of equations was solved using an implicit difference scheme over time with linearization in each time layer and in each iteration. The corresponding boundary-value problems were solved by the matrix sweep method. The step of integration with respect to time was set automatically based on the preset accuracy of approximation. The space grid was variable, and it was modified on passing from one layer to another to satisfy the solution smoothness condition. The computational program allowed the rate constant of any process step to be changed at any preset time during combustion, thus making it possible to assess the role of this step in combustion.

In these calculations combustion was assumed to be initiated by a heat pulse (900 K, 8 cm) in a hydrogen–air mixture (1 : 1) at atmospheric pressure at $T_0 =$ 300 K. Calculations carried out for temperature steps (initiation zone lengths) of 4 and 2 cm demonstrated that the parameters of the stationary wave at these step lengths are the same. For the initiation stage, the initial conditions for temperature were formulated as a step: $T(x,0) = T$, $0 \le x \le x_1$, $T(x,0) = T_0$, $x_1 \le x \le L$, where T_1 belongs to the region of chain ignition at a given pressure and the x_1 value is selected so that the wave is formed. The product Tx_1 has a critical value above which the mixture ignites and, after a sort period of time, a steady-state flame travels through the mixture, characterized by invariable maximum values of temperature and reactive species concentrations along the tube. The heats of reactions were taken from [4, 31–33]. The value of α was calculated via a familiar formula [3] to be 0.5×10^{-3} cal $(cm^3\ K\ s)^{-1}$ at 900 K.

It was assumed that $c_p = \sum c_i n_i$, where n_i is the mole fraction of the *i*th component in the mixture. The temperature dependences of the heart capacities of the components (c_i) were represented as polynomials [33]. Since a flat flame was considered and, accordingly, the natural changes in its shape were not taken into account, we did not aim at attaining quantitative agreement between the calculated and observed flame speeds.

RESULTS AND DISCUSSION

Calculations demonstrate that, in the initiation zone after producing a heat pulse, the mixture is in the self-ignition region. Accordingly, combustion develops and the temperature rises rapidly to reach its maximum value of ~2400 K. The concentrations of $OH^{\cdot}$, O, and H increase sharply to $\sim 10^{-7}$–10^{-6} mol/cm^3 (1–10% of the total mixture concentration), and these species are distributed over the entire initiation zone owing to diffusion.

It is clear from Figs. 1 and 2 that flame propagation along the reactor comes to a steady state 0.015 s after the initiation of combustion (between points *2* and *3* in time): the wave has a constant temperature. The maximum concentrations of reactive intermediates are also invariable from one cross section to another. By way of example, Fig. 2 shows the H atom concentration profile as a sharp peak with a constant height moving along the cylinder. In each cross section, the H concentration begins to grow with an increasing self-acceleration, as in the case of ignition. The calculated maximum concentration of H atoms (Fig. 2), steady along the reactor, is in good agreement with the concentration measured by Korobeinichev et al. [34]. The steady-state concentration profile moves with a constant velocity of ~2.8 m/s, which is also close to the observed value. Naturally, the steady-state values of the flame speed and other flame parameters remain invariable as the reactor length is increased. By the time the flame front travels some distance (e.g., 50 cm), there is a decrease in temperature in the initiation zone, which is due to O_2 consumption and gas cooling.

These results are consistent with the interpretation of the laminar flame as layer-by-layer ignition (see, e.g., [2, p. 181, images 5.15, 5.20, 5.27, 5.28; 9, p. 80]).

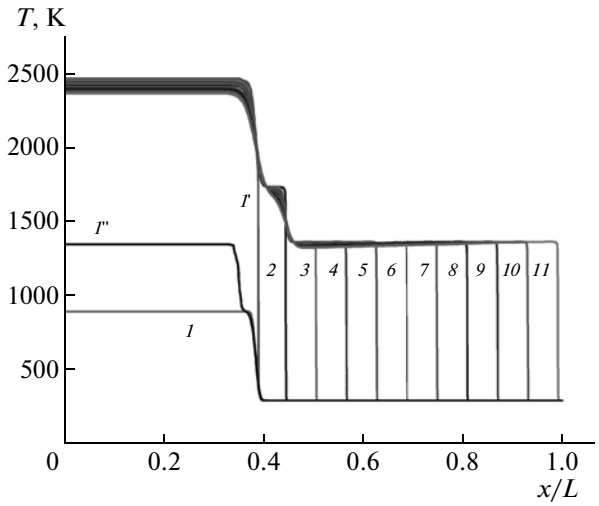

Fig. 1. Temperature profiles along the reactor length (dimensional longitudinal coordinate x/L) at various points in time (s): (*1*) 0, (*1''*) 0.01081, (*1'*) 0.01117, (*2*) 0.0135, (*3*) 0.017543, (*4*) 0.021578, (*5*) 0.02561, (*6*) 0.029647, (*7*) 0.03368, (*8*) 0.037716, (*9*) 0.04175, (*10*) 0.045785, and (*11*) 0.04982. In the wave, $T_{max} = 1375$ K.

Thus, the calculation based on the above branched-chain mechanism with a limited number of elementary reactions and on rate constants and thermal and gas-kinetic parameters available from the reference literature provides a good fit to the observed flame speed and other flame characteristics. Therefore, the above reaction network can be used to study the role of the competition between chain branching and chain termination in flame initiation and propagation and to elucidate the contributions from separate elementary reactions to combustion.

Key Role of the Competition between Chain Branching and Chain Termination in the Formation and Propagation of a Steady-State Flame

In order to understand the role of the competition between the free valence multiplication and disappearance steps in the formation and propagation of a steady-state flame, we excluded reactions (I) and (IX), which multiply reactive species, from one series of calculations. The results of these calculations demonstrated that, in the absence of these elementary reactions, the combustion intensity is much lower than in their presence for the same initial conditions and the same way of initiation. As is clear from Fig. 3, without reactions (I) and (IX) taken into account, the ignition process after initiation proceeds less rapidly and the maximum concentration of hydrogen atoms is one order of magnitude lower. The steady-state combustion wave forms later, and its velocity is lower by a factor of 10. Note that, since reactions (I) and (IX) are endothermic (their heats are 67 and 213 kJ/mol, respectively [31–33]), the exclusion of these reactions from the mechanism implies a considerable increase in the heat of the overall process. However, because in the absence of these reactions chain propagation is solely due to reactions (II), (V), (VI), and (VIII), which do not multiply free valences, the rate of the chain process turns out to be much lower. As a consequence, the ignition and steady-state combustion

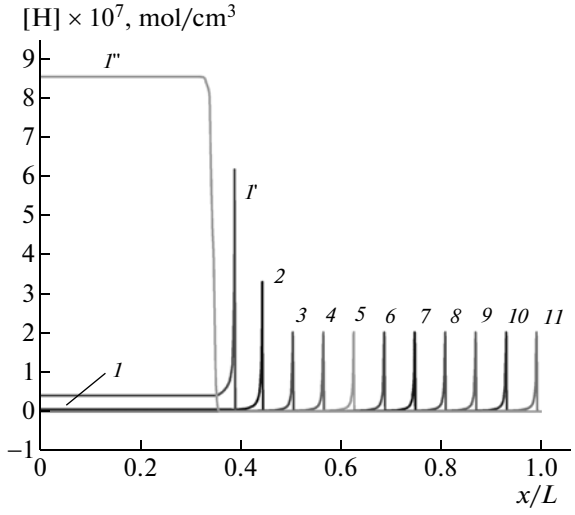

Fig. 2. Hydrogen atom concentration profiles along the reactor length (dimensional longitudinal coordinate x/L) at various points in time (s): (*1*) 0, (*1''*) 0.01081, (*1'*) 0.01117, (*2*) 0.0135, (*3*) 0.0175, (*4*) 0.0215, (*5*) 0.0256, (*6*) 0.0296, (*7*) 0.0337, (*8*) 0.0377, (*9*) 0.0417, (*10*) 0.0458, and (*11*) 0.0498. The wave velocity is ~3 m/s.

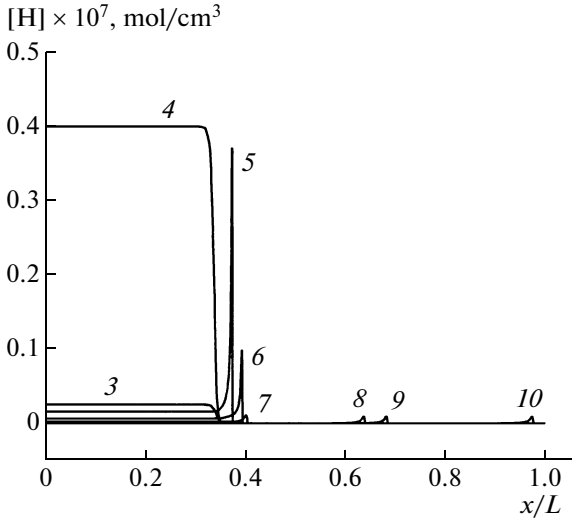

Fig. 3. Hydrogen atom concentration profiles along the reactor length (dimensional longitudinal coordinate x/L) at various points in time (s), calculated without reactions (I) and (IX) taken into account: (*3*) 0.02738, (*4*) 0.02742, (*5*) 0.02835, (*6*) 0.0298, (*7*) 0.0345, (*8*) 0.212, (*9*) 0.247, and (*10*) 0.467.

intensities are also much lower. In spite of its increased exothermicity, the overall reaction is slowed down, and so is heat evolution. This causes a decrease in self-heating, whose value is thus determined primarily by the ratio between the chain branching and chain termination rates.

In order to evaluate the total contribution from free valence multiplication reactions (I) and (IX) and positive chain interaction (VIII), these reaction were excluded from the mechanism in one series of calculations. Note that the exclusion of these reactions raises the heat of the overall reaction by 113 kJ/mol. In spite of this fact, with this reduced mechanism the temperature falls sharply in the initiation zone and the process does not develop at all, indicating that, without elementary reactions (I), (IX), and (VIII), the chain propagation reactions (II), (III), (V), and (VI) cannot sustain initiated combustion. These reactions alone do not ensure the combustion and heat evolution rates required to reach the temperature necessary for layer-by-layer chain ignition and flame propagation. The heat evolution rate becomes significant only under conditions of intensive chain branching and propagation ensuring a high process rate owing to the low activation energies of the reactions of the atoms and radicals. If only reaction (X) is ignored, the flame temperature will be only 5% lower. A similar result was obtained in our earlier computational study of the role of reactions (I), (VIII), and (IX) in hydrogen combustion under static conditions [30]. Solution of the undistributed set of equations demonstrated that the termination of chain branching by diminishing the rate constants of these reactions causes a sharp and large decrease in the combustion intensity.

Reaction (VIII), along with the free valence multiplication events, contributes greatly to the development of reaction chains. In this reaction, the low-active radical $HO_2^{\bullet}$ is replaced by the $OH^{\bullet}$ radical, an active chain carrier, and reactive species are thus regenerated.

The above results are in good agreement with experimental data indicating that, without establishing the chain avalanche conditions, it is impossible to initiate ignition and flame propagation by, e.g., a spark or an incident shock wave even at high initial temperatures up to at least 1450 K [18–22, 35, 36]. The initial temperature necessary for ignition was produced by adjusting the velocity of the incident shock wave. Figure 4 presents experimental data [36] indicating that, as the chain termination rate is increased using minor amounts of inhibitors, the initial temperature necessary for ignition and flame propagation rises.

It is clear from Fig. 4 that the mixture igniting in the absence of an inhibitor at 900 K is nonignitable in the presence of, e.g., 1% propene not only at this temperature, but also 150 K above.

Thus, the above results demonstrate that the exclusion of reactions (I), (VIII), and (IX) or the introduction of an inhibitor makes ignition and flame propagation impossible not because of the decrease in temperature, but because of the chain termination rate exceeding the chain branching rate. The decrease in temperature is a consequence of the weakening or disappearance of the chain avalanche.

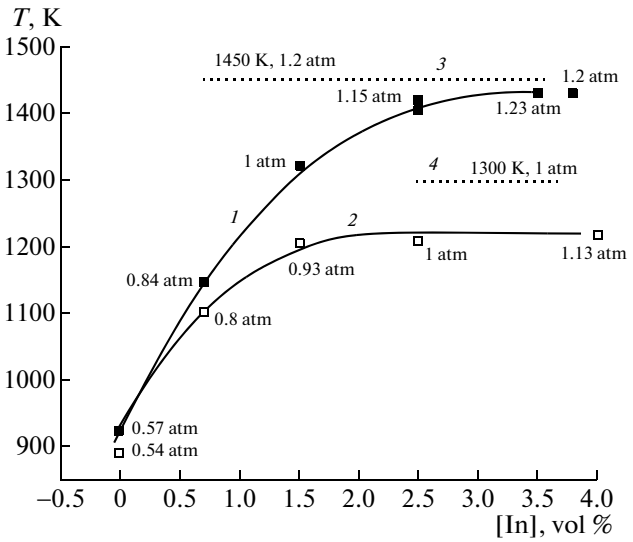

Fig. 4. (*1*, *2*) Minimum initial self-ignition temperature of the $2H_2 + O_2$ mixture with argon as a function of the inhibitor concentration: (*1*) C_3H_6 and (*2*) i-C_3H_5OH. (*3*, *4*) Self-ignition temperatures of (*3*) propylene and (*4*) isopropanol in air [20].

The calculations demonstrated that the exclusion of the quadratic-law hydrogen atom recombination reaction (X) reduces the flame temperature only by 5%. This is accompanied by an equally small change in the flame propagation rate. Therefore, the role of this reaction in developing combustion is insignificant, because heat evolution is mainly due to water formation rather then H atom recombination.

Simulation of Chain Termination through Inhibition

In order to simulate the relative contributions from reaction chains and self-heating to lame propagation, we studied the effect of an inhibitor on combustion parameters, as was done in our experimental studies [18–22, 35, 36]. The inhibitor was propene, whose molecules are known to add hydrogen atoms actively:

$$H + C_3H_6 = C_3H_7^{\bullet}. \qquad \text{(XI)}$$

The resulting propyl radicals are almost uninvolved in chain propagation, so reaction (XI) causes chain termination. In addition, $C_3H_7^{\bullet}$ radicals regenerate part of the C_3H_6. The rate constant of reaction (XI) is $1.13 \times 10^{13}\exp(-820/T)$ cm^3 mol^{-1} s^{-1} [37], much larger than the rate constant of chain branching. As a consequence, small amounts of propene effectively suppress the combustion, explosion, and detonation

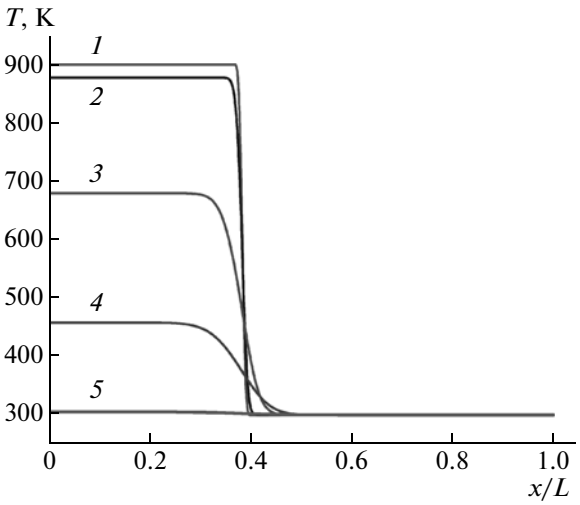

Fig. 5. Temperature profiles along the reactor length (dimensional longitudinal coordinate x/L) for the initial mixture containing 1% inhibitor at various points in time (s): (*1*) 0, (*2*) 0.0233, (*3*) 0.276, (*4*) 0.79, and (*5*) 2.32.

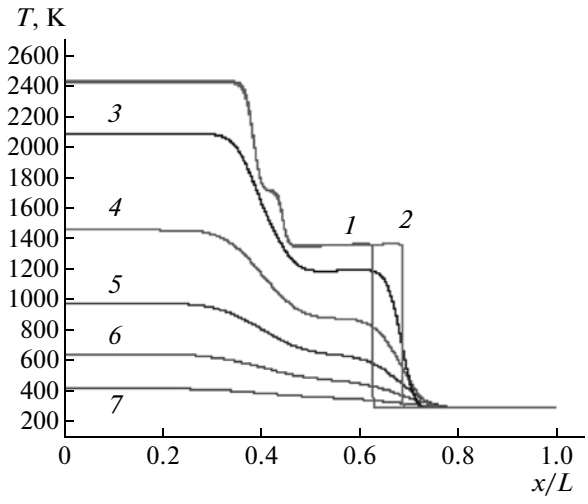

Fig. 6. Temperature profiles along the reactor length (dimensional longitudinal coordinate x/L) at various points in time (s) in the case of 3% inhibitor added 0.02965 s after the onset of the reaction: (*1*) 0.02561, (*2*) 0.02965, (*3*) 0.1621, (*4*) 0.5, (*5*) 0.9144, (*6*) 1.439, and (*7*) 2.23.

of hydrogen– and syngas–air mixtures [18, 19, 21, 22, 35, 38–40].

Our calculations demonstrated that, upon the introduction of 3 or 1% propene into the gas mixture, no ignition takes place, the maximum temperature in the initiation zone falls down to the initial temperature, and the H concentration does not exceed 10^{-14} mol/cm^3 (~10^{-9}% of the mixture concentration). Thus, these propene concentrations prevent flame propagation (Fig. 5). The calculations also demonstrated that the introduction of the same amount of propene into the burning mixture quenches the flame (Fig. 6). Therefore, with this increased chain termination rate, the self-heating of the mixture cannot sustain combustion, although the chain termination reaction (XI) is exothermic. Upon the introduction of 0.5% propene, combustion does not cease, but it becomes less intensive and the wave velocity decreases by a factor of 1.5. Therefore, the difference between the chain branching and termination rates determines the steady-state flame speed as well.

The results of simulation are in good agreement with experimental data on the prevention of ignition and flame propagation. For example, according to our measurements [39], the minimum propene concentration preventing flame propagation in 50% H_2 + air mixture is close to 1%, just as is suggested by the data calculated in this work. The dependence of the concentration limits of flame propagation on the presence of minor admixtures is unambiguous evidence that, without the competition between chain branching and chain termination taken into account, it is impossible to explain these concentration limits.

As the H_2 concentration is decreased and, accordingly, the O_2 concentration is raised, the amount of inhibitor necessary to prevent flame propagation increases. This is in good agreement with the key role of the competition between chain termination and the chain branching reaction involving O_2. Indeed, as the O_2 concentration is increased, the ratio of the rate of reaction (I) to the rate of the additional chain termination reaction (XI) increases. Accordingly, a higher inhibitor concentration is required to prevent combustion, and this is confirmed by experimental observations.

Experimental data corroborate the above calculated data suggesting that, at inhibitor concentrations too small to suppress combustion, the flame speed does decrease. By way of example, we present, in Fig. 7, experimental data reported in our earlier article [40]. In that experiment, the combustion of a premixed 40% H_2 + air mixture in a closed metallic reactor was initiated with a spark. The measure of combustion intensity was the increase in pressure caused by self-heating. The experimental details are presented in [40]. The decrease in the difference between the chain branching and termination rate caused by inhibition reduces the intensity of the chain avalanche and, accordingly, decreases the flame temperature and the rate of its growth.

All relevant experimental data also demonstrate that the effects of equal amounts of admixtures are different, depending on their chemical nature [18, 22, 35, 36, 40]. The data presented in Fig. 7 were obtained for inhibitors differing in their capacity to terminate reaction chains. Owing to the presence of a double bond in its molecule, propene can add hydrogen atoms and, as a consequence, reacts more rapidly than isopropanol [30, 36]. Reacting with the latter, atomic hydrogen abstracts an H atom from its molecule to

yield H_2. The heats of combustion of these inhibitors, as well as their concentration limits of flame propagation, are practically equal [5, 31–33, 41]. Therefore, the difference between the effects of these compounds on combustion is due only to the different effects of their reactions on the ratio between the chain branching and chain termination rates.

Until recently, combustion theory considered the self-acceleration of the reaction to be a result of self-heating alone, and, accordingly, thermal ignition was considered to be the only and necessary condition for the existence of concentration limits of flame propagation (see, e.g., [3, 4, 9, 42]). Now we can see that these views are in conflict with experimental data, including those presented in Fig. 4, and with the results of the calculations reported here. The effect of inhibitors on the concentration limits of flame propagation is evidence that these limits are defined by the equality of the chain branching and termination rates. These experimental data also demonstrate that the combustion theories ignoring the competing reactions cannot account for the dependence of the concentration limits on the mixture composition.

The difference between the chain branching and termination rates also determines the intensity of combustion. At a given heat removal rate and temperature, this difference depends on the mixture composition and on the nature of the admixture, and so do the corresponding combustion intensities. In filtration combustion, the difference between the branching and termination rates also depends on the rates and nature of the heterogeneous reaction of reactive species.

More examples of the discrepancy between experimental data and the theory ignoring the branched-chain nature of combustion are given in [19, 36, 43]. The fact that methane–air combustion is characterized by narrower concentration limits of flame propagation than hydrogen-air combustion, which was inconceivable within previous theories, was successfully accounted for in terms of self-inhibition in methane combustion and, hence, a very small excess of the chain branching rate over the termination rate [42]. In our earlier work [44], taking into consideration the participation of methane in chain termination, we simulated the stronger effect of methane versus inert gases on the flame speed.

The results of simulation of the quenching of a developed flame by adding an inhibitor are in good agreement with the experimental data demonstrating that the introduction of a small amount of an aerosol fire suppressant into the hydrocarbon combustion zone at atmospheric pressure quenches the flame [45]. The same amount of the same inhibitor introduced into a sodium vapor flame does not affect the process because this vapor burns via a nonchain mechanism.

Thus, the above calculations on combustion, as well as experimental data, demonstrate that the competition between the reactive intermediate multiplication and disappearance reactions determines all basic parameters of the process, including the chain avalanche appearance conditions, the combustion temperature, the reaction rate, and the flame speed. There is a positive feedback between self-heating and the chain avalanche intensity. In laminar flame propagation, self-heating ensures a temperature rise sufficient for chain ignition in the layer next to the combustion zone.

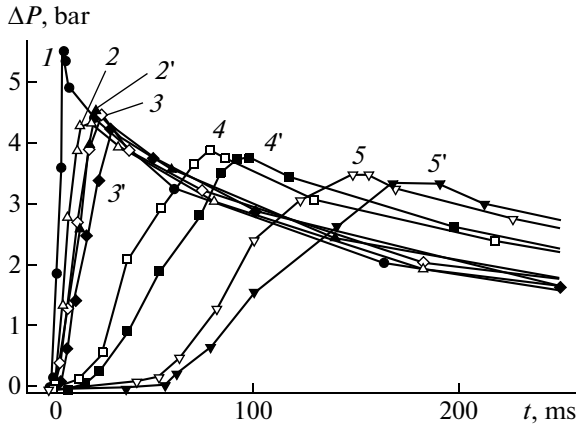

Fig. 7. Effect of (*2*–*5*) isopropanol and (*1'*–*5'*) propylene admixtures on the pressure variation in the combustion of the 40% H_2 + air mixture [40]. Amount of admixture (vol %): (*1*) 0, (*2*, *2'*) 0.75, (*3*, *3'*) 1.0, (*4*, *4'*) 1.5, and (*5*, *5'*) 2.0.

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REFERENCES

1. Semenov, N.N., *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti* (Topics in Chemical Kinetics and Reactivity), Moscow: Akad. Nauk SSSR, 1958.
2. Lewis, B. and von Elbe, G., *Combustion, Flames and Explosions of Gases*, New York: Academic, 1961.
3. Frank-Kamenetskii, D.A., *Diffuziya i teploperedacha v khimicheskoi kinetike* (Diffusion and Heat Transfer in Chemical Kinetics), Moscow: Nauka, 1987.
4. Lewis, B. and von Elbe, G., *Combustion, Flames and Explosions of Gases*, New York: Academic, 1987.
5. *Fizicheskaya entsiklopediya* (Encyclopedia of Physics), Moscow: Sovetskaya Entsiklopediya, 1988, vol. 1, p. 267.
6. Lozovsky, D., Buckmaster, J., and Konny, P., *Combust. Flame*, 1994, vol. 97, no. 2, p. 301.
7. *Khimicheskaya entsiklopediya* (Encyclopedia of Chemistry), Moscow: Sovetskaya Entsiklopediya, 1998, vol. 5, p. 345.

8. Purmal, A.P., *A, B, V ... khimicheskoi kinetiki* (ABC of Chemical Kinetics), Moscow: Akademkniga, 2004.
9. Zel'dovich, Ya.B., Barenblatt, G.I., Librovich, V.B., and Makhviladze, G.M., *Matematicheskaya teoriya goreniya* (Mathematical Theory of Combustion), Moscow: Nauka, 1980.
10. Kakutkina, I.A. and Babkin, V.S., *Fiz. Goreniya Vzryva*, 1998, vol. 34, no. 2, p. 9.
11. Kislov, V.M., Salgansky, E.A., and Manelis, G.B., *Proc. Int. Seminar on Nonequilibrium Processes*, Moscow: Torus, 2005, p. 247.
12. Salgansky, E.A., Polianczuk, E.V., and Manelis, G.B., *Proc. Int. Seminar on Nonequilibrium Processes*, Moscow: Torus, 2005, p. 231.
13. Lovachev, L.A., Basevich, V.Ya., Kogan, A., and Neigauz, M.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, no. 9, p. 1256.
14. Maas, U. and Warnatz, J., *Combust. Flame*, 1988, vol. 74, no. 1, pp. 53, 102.
15. Gontkovskaya, V.T., Gordopolova, I.S., and Ozerkovskaya, N.I., *Fiz. Goreniya Vzryva*, 1988, vol. 24, no. 1, p. 53.
16. Warnatz, J., Maas, U., and Dibba, R., *Combustion: Physical and Chemical Aspects, Modeling, Experiments, Formation of Pollutants*, Berlin: Springer, 2001.
17. Petrova, L.D., Azatyan, V.V., Baratov, A.N., Vogman, L.P., and Makeev, V.I., in *Gorenie i vzryv* (Combustion and Explosion), Moscow: Nauka, 1977, p. 526.
18. Azatyan, V.V., Andreeva, N.V., and El'natanov, A.I., *Khim. Fiz.*, 1988, vol. 7, no. 6, p. 821.
19. Azatyan, V.V., *Kinet. Katal.*, 1999, vol. 40, no. 6, p. 818 [*Kinet. Catal.* (Engl. Transl.), vol. 40, no. 6, p. 741].
20. Ivanova, A.N., Andrianova, Z.S., and Azatyan, V.V., *Khim. Fiz.*, 1998, vol. 17, no. 8, p. 91.
21. Azatyan, V.V., Wagner, G.Gg., and Vedeshkin, G.K., in *Gaseous and Heterogeneous Detonations*, Roy, G., Frolov, S., Kailasanath, K., and Smirnov, N., Eds., Moscow: ENAS, 1999, p. 331.
22. Azatyan, V.V. and Merzhanov, A.G., *Tyazhel. Prom–st.*, 2001, no. 7, p. 40.
23. Bunev, V.I. and Zamashchikov, V.V., *Fiz. Goreniya Vzryva*, 2003, vol. 39, no. 3, p. 121.
24. Gel'fand, B.E., *Fiz. Goreniya Vzryva*, 2002, vol. 38, no. 5, p. 101.
25. Azatyan, V.V., Bolod'yan, I.A., Kopylov, S.N., Rubtsov, N.M., and Shebeko, Yu.N., *Fiz. Goreniya Vzryva*, 2003, vol. 39, no. 3, p. 127.
26. Azatyan, V.V., Kalachev, V.I., and Masalova, V.V., *Fiz. Goreniya Vzryva*, 2006, vol. 47, no. 4, p. 498.
27. Azatyan, V.V. and Merzhanov, A.G., *Khim. Fiz.*, 2008, vol. 27, no. 11, p. 93.
28. Azatyan, V.V., Baklanov, D.I., Bolod'yan, I.A., Vedeshkin, G.K., Ivanova, A.N., Naboko, I.M., Rubtsov, N.M., and Shebeko, Yu.N., *Kinet. Katal.*, 2009, vol. 50, no. 2, p. 176 [*Kinet. Catal.* (Engl. Transl.), vol. 50, no. 2, p. 156].
29. Azatyan, V.V. and Semenov, N.N., *Kinet. Katal.*, 1972, vol. 13, no. 1, p. 17.
30. Azatyan, V.V., Andrianova, Z.S., and Ivanova, A.N., *Kinet. Katal.*, 2010, vol. 52, no. 3, p. 358 [*Kinet. Catal.* (Engl. Transl.), vol. 52, no. 3, p. 337].
31. Baulch, D.L., Bowman, C.T., Cobos, C.J., Cox, R.A., Just, Th., Kerr, J.A., Pilling, M.J., Stocker, D., Troe, J., Walker, R.W., and Warnatz, J., *J. Phys. Chem. Ref. Data*, 2005, vol. 34, no. 3, p. 757.
32. Baulch, D.L., Cobos, C.J., Cox, R.A., Stocker, D., Troe, J., Walker, R.W., and Warnatz, J., *J. Phys. Chem. Ref. Data*, 1994, vol. 23, no. 3, p. 59.
33. *Termodinamicheskie svoistva individual'nykh veshchestv* (Thermodynamic Properties of Individual Substances), Glushko, V.P., Ed., Moscow: Akad. Nauk SSSR, 1962.
34. Korobeinichev, O.P., Shmakov, A.G., and Rybitskaya, I.V., *Kinet. Katal.*, 2009, vol. 50, no. 2, p. 170 [*Kinet. Catal.* (Engl. Transl.), vol. 50, no. 2, p. 156].
35. Azatyan, V.V., Shebeko, Yu.N., Kopilov, S.N., Navzenya, V.Y., Shebeko, D.Y., and Zamyshevskii, E.D., *Proc. 3rd Asia–Oceania Symp. on Fire Science and Technology*, Singapore, 1998, p. 131.
36. Azatyan, V.V., Pavlov, V.A., and Shatalov, V.A., *Kinet. Katal.*, 2005, vol. 46, no. 6, p. 835 [*Kinet. Catal.* (Engl. Transl.), vol. 46, no. 6, p. 789].
37. Tzang, W., *Ind. Eng. Chem.*, 1992, vol. 31, p. 3.
38. Azatyan, V.V., Naboko, I.M., Petukhov, V.A., Gusev, P.A., Merzhanov, A.G., Rubtsov, N.M., Solntsev, O.I., Fortov, V.E., and Tsvetkov, G.I., *Dokl. Akad. Nauk*, 2004, vol. 394, no. 1, p. 61 [*Dokl. Phys. Chem.* (Engl. Transl.), vol. 394, part 1, p. 1].
39. Avetisyan, A.A., Azatyan, V.V., Kalachev, V.I., Masalova, V.V, and Piloyan, A.A., *Kinet. Katal.*, 2007, vol. 48, no. 1, p. 12 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 1, p. 8].
40. Azatyan, V.V., Borisov, A.A., Kalachev, V.I., Mailkov, A.E., Masalova, V.V., and Troshin, K.Ya., *Combustion and Atmospheric Pollution*, Moscow: Torus, 2003, p. 41.
41. *Pozharo-vzryvobezopasnost' veshchestv i materialov i sredstva pozharotusheniya: Spravochnik* (Fire and Explosion Safety of Substances and Materials and Fire-Extinguishing Means: A Handbook), Korol'chenko, A.Ya. and Baratov, A.N., Eds., Moscow: Khimiya, 1990, vol. 1.
42. Buckmaster, J.D. and Jordan, G., *Combust. Flame*, 1991, vol. 84, p. 11.
43. Azatyan, V.V., Navtsenya, V.Yu., Bolod'yan, I.A., and Shebeko, Yu.N., *Zh. Fiz. Khim.*, 2002, vol. 76, no. 5, p. 775 [*Russ. J. Phys. Chem.* (Engl. Transl.), vol. 76, no. 5, p. 677].
44. Azatyan, V.V., Shebeko, Yu.N., and Shebeko, A.Yu., *Pozharobezopasnost*, 2008, no. 2, p. 4138.
45. Azatyan, V.V., Bolod'yan, I.A., Shebeko, Yu.N., and Navtsenya, V.Yu., *Zh. Fiz. Khim.*, 2003, vol. 72, no. 3, p. 449 [*Russ. J. Phys. Chem.* (Engl. Transl.), vol. 72, no. 3, p. 385].