

Accelerated Diffusion of Chain Carriers and Kinetic Features of Heterogeneous Processes in Gas-Phase Chain Reactions

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Abstract—In gas-phase combustion processes, the regeneration of free atoms and radicals in chain propagation reactions enhances the diffusion flux of these species from the flame zone. In flame propagation in tubular reactors and in filtration combustion, this effect facilitates the access of chain carriers to the surface even at atmospheric pressure, increases the role of heterogeneous reactions (primarily chain termination), and enhances heat removal due to heterogeneous recombination.

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Since the discovery of chain reactions, it has generally been believed that the branched chain mechanism and atom and radical multiplication and loss reactions in gas-phase combustion become significant only at pressures tens or hundreds times lower than atmospheric pressure, when there is no significant self-heating of the reaction mixture. Gas combustion at higher pressures has been considered to result from the increasing acceleration of self-heating alone (see, e.g., [1–4]). Even now, this view is dominant. Both critical ignition conditions for gas mixtures (including hydrogen + oxygen) at atmospheric pressure and the laws of developing combustion are thought to be only a consequence of the competition between heat generation and heat removal (see, e.g., [1–9]). In some studies using numerical methods in the solution of sets of kinetic equations, various reactions of atoms and radicals are included in the reaction network. However, in the same or later publications of the same authors, ignition and combustion are considered to result from self-heating alone when the gas pressure exceeds a few hundredths of atmospheric pressure [7]. The burning gas phase is usually in contact with a solid surface. Since gas-phase combustion at pressures above several kilopascals is represented as a single-step reaction, the analytical expressions describing the system, such as the energy balance equation, disregard the heterogeneous reactions of atoms and radicals even in filtration combustion [6–9], in which the ratio of the surface area to the gas volume is fairly large.

At the same time, in a series of our works, including [10–14], it was demonstrated that a chain avalanche is a necessary condition for the gas-phase combustion of hydrogen-containing and many other compounds not only at several hundredths or thousandths of atmospheric pressure, but also at any higher pressure, and at

temperatures up to at least 1450 K. It was also demonstrated that self-heating is not a necessary condition for chain ignition even at atmospheric pressure. Self-heating is significant only in developed chain combustion and enhances the chain avalanche [10, 11].

At appreciable rates of the recombination of chain carrier atoms and radicals on the reactor walls, this process is not only a significant energy removal channel but, what is more important, a chain termination process. Along with recombination, other chain carrier reactions governing the combustion process take place on the surface (see below). Obviously, the character of the heterogeneous reactions of atoms and radicals, as well as the chain nature of the overall process, determines the concentration kinetic equations and the energy balance equation. The role of heterogeneous reactions in combustion at atmospheric pressure is also considered to be insignificant in numerical simulations of gas combustion, even when various reactions of atoms and radicals are taken into account. This is in part due to the fact that, at atmospheric pressure, the rate of chain termination on the reactor walls calculated in the conventional way is much lower than the rate of the gas-phase steps determining the combustion process. In such calculations, the characteristic time of heterogeneous chain termination is taken to be equal to the average time required for a diffusing active species to travel the average distance separating it from the reactor wall.

By contrast, our analysis has demonstrated that, owing to the periodic regeneration of chain carriers, the access of free valence to the surface (for example, at atmospheric pressure) is easier through the relay-race transfer of free valence from one species to another than through diffusion. Accordingly, the role of heterogeneous reactions in combustion is more significant than was believed earlier.

Furthermore, the relay-race diffusion of a free valence plays an important role in so-called nonthermal flame propagation [1, 15]. In this kind of combustion, the active species diffusing into the fresh mixture react with one another, giving rise to a chain avalanche even outside the self-ignition region. The specific features of relay-race diffusion in polymer oxidation and polymerization processes are detailed in [16, 17].

This work is devoted to free valence diffusion to the reactor walls in chain combustion and to the role of heterogeneous reactions in flame propagation in hydrogen-air mixtures at an initial pressure of 0.1 MPa. As distinct from the processes considered in [15], hydrogen combustion involves no reactions between chain carriers capable of initiating nonthermal flame propagation. The mechanism and role of the diffusion of free valence in H_2 oxidation differs radically from those of relay-race diffusion in processes involving polymers.

Free Valence Diffusion in Chain Combustion

According to Brownian motion theory, the time t_d taken by a diffusing particle to travel the distance x is given by the formula

$$t_d = \frac{x^2}{4D}, \quad (1)$$

where D is the diffusion coefficient [18].

If we define the diffusion velocity (V_d) as the average distance traveled by the diffusing particles per unit time, we will obtain the following equation from expression (1):

$$V_d = \frac{dx}{dt} = \frac{2D}{x}. \quad (2)$$

It is clear from Eq. (2) that V_d decreases hyperbolically as the distance increases (Fig. 1).

Once the diffusing chain carriers in a chain process have traveled some distance δ , they react to be replaced by the same reactive species; that is, they are regenerated. Due to the fact that the chain carriers are highly reactive and, accordingly, can travel only a short distance (δ) before the regeneration event, their diffusion velocity has time to decrease only slightly. The diffusion velocity of the identical chain carrier resulting from this reaction will decrease by an equally small value before this chain carrier reacts (see the sawtooth curve in Fig. 1). Thus, the free valence transferred by the relay-race mechanism from one chain carrier to another diffuses at the average velocity defined by the distance δ . In turn, this distance is determined by the characteristic time of the chain carrier regeneration reaction, which is given by

$$t_g = \frac{1}{k_r[B]}, \quad (3)$$

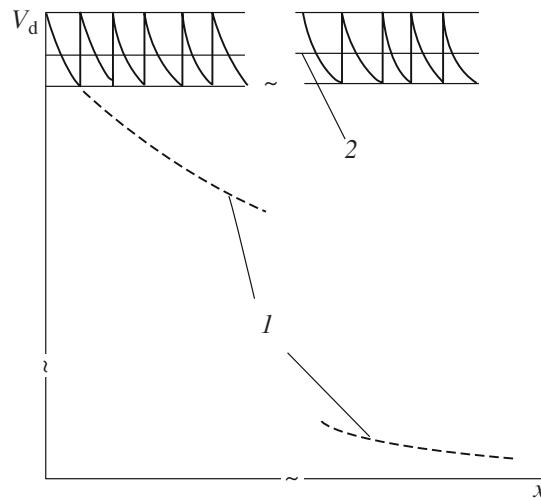


Fig. 1. Diffusion velocity versus the distance traveled (x): (1) the diffusing species are not involved in the chain process; (2) the diffusing species are chain carriers.

where k_r is the effective rate constant of the rate-limiting step of chain carrier regeneration and $[B]$ is the concentration of the initial reactant involved in this step.

The chain multiplication of reactive species raises the free valence flux to the surface relative to the same flux in the nonbranched chain process. The multiplier standing before k_r , which accounts for the degree of branching, lies between 1 and 2.

Substituting t_g from Eq. (3) into Eq. (1) and replacing x with δ , we obtain the following expression for the distance traveled by a diffusing chain carrier before its regeneration:

$$\delta = 2 \sqrt{\frac{D}{k_r[B]}}. \quad (4)$$

Replacing x with the chain carrier diffusion path length δ in Eq. (2) and taking into account Eq. (4), we arrive at the following equation for the relay-race diffusion velocity:

$$V_\delta = \sqrt{Dk_r[B]}. \quad (5)$$

The subscript δ in V_δ indicates that this quantity is actually the velocity of diffusion through the distance δ . It is clear from Eq. (5) that, up to the constancy of $[B]$ in the flame front moving toward the wall, V_δ can be considered to be approximately constant at a fixed temperature. In view of Eq. (5), the time taken by the chain carriers diffusing by the relay-race mechanism to travel the average distance equal to the distance between the reactor center and the wall can be represented as

$$t_r^{\text{relay}} = \frac{r}{2\sqrt{Dk_r[B]}}, \quad (6)$$

where r is the reactor radius.

Obviously, since the rate of the heterogeneous reaction is limited by the diffusion velocity, this reaction is actually first-order. Therefore, considering the rate-limiting role of relay-race diffusion, we can represent the rate of the heterogeneous reaction as the reciprocal of the characteristic time of this process:

$$k_r^{\text{relay}} = \frac{2\sqrt{Dk_r[B]}}{r}. \quad (7)$$

As distinct from expression (7), the expression for the rate constant of the heterogeneous decay of chain carriers in diffusion-controlled chain termination in the absence of relay-race diffusion appears as follows for a cylindrical reactor of diameter d [1]:

$$k_r = 23.2D/d^2. \quad (8)$$

It is clear from expressions (7) and (8) that, unlike k_r , k_r^{relay} is proportional to the square root of $Dk_r[B]$. Since the diffusion coefficient is inversely proportional to the gas mixture concentration and appears as the product $D[B]$ in expression (5), the relay-race diffusion velocity is pressure-independent. It is clear from expression (7) that, for the same reason, k_r^{relay} is also pressure-independent.

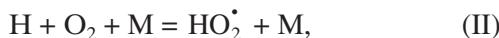
Note that expression (5) is similar to the formula obtained by Zel'dovich et al. [19, p. 244] by solving a differential equation of the heat conductivity type under certain assumptions as to the spatial distribution of reactive species. However, as distinct from expression (5), the formula reported by Zel'dovich et al. [19] contains a first-order rate constant in place of $k_r[B]$. Accordingly, the diffusion velocity in this formula is inversely proportional to \sqrt{P} , unlike the diffusion velocity in expression (5).

Note that, unlike k_r^{relay} , k_r defined by formula (8) is proportional to D and is, accordingly, inversely proportional to pressure. As a consequence, in the narrow pressure range below 1–1.5 kPa, $k_r > k_r^{\text{relay}}$. Accordingly, for reactors 4–7 cm in diameter, the k_r values calculated using formula (8) are in agreement with the observed values of the first ignition limit, for example, for $\text{H}_2 + \text{O}_2$ mixtures in the diffusion-controlled region of chain termination.

In the combustion of $\text{H}_2 + \text{O}_2$ mixtures at atmospheric pressure, the chain branching reaction



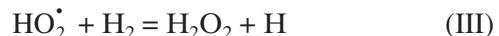
is in competition with the trimolecular formation of the HO_2^\bullet radical,



which is unreactive in this system and mainly undergoes recombination on the surface [3]. In reaction (II),

the third reactant M is the species removing the recombination energy.

As the HO_2^\bullet radicals move to the surface, part of them participate in the reaction



and are then regenerated via reaction (II). Reaction (III) is rate-limiting because of its comparatively high activation energy (~ 110 kJ/mol). Therefore, when the HO_2^\bullet radical is considered as the diffusing species, the component B in the above expressions should be the hydrogen molecule.

Under the conditions examined, the rate of hydrogen atom adsorption,



is much lower than the rates of the competing chain branching and termination reactions taken separately, but it is comparable with the difference between the rates of these reactions, particularly near the critical conditions. Since the kinetics of the chain process is mainly determined by this difference, reaction (IV) can exert a significant effect on the overall combustion process.

Let us compare the k_4^{relay} and k_4 values for the combustion of 7% H_2 in air at 850 K and an initial pressure of 0.1 MPa in a cylindrical reactor 12.6 cm in diameter. The experimental data obtained under these conditions are reported below. The diffusion coefficient of H atoms in this mixture at 293 K and 0.1 MPa is approximately equal to $1 \text{ cm}^2/\text{s}$ [20, 21]. Since the diffusion coefficient of H atoms in a constant volume is proportional to $T^{1.6}$ [21], $D = 5.5 \text{ cm}^2/\text{s}$ at 850 K. The initial O_2 concentration under the above conditions is $2.65 \times 10^{-6} \text{ mol/cm}^3$. The rate-limiting step of the regeneration of hydrogen atoms is reaction (I), whose rate constant is $1.9 \times 10^{14} \exp(-8350/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [22] (here, the activation energy units are kelvins). Hence, for $T = 850 \text{ K}$, $k_1 = 9.3 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Substituting the above values of D , r , k_r , and O_2 concentration into expression (7), we obtain $k_4^{\text{relay}} = 120 \text{ s}^{-1}$. At the same time, the k_4 value calculated using expression (8) is 0.8 s^{-1} , which is smaller than k_4^{relay} by a factor of 150. This large excess of k_4^{relay} over k_4 is due to the comparatively large value of the rate constant of reaction (I).

The smaller the extent of regeneration of chain carriers, the smaller the difference between k_r^{relay} and k_r .

By way of example, compare the k_r^{relay} and k_r values for HO_2^\bullet adsorption,



for the combustion of 7% H_2 in air under the above conditions. The HO_2^\cdot diffusion coefficient in this mixture at 293 K and 0.1 MPa is only slightly smaller than the O_2 diffusion coefficient and is close to $0.25 \text{ cm}^2/\text{s}$ [20, 21]. Since the HO_2^\cdot diffusion coefficient at a constant volume is proportional to $T^{1.7}$ [21], $D_{\text{HO}_2^\cdot} = 1.5 \text{ cm}^2/\text{s}$ at 850 K. The rate-limiting step of HO_2^\cdot regeneration is reaction (III) because of its comparatively high activation energy. The rate constant of this reaction is $3 \times 10^{13} \exp(-13100/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [22] (here, the activation energy is in kelvins). Hence, for $T = 850 \text{ K}$, $k_3 = 5.4 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The initial H_2 concentration under these conditions is $1.0 \times 10^{-6} \text{ mol/cm}^3$. In the mixture examined, which contains 7% H_2 , only part of the reaction (I) events actually cause chain branching. This is due to the fact that, because of the small H_2 content, part of the O atoms and OH^\cdot radicals resulting from reaction (I) have insufficient time to enter into the chain propagation reactions



and terminate the chain via the reaction opposite to reaction (I),



and via adsorption on the walls. This is why the above coefficient accounting for the chain termination fraction is between 1 and 2. In this calculation we take this coefficient to be 1.5. Substituting the above values of D , r , k_1 , and H_2 concentration into expression (7) and replacing the subscript "g" at the constants with the subscript "5," we obtain $k_5^{\text{relay}} \approx 1.3 \text{ s}^{-1}$. The rate constant k_5 calculated using expression (8) for $d = 12.6 \text{ cm}$ is 0.2 s^{-1} , which is smaller than k_5^{relay} by a factor of 6.5.

Chain Carrier Flux to the Surface over the Flame Traveltime

Obviously, the effect of the heterogeneous reactions on combustion will be possible if the chain carriers have sufficient time to reach the surface area with which the traveling flame front is currently in contact. For this reason, let us determine the longest distance from which the free valences propagating via reactions of alternating hydrogen atoms can reach the walls of a cylindrical reactor within the time taken by a laminar flame front to travel the distance l equal to the thickness of the combustion zone (Fig. 2). Substituting the values of D , k_1 , and O_2 concentration into Eq. (5), we obtain

$V_\delta^{\text{relay}} = 380 \text{ cm/s}$. The flame velocity in the mixture examined is approximately equal to 50 cm/s [3], and the combustion front thickness is $l \approx 0.1 \text{ cm}$. Hence, the time taken by the flame to travel the distance l is $2 \times 10^{-3} \text{ s}$. Within this period of time, the free valences dif-

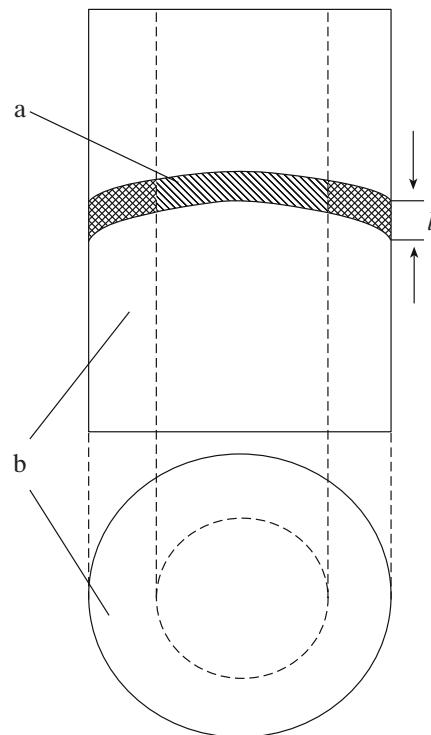


Fig. 2. Schematic representation of (a) the combustion front and (b) the cylindrical layer from which chain carriers have time to reach the reactor surface.

fusing with the velocity $V_\delta^{\text{relay}} = 380 \text{ cm/s}$ will travel a distance of $\Delta r \approx 0.75 \text{ cm}$. Therefore, the H atoms separated by a distance of $\leq 0.75 \text{ cm}$ from the wall of the cylindrical reactor will transfer their free valence to the wall within the flame traveltime. In a reactor 12.6 cm in diameter, the volume of the cylindrical layer corresponding to this distance is $>20\%$ of the reactor volume. Without relay-race diffusion, only the H atoms separated by 0.01 cm or a shorter distance from the wall would reach the wall within the same period of time. The volume of the corresponding cylindrical layer is below 0.5% of the reactor volume. Thus, without relay-race diffusion, the heterogeneous reactions cannot play any significant role in combustion.

Similar calculations have demonstrated that, in the mixture containing 7% H_2 , the flux of O atoms and OH^\cdot radicals to the surface is not lower than the flux of H atoms.

For a reactor 5 cm in diameter (usual size), the volume of the cylindrical layer corresponding to the relay-race diffusion distance $\Delta r \approx 0.75 \text{ cm}$ is above 50% of the reactor volume and the effect of the surface properties is even stronger.

Role of Heterogeneous Reactions in Combustion at Atmospheric Pressure

The rate of the hydrogen combustion reaction (w) under self-heating conditions is described by the fol-

lowing equation, which takes into account the homogeneous and heterogeneous chain termination reactions [10, 12]:

$$w/[O_2] = k_1 n_0 \exp \int_{t_0}^t \{ 2k_1^0 [O_2] \beta \exp(-E_1/RT) - k_2 [O_2] [M] \eta - k_4^{\text{relay}} \} dt, \quad (9)$$

where k_1^0 is the preexponential factor of the rate constant of reaction (1), E_1 is the activation energy of this reaction, β is the fraction of O atoms and OH[·] radicals participating in the chain propagation reactions (V) and (VI), k_2 is the effective rate constant of reaction (II), t_0 is the point in time after which the role of the reaction between the initial reactants is insignificant, n_0 is the chain carrier concentration at the point in time t_0 (which is actually the combustion onset time), k_4^{relay} is the rate constant of heterogeneous chain termination, η is the fraction of HO₂[·] radicals that have not entered reaction (III) and will lead to chain termination, and T is temperature.

It is clear from relationship (9) that the role of heterogeneous chain termination in combustion is determined by the balance between k_4^{relay} and the difference between the first two terms of the integrand:

$$2k_1^0 [O_2] \beta \exp(-E_1/RT) - k_2 [O_2] [M] \eta.$$

This difference is usually much smaller than either term. Therefore, a change in the chemical properties of the surface that has an effect on k_4^{relay} can cause an appreciable change in the integrand and, accordingly, in the overall process rate, particularly near the concentration limits of ignition, where the chain branching and termination rates are similar.

Below, we will present an experimental verification of the inference that the heterogeneous reactions of chain carriers play a significant role in combustion at atmospheric pressure.

EXPERIMENTAL PROCEDURE, MEASUREMENTS, AND DISCUSSION

Reactions were carried out in an airtight, cylindrical, stainless-steel reactor 12.6 cm in diameter and 25.2 cm in height. The components were mixed in the reactor using a partial pressure-based method with a relative accuracy of 1%. Before gas admission, the reactor was pumped to 2 Pa. The initial mixture pressure and temperature were 0.1 MPa and 293 K, respectively. The mixture was ignited with a 3.6-J spark at the lower end of the reactor after the time necessary for the perfect mixing of the components (20 min). From the ignition point until the completion of combustion, we performed simultaneous rapid recording of the gas

pressure and luminescence. The signal from the piezoelectric pressure gauge was amplified and was then recorded with an S9-8 dual-beam memory oscilloscope. The discretization time was 2 μ s. Flame chemiluminescence between 300 and 600 nm was recorded on an oscilloscope using an FEU-39 photomultiplier. After each run, the reactor was pumped down to ~ 3 Pa. This experimental procedure is detailed in an earlier publication [23].

Since the number of moles of the gas mixture decreases steadily during H₂ oxidation, the increase of pressure (ΔP) observed during combustion is due only to the increasing temperature. Obviously, the gas temperature in the moving flame, which is the place where heat is generated, is higher than the temperature of the unburnt gas. Therefore, ΔP characterizes the temperature rise averaged over the reactor volume (and the average temperature as well). This temperature rise is determined by the ratio between the rate of heat generation due to combustion and the rate of heat removal from the reactor. Thus, ΔP characterizes the rate of heat generation and, accordingly, the rate of the combustion reaction. This is why the gas mixture pressure and the chemiluminescence intensity increase synchronously at an increasing rate (the initial portions of the kinetic curves are concave upward) and reach their maxima almost simultaneously.

In order to elucidate the role of the heterogeneous reactions, we varied the chemical properties of the surface. For this purpose, the reactor surface in some experiments was coated with a thin film of boric acid: the reactor was rinsed with a boric acid solution and then dried. To make sure that the data obtained are reproducible, measurements for the boric acid-coated surface were alternated with measurements for the untreated surface in the same reactor. To remove the boric acid coating, the reactor was rinsed with a sodium carbonate solution and water and was then dried.

Combustion of hydrogen-lean mixtures. The lower hydrogen concentration limit for the propagation of flame in hydrogen-air mixtures is known to be 5%. The intensity of the combustion of 7 or 8% H₂ + air is always much lower in the reactor treated with boric acid than in the untreated reactor (Figs. 3, 4). Indeed, the slope of the kinetic curve, which is a measure of the rate of the combustion reaction, is always much smaller in the boric acid-treated reactor. Furthermore, combustion over boric acid stops earlier: the pressure peaks are lower, and the areas under the kinetic curves are smaller. The boric acid coating on the surface exerts a similar effect on the luminescence curves.

Furthermore, the treatment of the surface with boric acid has an effect on the critical ignition and flame propagation conditions. In the reactor whose surface is coated with boric acid, as distinct from the untreated reactor, it is impossible to ignite a 6% H₂ + air mixture at a spark energy of 3.6 J. Since the heat removal rate is independent of the chemical properties of the reactor

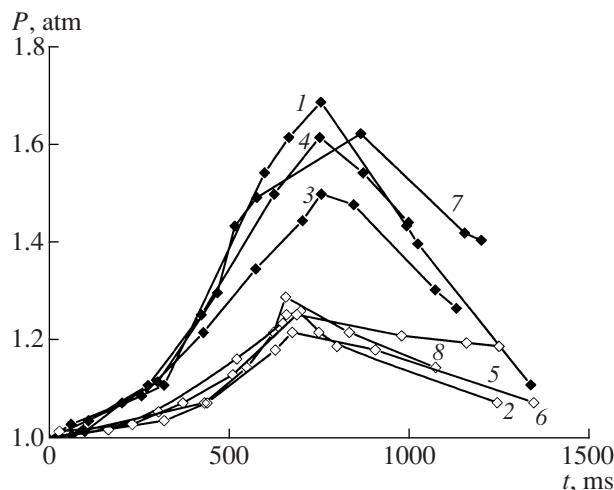


Fig. 3. Combustion kinetics as pressure variation for a 7% H_2 + air mixture: (1, 3, 4, 7) untreated reactor surface; (2, 5, 6, 8) reactor surface coated with boric acid. The curve numbering shows the order of runs.

surface, it is quite obvious that the observed inhibition of the combustion reaction by boric acid is due to the increased rate of the heterogeneous termination of reaction chains. The results of these experiments, which demonstrate that the ignition conditions at atmospheric pressure are primarily determined by the competition between chain branching and termination rather than by the increasing self-heating, are in good agreement with our earlier data [10–14]. The above data are also in good agreement with our data demonstrating the chain character of hydrogen ignition in air at atmospheric pressure and illustrating the time lag between luminescence rise curves and temperature rise curves during combustion [11, 23].

The conventional views of flame propagation, which disregard the chain character of this process, cannot explain the above observations.

The weakening of the effect of the boric acid coating observed upon passing to the 8% H_2 + air mixture is due to the following. As the H_2 concentration in the initial mixture is raised, the fraction of O atoms and OH^\bullet radicals participating in reactions (V) and (VI) increases (i.e., β grows), resulting in a decrease in the contribution from k_g^{relay} to the exponent in relationship (9). This is manifested as more intensive combustion. As a consequence, the time taken by the flame to travel the distance considered above (thickness of $l = 0.1$ cm) is shorter. Accordingly, the volume of the cylindrical layer from which H atoms reach the surface is smaller. As a consequence, the difference between the combustion rates in the untreated and boric acid-treated reactors is much smaller.

It follows from the above that, for reactors smaller in diameter, the role of the heterogeneous reactions of chain carriers will also be significant in the combustion

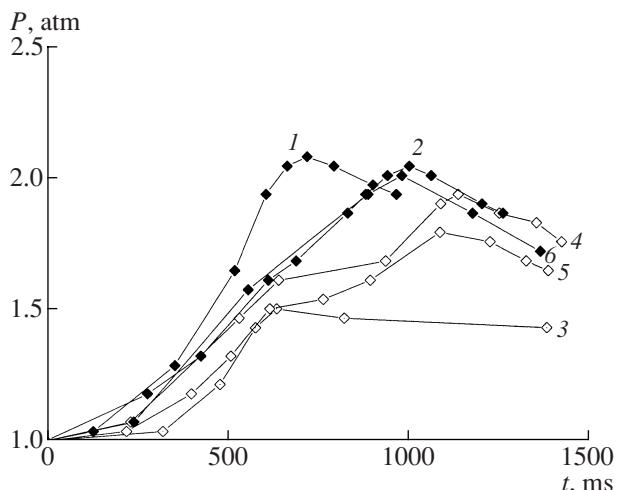


Fig. 4. Combustion kinetics as pressure variation for a 8% H_2 + air mixture: (1, 2, 6) untreated reactor surface; (3–5) reactor surface coated with boric acid. The curve numbering shows the order of runs.

of near-stoichiometric mixtures. Furthermore, since the propagation rate of hydrocarbon–air flames normally does not exceed the propagation rate of the 7% H_2 + air flame [3], it is expected that the combustion of these organic compounds will also be dependent on the chemical properties of the surface because of the effect of the heterogeneous reactions of reactive species.

Combustion of hydrogen-rich mixtures. Now let us consider the combustion of mixtures containing overstoichiometric amounts of hydrogen. In this concentration region, as distinct from the vicinity of the lower concentration limit, the main chain carrier reacting on the surface is the H atom because nearly all of the O atoms and OH^\bullet radicals are involved in reactions (VI) and (VII). Since the heterogeneous reactions of H atoms differ from the heterogeneous reactions of O, OH^\bullet , and HO_2^\bullet , it was expected that boric acid would exert a different effect on the combustion of hydrogen-rich mixtures. However, the data presented in Fig. 5 indicate that the boric acid coating on the reactor walls does not exert any significant effect. This can be explained by the fact that the mixture composition is far from the upper hydrogen concentration limit (75%). As a consequence, k_4^{relay} is so much smaller than the difference between the first two terms of the integrand in relationship (9) that the contribution from the heterogeneous reactions is smaller than in the case of the 7% H_2 + air mixture.

The effect of the boric acid coating on the characteristics of combustion is unambiguous evidence that, contrary to prevalent views, ignition and combustion at atmospheric pressure are caused by a chain avalanche and the reactions of atoms and radicals on the reactor walls play an important role in combustion. The significant effect of the heterogeneous reactions on combus-

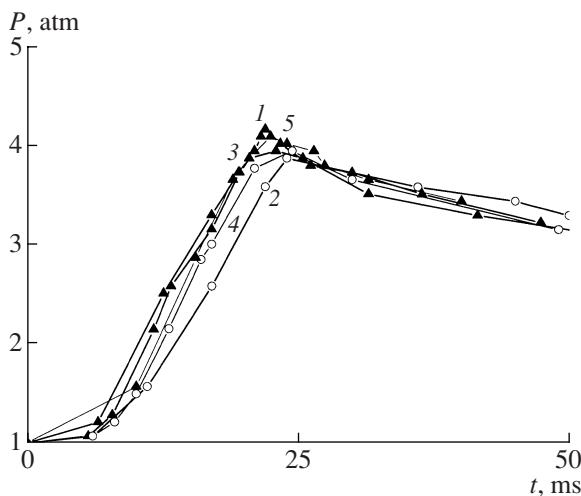


Fig. 5. Combustion kinetics as pressure variation for a 60% $\text{H}_2 + \text{air}$ mixture: (2, 4) untreated reactor surface; (1, 3, 5) reactor surface coated with boric acid. The curve numbering shows the order of runs.

tion under these conditions is due to the relay-race diffusion of reactive intermediates.

Character of the heterogeneous reactions capable of affecting combustion. The observed dependence of the characteristics of combustion at atmospheric pressure on the chemical properties of the reactor surface indicates that the rate of the heterogeneous reactions is determined to a considerable extent by the coefficient (probability) of adsorption of the intermediate species colliding against the surface. For this to be the case, it is necessary that the rate constant of the capture of the intermediate by the surface be smaller than the rate constant at which diffusion to the surface is the rate-limiting process [1]. Without relay-race diffusion, this condition is expressed as

$$\gamma v/d \leq 23.2D/d^2, \quad (10)$$

where v is the thermal velocity of the reactive species, γ is the coefficient of capture of the species by the surface, and d is the diameter of the cylindrical reactor. The right-hand side of Eq. (10) is equal to k_4 , the rate constant of diffusion-limited heterogeneous chain termination, which is given by formula (8) [1]. This formula does not take into account relay-race diffusion.

Substituting the above values of the variables into Eq. (10), we obtain, for H atoms, $\gamma < 3.8 \times 10^{-5}$. Since we examine a stainless steel reactor, this value is an obvious underestimation, especially because the reactor surface is rich in chromium oxide. The main cause of the smallness of the calculated γ value is that, as was noted above, the right-hand side of Eq. (10) disregards relay-race diffusion and is, therefore, an underestimation. If relay-race diffusion is taken into account, the condition for combustion depending on the properties of the surface will be expressed as

$$\frac{\gamma v}{d} \leq \frac{2\sqrt{Dk_1[\text{O}_2]}}{r}, \quad (11)$$

where the right-hand side is equal to k_4^{relay} given by formula (7).

Substituting the above parameters into relationship (11) yields $\gamma^{\text{relay}} \leq 6 \times 10^{-3}$. This value is more than two orders of magnitude larger than the γ value obtained without taking into account relay-race diffusion. Note, however, that this value still seems to be too small for the recombination of H atoms on stainless steel. Some heterogeneous reactions of atoms and radicals involve gaseous molecular reactants and release new chain carriers into the gas phase, implying heterogeneous chain propagation [26–28]. In this case, in spite of the rate-limiting role of diffusion in the access of H atoms to the surface, the rate of heterogeneous chain termination depends on the chemical properties of the surface [28]. Hydrogen atoms are also involved in the chemical modification of the surface, which is due to the displacement of metal atoms from solid salts into the gas phase [29]. These reactions along with heterogeneous recombination are significant factors in combustion.

Thus, because of the relay-race character of the diffusion of chain carriers in the combustion of gases in contact with a solid surface at atmospheric pressure, the intensity and energetic parameters of this process, as well as the concentration limits of flame propagation, are determined to a large extent by the heterogeneous reactions of the chain carriers. Obviously, the role of the heterogeneous reactions is particularly significant in filtration combustion, in which the gas–surface contact area is very large.

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