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Effect of processes at the reactor surface on the low-pressure hydrogen flame

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The interaction of the low-pressure flame of a $2H_2$—O_2 mixture with a quartz reactor surface was studied by the resonance fluorescence technique. The results confirmed the fundamental statement of N. N. Semenov´s theory concerning chain propagation in the gas and termination on the surface in the kinetic region of chain termination (quadratic decay in the heterogeneous negative chain interaction) and in the diffusion region (linear decay). The kinetic curves observed in the kinetic and diffusion chain termination regions on the wall were well matched using N. N. Semenov´s theory, taking into account the heterogeneous catalytic chain initiation and interaction processes occurring on the wall with a variable "rate constant." The interaction of chains on the wall markedly retards ignition in the gas in the kinetic region and has almost no influence on chain propagation in the gas in the diffusion region of the heterogeneous chain termination.

Key words: branched chain reactions, active sites, resonance fluorescence, hydrogen, oxygen.

The research into the combustion of oxyhydrogen, $2H_2$—O_2, begun by N. N. Semenov,[1] led subsequently to quantitative agreement between the theory and experiments carried out within ignition peninsula.[2] However, near the first ignition limit, deviations were observed, which were attributed to the effect of the reactor wall on the flame in the gas.[3—6] A reason for the discrepancy was sought for in either hypothetical chain branching on the reactor wall or in experimental errors.[2,3]

Models of the possible interaction of active sites (AS) in the branched chain processes (BCP) in the gas phase with the AS formed on the reactor surface in the heterogeneous catalytic processes (HCP) have been analyzed.[1,2,6]

The sensitive resonance fluorescence spectroscopy (RFS) technique used to study BCP revealed the error mentioned previously[3] and provided an agreement between the theory and experiments near the first ignition limit of oxyhydrogen.[7,8] Hence, the hypothesis of chain branching on the surface[4,7—14] used to interpret the experiment results[15—18] became unnecessary.

In this study, which continues a series of publications,[7—14] new data on the gas—surface interaction near the lower ignition limit were gained. By gas—surface interaction, we mean a state of the reaction system in which reactions between the AS in the gas and on the surface have a pronounced effect on the processes in both phases.

The purpose of this work is quantitative investigation of the BCP in the gas and HCP on the quartz surface with chain termination in the kinetic and diffusion regions.

Investigation procedure

The investigation strategy is based on N. N. Semenov´s BCP theory,[1,2] which we supplemented by new reactions: variable AS decay on the reactor wall and through-surface chain interaction.[7—14] Here we obtained quantitative information on the change in the rate "constant" for the heterogeneous decay of AS[11] and the rate "constant" for the heterogeneous chain initiation. Both reactions are catalyzed by the wall material.

The ignition of a portion of oxyhydrogen injected into a heated reactor was detected by a change in the intensity of the resonance fluorescence of hydrogen atoms and a pressure change in the reactor. At an RFS sensitivity threshold of ~10^8 atom cm^{-3}, AS were observed in the gas on both sides of the first ignition limit.[7—12] The pressure was measured by a precision method with a sensitivity threshold of ~$5 \cdot 10^{-5}$ Torr developed[4,9] to study low-pressure flames.

The intensity of the generation of AS in the gas was sufficient to change the surface properties and to affect chain initiation and, possibly, chain propagation on the wall. Factors that accelerate or retard hydrogen combus-

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tion in the gas and were neglected in previous works[1—4] were studied.[11,12]

The crucial role of the experimental equipment can be seen by comparing the results obtained by two groups of authors.[7—18]

The data and conclusions obtained by RFS with a sensitivity threshold of 10^8 particles cm^{-3} (see Refs 7—14) and by IR spectroscopy without detection of the BCP AS with a sensitivity threshold of 10^{14} particles cm^{-3} (see Refs 15—18) are different. In conformity with the scope of the procedure[15,16] not fully adequate to the task set, the principal result of the latter group of studies[15—18] is that possible heterogeneous processes are considered at a qualitative level. By using the procedure[7—14] that allowed direct detection of the AS both inside and outside the ignition peninsula, it was possible to study quantitatively the effect of the reactor wall on the combustion process in the gas and to measure the parameters of new reactions that correct the N. N. Semenov´s theory. The procedure used[7—14] provided the possibility of monitoring the appearance of foreign substances resulting from AS reactions with the vacuum grease in the reactor. The replacement of lubricated valves by lubricant-free valves induced a 10—30-fold decrease in the first limit, which made it possible to obtain and study the previously unknown (vacuum) flame of oxyhydrogen.[8,9]

The features of adapting the new highly sensitive instrumentation to extremely low-pressure flames have been described[8—10,19] and the scope of applicability of the reliable static method used to develop the BCP theory was analyzed.[1,2] It was shown[11,19] that the experimental errors[1,2] related to the foreign substances getting into the reactor do not exceed 3—8% and could not affect the fundamental conclusions of the classical works.

In our experiments, the error of RFS measurement of the hydrogen atom concentration includes the calibration error and indeterminable light self-reversal in the resonance radiation source and in the reactor. This error increases upon an increase in the AS concentration in the gas. Within 15%, the wings of the [H] = *f*(*t*) dependence and the peak position are not equally distorted.[8] The error in the pressure measurement by the membrane manometer did not exceed 1—2%.

Numerical modeling of oxyhydrogen combustion in the kinetic and diffusion chain termination regions and comparison with the experiment

Instead of the expected theoretical kinetic curves nearly symmetrical with respect to the point of the highest reaction rate, highly asymmetric curves in which the time-extended "tails" could not be quantitatively interpreted were recorded at the first limit in the kinetic region.[8,14] It was shown[15,16] that taking into account the heterogeneous interaction between the chains does not provide agreement between the theory and experiment. In order to eliminate this contradiction, it was proposed[15,16] to consider again the hypothesis[5] of chain branching on the reactor surface. However, a calculation in terms of a fuller scheme including heterogeneous chain initiation and chain interaction reactions resulted in agreement between the theory and experiments (Fig. 1)[14] without resorting to this hypothesis.

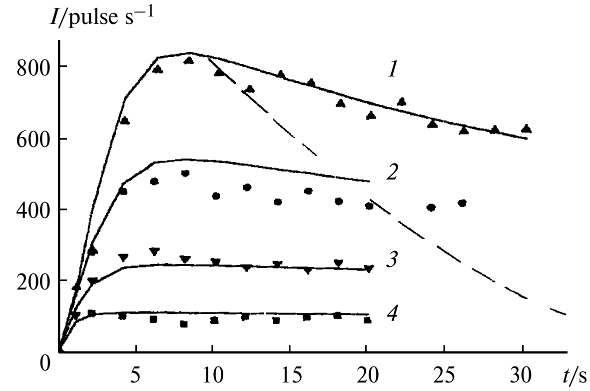

Fig. 1. Kinetic dependences of the concentration of atomic hydrogen *vs.* time for oxyhydrogen ignition near the first limit in a quartz reactor at a temperature of 500 °C and P_0/P_1 = 1.01 (*1*) 1.00 (*2*), 0.984 (*3*), 0.95 (*4*).[14] The first-limit pressure P_1 = 0.668 Torr, P_0 is the initial pressure of the mixture. Continuous lines correspond to calculations with allowance for chain initiation, dots show the experimental data.[7,14] The calculation presented by the dashed line was carried out in Ref. 15 and shows the deviation between the calculation and the experiment resulting from neglecting the chain initiation in the calculations. Here and in Fig. 2 the *y*-axis shows the fluorescence signal of the atomic hydrogen, where 1 pulse s^{-1} corresponds to [H] = 10^8 atom cm^{-3}.

Limited chain propagation in the gas in the kinetic region of chain termination under BCP and HCP competition in a quartz reactor[12,20]

A preliminary explanation of the appearance of asymmetric kinetic curves near the first limit in the kinetic region has been given in a study[12] in which the position of the first limit in experiments[14] was corrected. It should be noted that the gas-phase interaction of products formed in heterogeneous processes with BCP products is manifested as the lack of a clear transition of the limit predicted by the theory.[2] Curve *3* was accepted as the kinetic curve corresponding to the first ignition limit[14] (see Fig. 1). However, thorough analysis of the whole set of data[8,12,14] carried out in the present work showed that best agreement between the theoretical and experimental results is attained if curve *2* is taken as the "limiting" curve (see Fig. 1).

After refinement of the rate parameters of heterogeneous chain initiation, we estimated the extent to which heterogeneous interaction of the chains influences the process in the gas and found the ratio of the amounts of water formed in the reaction below and above the ignition limit. The effective rate constant for the heterogeneous decay of the H atoms (K_{het}) under conditions of negative heterogeneous interaction of chains has the form[7—9]

$$K_{\text{het}} = a + b[\text{H}], \qquad (1)$$

where a and b are the coefficients measured in the experiment.

Calculated curve *1* (see Figs 1 and 2) with a nonzero parameter of heterogeneous chain interaction b shows that a non-zero coefficient b and a high rate of chain initiation on the surface dictate the shape of the kinetic curves. If these factors are ignored, the calculation does not agree with the experiments even at a qualitative level. The ratio of the area of the shaded curvilinear triangle $0AB$ (see Fig. 2) to the area of the curvilinear trapezoid $ABCD$ is equal to the ratio of the amounts of water formed during 30-s combustion of hydrogen above and below the ignition limit. Burn-out of the mixture during BCP above the limit is 0.12% in 6 s. Complete burn-out in 30 s was ~1%. According to classical BCP scheme,[2] burn-out should be ~2% in this case. Thus, the reaction of hydrogen with oxygen that started as a gas-phase branched chain reaction above the first limit was retarded already after 0.12% burn-out and transformed into the mode of catalytic afterburning on the wall. In the case of "classical" ignition, the ratio of the areas located below $[\text{H}] = f(t)$ on the left and on the right of the [H] maximum (line $A'B'$, see Fig. 2) should not differ much from unity for any chain termination mode, as shown by curve *2* (see Fig. 2).

It can be seen from Figs 1 and 2 how much the classical kinetic BCP curves are transformed in the kinetic region of chain termination due to the interaction of chains on the surface. As a result, the gas-phase chain branching reaction, whose rate is proportional to [H], becomes slower than quadratic chain termination on the reactor wall even at an initial stage of ignition. This happens when the hydrogen atom concentration is $\sim 10^{11}$ cm $^{-3}$, *i.e.*, only 2—3 times higher than their concentration at the first ignition limit.

The appearance of an early maximum $[\text{H}]_{\text{m}} = (2—3)[\text{H}]_{\text{l}}^{0}$ in experiments and in the calculation means that chain propagation no longer takes place due to an increase in the limit during the reaction (here $[\text{H}]_{\text{l}}^{0}$ is the quasi-steady-state concentration of H atoms directly below the initial first limit). The fast increase in the limit over a period of time characteristic of the gas reaction and subsequent slow relaxation to the initial limit with a time typical of surface relaxation are reflected in the calculations and in the experiments by asymmetric kinetic curves whose shape has long been debated.[7,14—16]

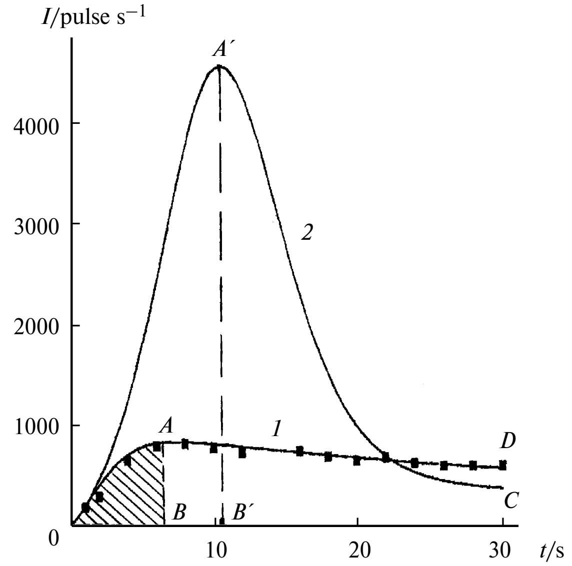

Fig. 2. Kinetic dependences of the concentration of atomic hydrogen for oxyhydrogen ignition near the first limit in a quartz reactor at a temperature of 500 °C and the first-limit pressure $P_{\text{l}} = 0.668$ Torr: $P_0/P_{\text{l}} = 1.01$, $b = 5 \cdot 10^{-12}$ cm^3 s^{-1} atom^{-1} (*1*); $P_0/P_{\text{l}} = 1.01$, $b = 0$ (*2*). Lines correspond to calculations[12] and the dots to the experiment.[7,14]

It has been suggested[3—6] that interaction of BCP and HCP may induce acceleration of BCP. The reactions between the BCP and HCP products were actually detected[7—14] but BCP was retarded rather than accelerated.

In addition to chain interaction on the wall, heterogeneous retardation of hydrogen combustion in the gas may be due to processes involving $\text{HO}_2^{\bullet}$ radicals (see Refs 3, 4, and 18), which give rise to hydrogen peroxide on the reactor surface and in the cold zone (detected experimentally).[21,22] However, taking account of these processes is not obligatory. Apparently, their contribution is low, as good agreement between the theory and experiments was attained[2,7—14] without inclusion of these processes into calculation schemes.

Thus, hydrogen combustion in the kinetic region of chain termination is controlled by the strong heterogeneous interaction between the chains, which precludes separation of the effect of other heterogeneous reactions on the process in the gas. The contribution of less significant catalytic reactions should better be studied using hydrogen combustion in the diffusion region of chain termination in which the flow rate of the AS to the decay site is determined by the diffusion coefficient.

Numerical modeling of oxyhydrogen combustion in the diffusion region of the heterogeneous chain termination

In experiments carried out in the diffusion region of chain termination, no isothermal combustion of oxyhydrogen has previously been obtained.[2,23] A dependence of the final degree of transformation (η_t) on the first-limit pressure (P_1) and the initial pressure (P_0)

$$\eta_t = 1 - (P_1/P_0)^2, \quad (2)$$

consistent with experimental results, has been established.[8,9] In this study, we compare the results of detailed calculations of the ignition kinetics with the results of an experiment carried out without self-heating of oxyhydrogen in the diffusion region of chain termination.

The lower limit in the diffusion region of chain termination was determined by using a new scheme of the heterogeneous decay of AS, namely, the "reactor with a spot" model.[8,9,19] The areas of chain propagation and termination were artificially separated in space. The ignition took place in a hot reactor 5 cm in diameter, and only a small portion of the AS decayed on the reactor walls. Their decay mainly took place on the liquid-nitrogen-cooled tube section meant for injecting oxyhydrogen into the reactor at a 50 cm distance from the reactor center. A 100-fold increase in the AS diffusion time to the decay place resulted in a very low pressure at the first limit (0.08 Torr) at which ignition in the diffusion region of chain termination was isothermal.

The standard treatment of the reactor wall by oxyhydrogen flashes before the main experiments (see Refs 1—4 and 15—18) in order to attain a low first limit and the kinetic region of chain termination actually gave rise to the diffusion mode of the heterogeneous decay of the AS.[19] Flash treatment cleaned only the heated reactor surface, while a grease spot on the valve adjacent to the reactor could not be removed. Therefore, the grease spot on the valve became the main site of AS decay at low pressures ($P < 0.4$ Torr),[8,19] and the major AS flow was directed there. It was shown[8,9,19] that a substantial portion of "new effects" interpreted[4,15—18] as new BCP features is due to the systematically ignored effect of vacuum grease in experiments with $P < 0.4$ Torr.

For $P < 0.4$ Torr (see Refs 4 and 15—18), after admission of the mixture into the reactor, the reaction products formed from AS and grease had time to interfere into the process before the end of the ignition.[19] At $P > 0.4$ Torr (see Refs 2 and 3), oxyhydrogen had time to burn, while remaining pure.[8]

In the cryogenic trap located between the reactor and the adjacent valve, the AS decayed before they could reach the grease spot. Freezing-out of water formed in the reaction allowed us to neglect the change in the gas composition and to consider the diffusion coefficient to be constant. At low pressures of gas mixtures, the correction related to the transfer of hydrogen atoms by a flow of water (Stefan flow) to the site where they decayed was negligibly small. An estimate has shown[9] that in the case of oxyhydrogen ignition at an initial pressure (P_0) exceeding the P_1 value by 25%, the correction was not more than 2%. When P_0 was higher than P_1 by 1.3%, the correction was 0.03%. (The conclusion[7—14] that the Stefan flow has a pronounced influence on the kinetics of hydrogen combustion[15,16] was not supported by calculations and could be valid only at a much higher pressure.)

The set of chemical kinetic equations describing the combustion of oxyhydrogen in the diffusion region of chain termination[2] has the following form:

$$d[H]/dt = 2K_0[H_2][O_2] + 2K_b[O_2][H] - a_{d1}[H]P_1/P, \quad (3)$$

$$d[O_2]/dt = -K_b[O_2][H] - K_0[H_2][O_2], \quad (4)$$

where K_0 is the rate constant for chain (radical) initiation on the quartz surface, K_b is the rate constant for chain branching ($H + O_2 = OH + O$), P_1 and P are the pressure at the first ignition limit and the current pressure, respectively, a_{d1} is the diffusion rate constant for the heterogeneous decay at the first limit. The current $[H_2]$ and $[O_2]$ values satisfy the equality $[H_2] = 2[O_2]$ to an accuracy of low radical concentrations. By passing to concentrations normalized to the initial concentration of dioxygen $[O_2]_0$ in the set of equations (3) and (4), we obtain

$$dx_2/dt = 2K_b{}^*x_1x_2 + 4K_0{}^*x_1{}^2 - a_{d1}x_2x_{11}/x_1, \quad (5)$$

$$dx_1/dt = -K_b{}^*x_1x_2 - 2K_0{}^*x_1{}^2, \quad (6)$$

where $x_1 = [O_2]/[O_2]_0$, $x_{11} = [O_2]_1/[O_2]_0$, $x_2 = [H]/[O_2]_0$, $K_b{}^* = K_b[O_2]_0$, $K_0{}^* = K_0[O_2]_0$, $[O_2]_1$ is the initial dioxygen concentration at the first limit. The initial conditions: $x_1 = 1$, $x_2 = 0$. The $[O_2]_0$ concentration in oxyhydrogen at a specified temperature and initial pressure values was determined using the ideal gas law: $P = 3[O_2]_0kT$, where k is the Boltzmann constant.

The set of equations (5) and (6) contains three reaction rate constants K_b, K_0, and a_{d1}. A reference book[24] recommends determining K_b by a formula that we used in the calculations:

$$K_b = 10^{14.19}\exp(-8420/T)\ \mathrm{cm^3\ s^{-1}\ mol^{-1}}. \quad (7)$$

The constants K_b and a_{d1} are related by the known expression for the lower ignition limit:

$$a_{d1} = 2K_b{}^* = 2K_bP_1/3kT. \quad (8)$$

For calculation of the constants a_{d1} and K_0, we used the results of experiments carried out at $T = 500$ °C and the pressures $P_1 = 0.075$ and 0.08 Torr at the first limit. The rate constant for chain initiation K_0 was the only varied parameter found from coincidence of the calculated and experimental times required to reach the maximum reaction rate after injection of the mixture into the reactor. According to relations (7) and (8), the set of equations (4) and (5) was solved with the following constants: $K_b = 5 \cdot 10^{-15}$ cm^3 s^{-1} mol^{-1}; $a_{d1} = 3.166$. The theoretical and experimental results (Fig. 3 and 4) were in

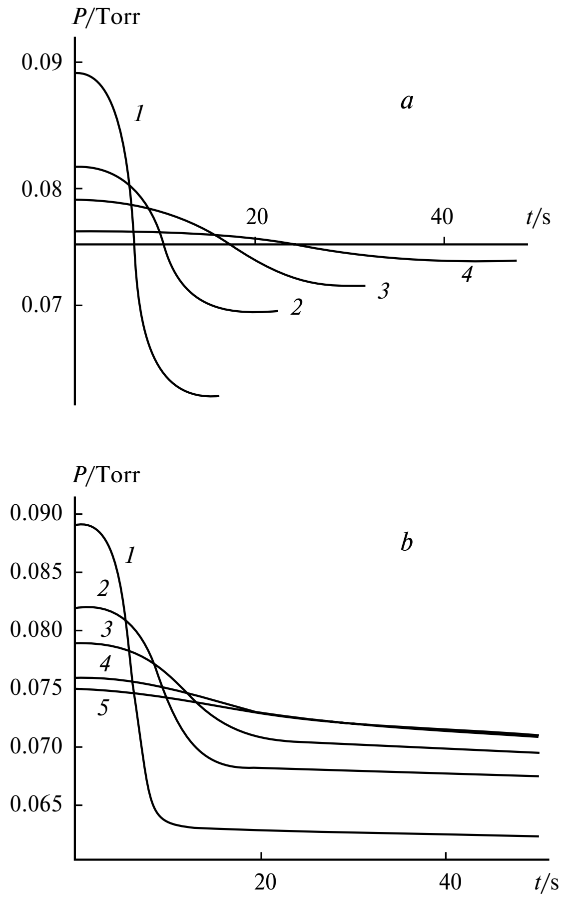

Fig. 3. Experimental (*a*) and calculated (*b*) variation of the pressure (*P*) *vs.* time (*t*) in a quartz reactor obtained for oxyhydrogen ignition in the diffusion region of chain termination at T = 500 °C and P_0/P_1 = 1.19 (*1*), 1.093 (*2*), 1.053 (*3*), 1.013 (*4*); P_1 = 0.075 Torr.[8,9] The pressure at the limit was determined as the average of two successive experiments with initial pressures differing by 1—2% in which nearly symmetrical kinetic curves were replaced by curves asymmetric with respect to the point corresponding to the highest reaction rate. Curve *5* was calculated for $P_0 = P_1$ = 0.075 Torr and is not parallel to the *x*-axis.

agreement at $K_0 = 1.5 \cdot 10^{-19}$ cm^3 s^{-1} molecule^{-1} for curve *1*, $K_0 = 1 \cdot 10^{-19}$ cm^3 s^{-1} molecule^{-1} for curves *2* and *3*, and $K_0 = 2.8 \cdot 10^{-20}$ cm^3 s^{-1} molecule^{-1} for curve *4*.

A fivefold increase in K_0 with an increase in the parameter P_1/P_0 from 1.014 to 1.19, which was found near the first limit as a result of solving the inverse problem, indicates apparently only that the new AS, presumably formed in the known heterogeneous chain initiation process, are transferred into the gas with a variable rate "constant." The rate of AS transfer to the bulk depends probably on the intensity of the reaction in the gas, which affects the atomic and radical populations of the surface. This result was obtained at fixed values of other constants, because in this case, it did not make sense to vary either the well-known rate constant for the AS decay, which depends only on the diffusion coefficient, or the equally well-known rate constant for chain branching.

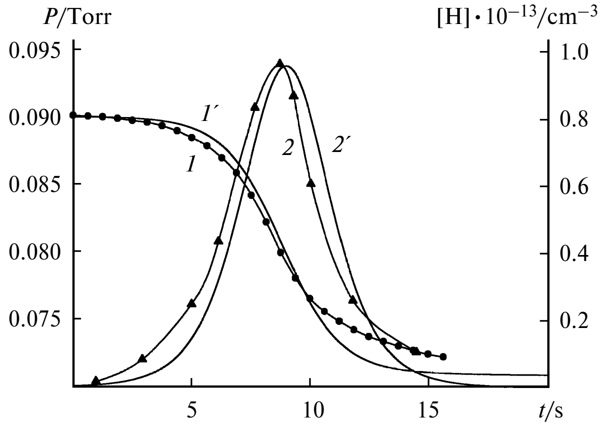

Fig. 4. Gas pressure (*1*, *1′*) and atomic hydrogen concentration (*2*, *2′*) *vs.* time for oxyhydrogen ignition in a quartz reactor obtained experimentally at P_1 = 0.08 Torr, P_0 = 0.09 Torr, T = 500 °C (*1*, *2*) and by calculations (*1′*, *2′*).

In the diffusion region, unlike the kinetic region, the quadratic chain termination on the wall does not affect the BCP in the gas, as the chain termination rate is linear with respect to [H] and depends only on the diffusion coefficient,[2] which did not change during ignition in our experiments.

Good agreement between experimental (see Fig. 3, *a*, curves *1—4*) and calculated (see Fig. 3, *b*, curves *1—4*) dependences of [H] on *t* as regards the shape and time scale indicates that the reaction scheme and the parameters found are close to true values.

Variation of the K_0 value for matching the times required to reach the maximum reaction rate in experimental (see Fig. 3, *a*) and theoretical (see Fig. 3, *b*) curves does not provide full coincidence. The deviations of the calculated results from the experiment are regular. The initial sections of the experimental kinetic curves exhibit on average a 40% higher reaction rate compared to the theoretical value. Conversely, at the final stage of ignition, the calculated reaction rate exceeds the experimental one. This can be seen from Fig 4, which reflects the time dependences of gas pressure and atomic hydrogen concentration obtained in a different series of experiments. The differences from the series shown in Fig. 3, *a* include recording of the atomic hydrogen pressure in the reactor and a slight change in the cooling mode of the surface spot on which the major portion of the AS decayed. It can be seen from the Figures that the highest reaction rate, the highest concentration of hydrogen atoms, and the final conversion degree are similar in the experiment and in calculations. However, matching of the curves $P = f(t)$ and [H] = $F(t)$ for the instant the reaction rate reaches a maximum demonstrated that the differences between the calculation and the experiment are confirmed by the pressure and RFS signal kinetic curves.[8]

When interpreting the detected interaction of active species in the gas—surface system, one should take into account the fact that the observed minor discrepancies between the theory and the experiment in the diffusion region of chain termination may be attributable not to chain initiation alone. Analysis[20] of the whole set of known data prompted the conclusion that, unlike heterogeneous chain branching, which has a low probability, the heterogeneous chain propagation is quite possible. A probable way is through-surface chain propagation with heteroatomic recombination of the H and O species. On ignition of oxyhydrogen, the concentration of the oxygen atoms at $T = 520$ °C is 20 times lower than the [H] value. The fraction of the hydroxy groups that enter the gas upon this heterogeneous chain propagation cannot be higher than 0.05, but this is sufficient for qualitative explanation of the observed minor discrepancies.[2,19]

Thus, for an initial stage of oxyhydrogen ignition, we found a reproducible accelerating influence of the gas-phase reaction on the formation of AS on the surface, which is manifested as acceleration of the heterogeneous chain initiation or propagation with a variable effective rate "constant". The reason for the replacement of the slight acceleration by an equal retardation of the reaction upon transition of the limit during ignition (see Fig. 4) is still unknown. This may be due, for example, to the nonlinear dependence of the rates of heterogeneous chain initiation or propagation reactions on the intensity of surface bombardment with the atoms generated from the low-pressure flame.

The K_0 value found for each experiment from coincidence of the instant where the highest reaction rate is attained according to calculations and the experiment should be interpreted as effective variable specific rate of chain initiation (or propagation), which is on average 1.5—2 times higher in the initial ignition period than at the final stage.

Results and Discussion

The discussion dealing with the surface effect on the low-pressure oxyhydrogen flame between two groups of researchers[3,4,7—18] proved to be useful and resulted in correction and development of some statements of N. N. Semenov´s theory.[1,2]

In one case, the conclusions[4,15—18] were based on experiments not provided with a procedure of AS monitoring. These conclusions were confirmed by an unusual strategy according to which both the experiment and its interpretation were focused on deviations from N. N. Semenov´s theory rather than on agreement. The accumulated array of inconsistencies between the experiment and the theory was interpreted as a general trend inherent in N. N. Semenov´s theory. It was concluded[18] that the linear approximation of the BCP theory,[1] which does not take into account the heterogeneous chain branching, can describe only the ignition limit but not the course of the reaction in time (see Ref. 18, p. 183 and references cited therein).

However, works of N. N. Semenov´s group published in the early 1980s[7,8,14] reported the discovery of an inhibitor formed in the reaction of the AS from the low-pressure flame with vacuum grease at the valves adjacent to the reactor and also the fact that the burn-out of the inhibitor, neglected in the earlier interpretations, was responsible for the previously considered[4,15—18] acceleration of the reaction; this was erroneously considered[4] as evidence for heterogeneous chain branching.

Studies[7—14,19,20] based on a monitoring procedure of the AS in the reaction area were focused on quantitative agreement between the theory and experiments and included experimental measurements of the parameters of new heterogeneous reactions.

Back in 1958, N. N. Semenov demonstrated that a calculation based on the linear approximation of the theory coincides with the experiments within the ignition peninsula and called this coincidence "excellent" (see Ref. 2, p. 519).

In the present study and in some publications,[8,9,19,20] good agreement between the calculated and experimental data was also attained near the ignition limit in the diffusion and kinetic regions of heterogeneous chain termination.

Therefore, both N. N. Semenov´s views and the later success[7—14,19,20,25] made the versatility of the BCP theory more and more obvious.[1,2] This theory provides rather accurate quantitative description of both the process in the peninsula[2] and the ignition limit,[19,20] and also the interaction kinetics of BCP and HCP.[25]

The results of previous studies[7—14,19,20,25] and the present work ultimately eliminate the question of serious discrepancies between the experiment and N. N. Semenov´s theory.

As a result, the potential of quantitative description of the low-pressure flame kinetics whose foundations were laid by N. N. Semenov[1] markedly increased. Recently,[12] a quantitative agreement between the experimental and theoretical data for the ignition of oxyhydrogen according to the BCP—HCP scheme was obtained for the first time. According to this scheme, of the four parameters describing the process, three refer to heterogeneous catalytic reactions (heterogeneous chain initiation, interaction, and termination). In the latter case, the gas phase chain branching was the only reaction taking place in the gas phase; even near the first limit, this could not compete with heterogeneous catalytic reactions of negative chain interaction.

N. N. Semenov´s and V. V. Voevodsky´s hypothesis of the existence of an interaction region between the BCP in the gas and the HCP on the reactor wall[6] was confirmed by examining hydrogen combustion in the kinetic region of chain termination in which the surface substantially retards the gas-phase part of the process.

As the first limit (P_1) decreased from 0.1 to 0.003 Torr and upon transition to the previously unknown region of extremely low-pressure oxyhydrogen flames, the fraction of particle collisions with the surface increased by almost two orders of magnitude, and the chain branching constant calculated from the kinetic curves remained invariable.[8,9] This fact confirmed once again, for a particular case, the artificial nature of the hypothesis of heterogeneous chain branching on quartz.

The spot reactor model for a nonuniform distribution of the probability of heterogeneous AS decay (ε) over the reactor surface[8,19] supplemented the model of uniform distribution of ε over the surface developed by N. N. Semenov.[2] Using this model, the interpretation of experiments[2] proposed later,[3] which was first poorly consistent with the theory, was reduced to a noncontradictory partial case of the theory. A strange combination of the observed[2] reaction rate twice as high as the calculated value and normal (not higher) burn-out observed in the same experiments was attributed[3] to heterogeneous chain branching. This contradiction was eliminated after experimental discovery[8,19] of the diffusion mode of chain termination[2] induced by the above-described specific cleaning of the reactor with flashes ensuring the formation of an AS flow from the reactor to the vacuum grease spot on the valve adjacent to the reactor. (This specificity was not taken into account in the calculations,[2—4] and the experiments[2] were considered to be carried out in the kinetic region of chain termination.)

The slight deviations from the theory observed for hydrogen combustion in the diffusion region are apparently due to low-pressure flame activation of heterogeneous chain initiation and propagation catalyst.

Quantitative description of the isothermal ignition of oxyhydrogen in the diffusion region of chain termination requires only three parameters, namely, the measured chain initiation rate and the tabulated chain branching constant and the diffusion coefficient.

This is the simplest known flame. When the initial pressure of the mixture is higher by more than 3—5% and less than 300% than P_1, it is not necessary to take into account the chain initiation and gas-phase interaction,[2,3,8] a quantitative agreement between the theory and experiments being attained by taking into account only two parameters, the diffusion coefficient of the H atoms and the rate constant for chain branching. The AS that emerge from the surface and are not taken into account by the theory are responsible for minor deviations, thus slightly accelerating the BCP in the gas in the initial ignition phase (above the limit) and retarding the process in the final phase (below the limit).

The main outcome of the series of studies considered[7—14,19,20] and the present study is elimination of virtually all significant discrepancies between the theory and experiments, whose interpretation at a qualitative level was accompanied by long debates.[3—18] Different modes of the standard reaction of hydrogen with oxygen are now described quantitatively without resorting to hypotheses that are difficult to verify.

The activation of the catalyst surface by bombardment with atoms and radicals coming from the flame zone has not been adequately studied and this research should be continued.

It appears promising to study the catalytic potential of a fresh quartz surface condensed on the reactor wall during silane combustion. An enhanced luminescence of the reactor wall after burning of silane[17] may be indicative of a heterogeneous catalytic reaction in which AS are formed on the surface and then emerge to the gas in chain initiation,[2,4] propagation,[3,22] or branching[3,6] processes. This study could be carried out by RFS. However, heterogeneous formation of AS accompanied by extensive luminescence of the surface but without significant emergence of the AS to the bulk, reported previously,[20,26] is also possible.

We hope that the question of influence of heterogeneous heteroatomic recombination of the hydrogen and oxygen atoms on the gas-phase hydrogen combustion could be answered after an RFS study of the low-pressure flame of hydrogen-depleted mixtures in which, unlike the flame of a stoichiometric mixture, the concentrations of H and O atoms are similar.

Quartz is a weak catalyst. One can hope that ethane chlorination on the surface of a more active catalyst, $ZnCl_2$, proposed previously[6] is actually a branched-chain reaction. This should also be verified experimentally by means of RFS.

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