

Kinetics of Hydrogen Oxidation Near the Lower Explosion Limit

E. N. ALEKSANDROV, V. S. ARUTYUNOV, I. V. DUBROVINA,
and S. N. KOZLOV

*Institute of Chemical Physics, U.S.S.R. Academy of Sciences, 177344 Moscow,
Union of Soviet Socialist Republics*

Abstract

Kinetics of hydrogen oxidation near the lower explosion limit in the kinetic region of chain termination has been studied. Major effects, causing deviations of the reaction kinetics from calculations by the linear theory of branched chain processes, are shown to be (1) the inhibition of the reacting mixture by the products of interaction of active centers with vacuum grease or with impurities contained in it and (2) the heterogeneous negative interaction of reaction active centers. The kinetics of hydrogen oxidation in this region has been calculated with consideration of the heterogeneous negative chain interaction. A set of parameters has been obtained that make it possible to determine by the shape of the kinetic curves the sign and the value of nonlinear interaction of chains near the lower explosion limit. It has been shown that the experimental data are in good agreement with the calculations, provided the heterogeneous negative chain interaction is taken into consideration and the inhibiting effect of impurities is eliminated. The rate of heterogeneous generation of chains on a quartz surface treated with hydrofluoric or boric acid has been determined.

Introduction

Hydrogen oxidation is a model reaction for experimental verification of branched chain process (BCP) theory developed by Semenov [1-3]. This theory explains qualitatively the main features of BCP and also provides a satisfactory quantitative description of hydrogen combustion in some regions [4,5]. However, near the lower explosion limit for chain termination in the kinetic region, where the contribution of nonlinear homogeneous processes is negligibly low, some phenomena have been observed that the linear theory of BCP cannot explain. In some cases the observed extent of conversion was significantly lower [6] or higher [7,8] than calculated values. High conversions were accompanied by long induction periods that did not correlate with experimental values of activation energy of heterogeneous chain generation [9] dominating at temperatures lower than 600°C. In refs. 10 and 11 kinetic curves with strongly stretched rear slopes have been

obtained. These curves indicate that for a considerable time after the maximum rate of reaction has been achieved, the drop of hydrogen atom concentration proceeds at an almost constant rate. In this region pulsations of hydrogen combustion have also been observed [12].

Some of the above-mentioned phenomena and the high conversions are attributed to a more active role of reactor surface in hydrogen oxidation than that assigned by linear BCP theory [8]. In ref. 8 it was assumed that high conversions were due to the nonlinear character of heterogeneous termination of active centers (AC), i.e., to a decrease in the probability of heterogeneous termination during combustion or possibly to the heterogeneous chain branching. The possibility of heterogeneous chain branching was considered by Semenov in the 1930s [2] and has been applied to the process of hydrogen oxidation in [13].

The aim of this work was to analyze incongruities between theory and experiment to find out the causes of these incongruities and to acquire a better understanding of the role of the heterogeneous processes in the kinetics of hydrogen oxidation near the lower explosion limit.

Experimental

The development over the past years of highly sensitive experimental techniques, such as resonance fluorescence, allow one to monitor reaction intermediates even beyond the self-ignition region. Besides the resonance fluorescence of hydrogen and oxygen atoms, the change in pressure during combustion was followed using a glass membrane manometer of 10^{-4} -torr sensitivity [12]. Experiments were performed in quartz reactors (36 and 55 mm i.d.) that were treated with either boric or hydrofluoric acid (Fig. 1). The resonance fluorescence technique is described in detail elsewhere [11]. The atom concentration was absolutely calibrated to within an accuracy of a factor of 2. In experiments with formation of high H-atom concentrations ($[H] > 10^{12} \text{cm}^{-3}$), the kinetics was followed by resonance light absorption at the H_{α} line [14]. The reactor placed in a heater had three inlets for addition of reagents and for resonance fluorescence excitation and de-

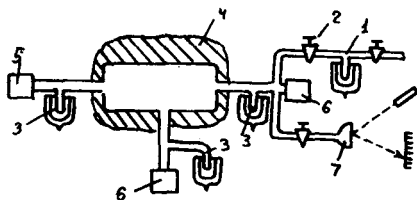


Figure 1. Experimental Setup: (1) transfer vessel, (2) inlet valve, (3) freezing traps, (4) heating oven, (5) resonance flow lamp, (6) Geiger counters, (7) glass diaphragm manometer.

tection. A stoichiometric hydrogen-oxygen mixture was introduced in the reactor from transfer vessel 1 by the valve 2. The transfer vessel had an appendage constantly cooled by liquid nitrogen to remove admixtures from the reaction mixture and to prevent vacuum grease vapors, vacuum oil, and mercury vapors from penetrating the reactor. Only Apiezon vacuum grease with a low vapor pressure was used. The temperature in the reactor was maintained to within $\pm 4^\circ\text{C}$. Before the experiments were performed, the reaction vessel surface was treated by numerous explosions of the hydrogen-oxygen mixture to ensure quantitative reproducibility of results.

Results and Discussion

The Foundation of Inhibitor in Mixture

We reproduced not only the values of the lower explosion limit, but also the very high conversions given in refs. 7 and 8, which immediately at the explosion limit amount to 40%. However, the kinetic curves for H-atom concentration, both above and below the limit (Fig. 2), indicate that an inhibitor is present in the system during the course of a reaction. A simple experiment confirmed this. When a mixture is injected into a reactor at a pressure up to 30% below the limit, a signal of resonance fluorescence of H-atoms appears, then rapidly decreases to the noise level and remains at this level for an infinitely long time (Fig. 3). However, the mixture can be easily exploded if an appendage, soldered to one of the inlets, is immersed in liquid nitrogen. A few seconds after the immersion, the mixture explodes, revealing the growth of H-atom concentration accompanied by a large pressure

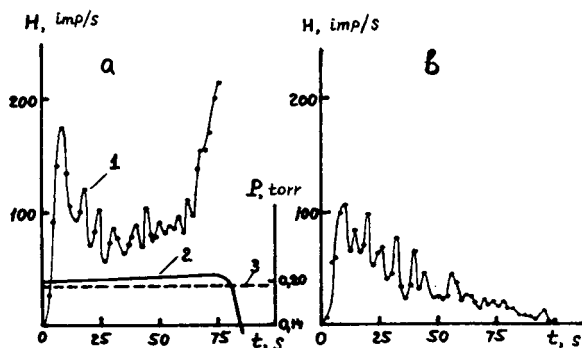


Figure 2. Dependence of H-atom concentration (curve 1) and pressure (curve 2) on time for experiments without nitrogen-cooled traps. Hydrofluoric-acid-treated vessel, $d = 55$ mm, $T = 420^\circ\text{C}$: (a) $P_0/P_1 = 1.026$, (b) $P_0/P_1 = 0.98$, pressure does not decrease. (3) Position of the lower explosion limit.

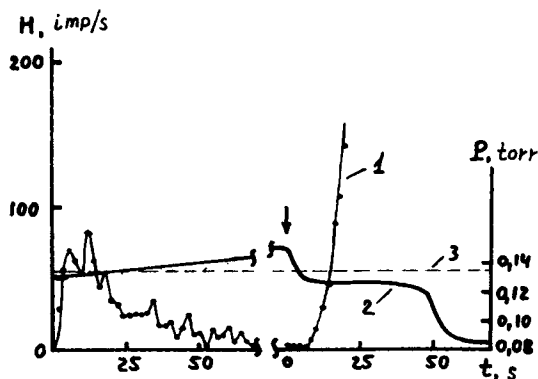


Figure 3. Effect of cooling trap on H-atom concentration and pressure change in the mixture at $P_0 < P_1$. Boric-acid-treated vessel, $d = 55$ mm, $T = 424^\circ\text{C}$. (1) Change in H-atom concentration, (2) pressure change curve, (3) Position of the explosion limit P_1 . Time interval between the two parts of the figure is ca. 10 min. Arrow shows the instant when the freezing starts.

drop (Fig. 3). (The insignificant rise of pressure in Fig. 3 is apparently due to the desorption of residual gases and the generation of an inhibitor, both of which were frozen in liquid nitrogen). The extent of conversion for such "below-the-limit" mixtures amounts to tens of percent. The two-stage feature of the process [Fig. 2(a)], the initial self-accelerating rise of H-atom concentration even in the below-the-limit mixtures (Figs. 2 and 3), and the long induction periods [Fig. 4(a)] typical also

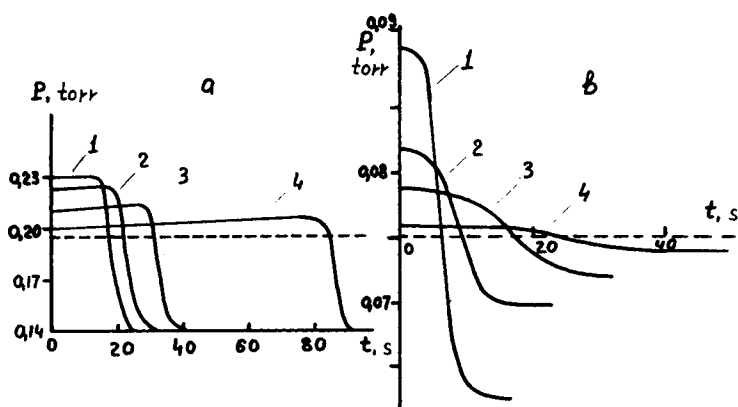


Figure 4. Pressure change in reactors without traps (a) and with nitrogen-cooled traps (b). Boric-acid-treated reactor $d = 55$ mm. (a) $T = 420^\circ\text{C}$, $P_1 = 0.195$ torr: (1) $P_0/P_1 = 1.18$, (2) $P_0/P_1 = 1.10$, (3) $P_0/P_1 = 1.092$, (4) $P_0/P_1 = 1.025$; (b) $T = 490^\circ\text{C}$, $P_1 = 0.075$ torr: (1) $P_0/P_1 = 1.19$, (2) $P_0/P_1 = 1.093$, (3) $P_0/P_1 = 1.053$, (4) $P_0/P_1 = 1.013$.

for ref. 8 prove that an inhibitor is present in the system. This inhibitor is apparently formed by the action of AC during the chain-branching reaction.

The most probable source of an inhibitor is vacuum grease or admixtures dissolved in the grease. To prevent such impurities from entering the reactor, all three inlets were equipped with appendages (Fig. 1), which were immersed in liquid nitrogen. As a result, the self-ignition process changed significantly. Self-ignition delays and the two-stages of the kinetics disappeared. The pressure curves acquired a shape almost symmetrical in relation to the self-ignition pressure [Fig. 4(b)]. Accordingly, the extent of conversion changed. (For its calculation, the forming water was frozen, and the pressure of the nonreacted mixture was measured). The final extent of conversion η_f , thus obtained was even lower than the values predicted by the linear theory of BCP [2,3] using the expression

$$(1) \quad \eta_f = -\frac{P_1}{P_0} \ln(1 - \eta_f)$$

where P_0 and P_1 are the initial pressure and the pressure at the lower explosion limit (Fig. 5).

Even more convincing were the results of an experiment conducted in a "greaseless" reactor (36 mm i.d.) treated with boric acid. In this reactor all valves were made of glass and Teflon. Indium O-ring gaskets

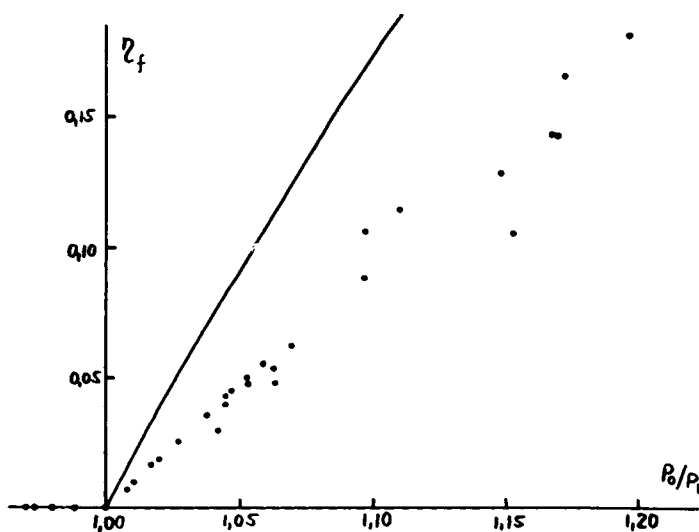


Figure 5. Final extent of conversion η_f of the $2\text{H}_2 + \text{O}_2$ mixture in quartz reactor treated with hydrofluoric acid, $T = 500 \pm 4^\circ\text{C}$. Solid curve corresponds to eq. (1).

were used to seal the optic windows. The traps, which were cooled by solid CO_2 , prevented the penetration of impurities into the reactor even at the experiments' intermissions. The lower explosion limit in this reactor dropped approximately an order of magnitude compared with the one having vacuum grease connections and was equal to 0.02 torr at $T = 400^\circ\text{C}$ (Fig. 6). An independently determined probability of heterogeneous decay of H atoms decreased up to ca. 10^{-6} [14]. As in the preceding case, the extents of conversion were lower than the theoretical values (1).

Thus, low-pressure combustion turned out to be a complex process because the full volume of the reactor, including its adjacent cold parts with vacuum grease valves, is in a rarefied flame zone. Subjected to the monotonous diffusion of atoms and radicals from the reacting zone, the vacuum grease becomes a source of inhibitor. Some changes in vacuum grease may occur as a result of its interaction with the acid vapors used in the preliminary treatment of the reactor.

This phenomenon could be neglected at relatively high pressures when the time of AC diffusion to the nearest vacuum-greased valve is essentially higher than the characteristic time of reaction [4,6]. However, when the characteristic times of the diffusion and the reaction are reversed [7,8], disregarding this phenomenon may lead to misinterpretation of the experimental data.

The generation of inhibitor can be prevented by using either greaseless

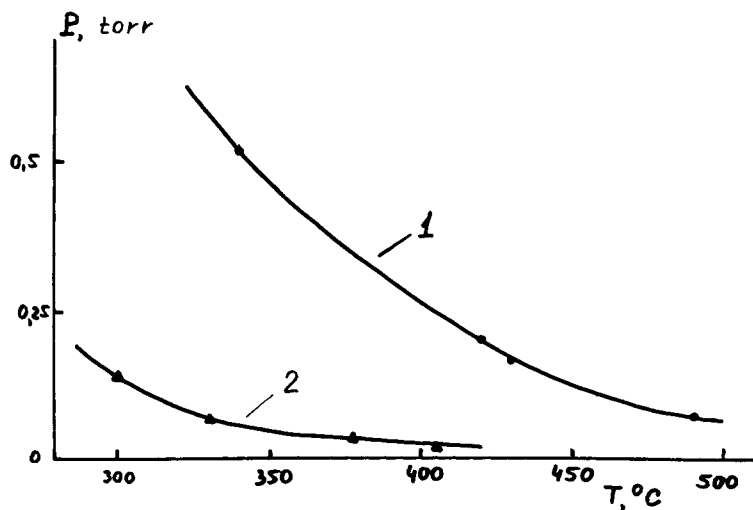


Figure 6. Position of the lower explosion limit for the $2\text{H}_2 + \text{O}_2$ mixture in the quartz reactor treated with boric acid: (1) reactor equipped with vacuum-greased valves, $d = 55$ mm; (2) reactor with Teflon valves having no contact with vacuum grease, $d = 36$ mm.

valves or nitrogen-cooled traps placed between each valve and the reactor. The nitrogen-cooled traps are preferable because they also freeze the water that is formed* and eliminate any possible effects caused by the change in surface properties as a result of adsorption of water vapor.

The nitrogen-cooled traps lead to certain increases in the effective heterogeneous AC decay rate in the reactor. However, in the kinetic region of chain termination, nonuniformities of distribution of AC in the reactor are insignificant and do not affect the combustion process very much. Therefore, the nitrogen-cooled traps do not alter the general features of combustion, at least while the AC decay occurs mainly on the reactor walls. At our conditions ($P \approx 1$ torr; $T \approx 500^\circ\text{C}$), in the quartz reactor treated with hydrofluoric acid, the rate of H-atom heterogeneous decay (the probability of recombination per collision $\approx 10^{-4}$) is almost an order of magnitude higher than the rate of decay as a result of diffusion and freezing in nitrogen-cooled traps located ca. 25 cm from the reactor center.

The Negative Heterogeneous Chain Interaction at Hydrogen Oxidation

The elimination of the inhibiting influence of the vacuum grease made it possible to discover the strong negative heterogeneous chain interaction at hydrogen oxidation. The kinetic curves for H-atom concentration in greaseless [11] or trap-equipped reactors (Fig. 7) appeared to have a strongly stretched rear slope, indicating that for a long time the reaction proceeds at an almost constant rate. These curves differ markedly from the almost symmetrical bell-like curves of the linear BCP theory [2,3]. Moreover, the extent of conversion is obviously below the calculated values (Fig. 5). This could be explained as a result of considerable influence of heterogeneous negative chain interaction. The latter is induced by increasing the rate of AC heterogeneous decay by a factor of 1.5 to 2 while increasing the H-atom concentration in a vessel by a few orders of magnitude during the explosion. This phenomenon is probably caused by an increase in the surface adsorption of atoms and by a corresponding change in the recombination mechanism. Such changes in heterogeneous recombination rates have already been observed at low temperatures on some metallic surfaces [15]. The arising dependencies on concentration have been analyzed in ref. 16.

* If there are no such traps, a considerable amount of water is adsorbed by the reactor walls. The amount of water adsorbed depends on its concentration in the reactor; thus, evaluating the extent of conversion by the change in pressure becomes a complicated matter.

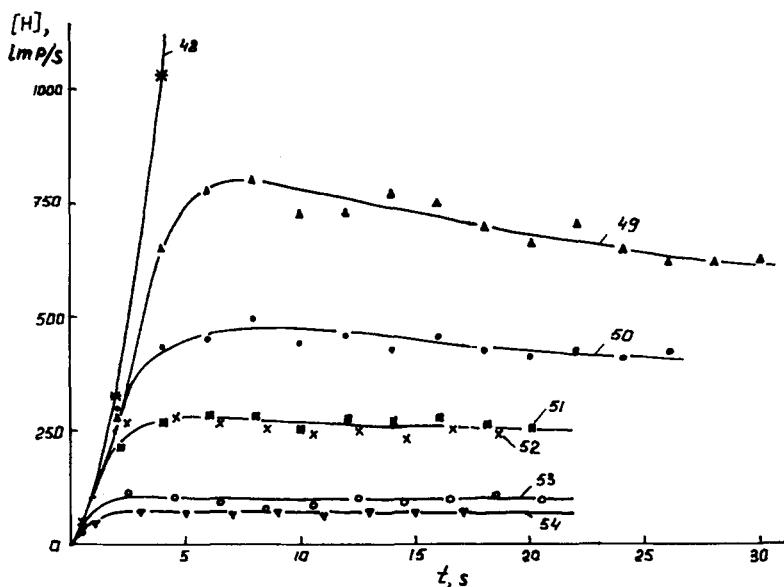


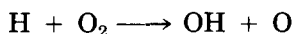
Figure 7. Kinetic curves for H-atom concentration in quartz reactor treated with hydrofluoric acid. Run numbers correspond to those in Table I. One pulse/s corresponds to ca. 10^8 atoms/cm³.

Direct measurements of the probability of heterogeneous H-atom decay at $T \sim 20$ and 500°C in a wide range of atom concentrations (from 10^8 to 10^{14} cm⁻³) were carried out in the same quartz vessels treated with hydrofluoric or boric acid in which the hydrogen oxidation had been studied [14]. In all instances, the H-atom heterogeneous decay probability increased by a factor of 1.5–1.8 as the H-atom concentration increased from 10^{10} to 10^{12} cm⁻³.

Such a small change in the rate of H-atom heterogeneous decay, hardly evident even in specially designed experiments, may considerably affect the kinetics of the branched chain reaction. The lower explosion limit for the hydrogen oxidation reaction is determined by the following expression:

$$(2) \quad 2k_b[\text{O}_2]_1 = k_{\text{het}}$$

where k_b is the rate constant of the chain branching



k_{het} is the rate constant of H-atom heterogeneous decay, and $[\text{O}_2]_1$ is the oxygen concentration at the lower explosion limit.

At the immediate vicinity of the explosion limit the concentration of atoms is about 10^{10} cm⁻³ (Fig. 7). Increasing the rate constant of

H-atom heterogeneous decay by only a few percent during the course of chain explosion can quickly halt the explosion. This may happen long before all the oxygen needed according to the linear BCP theory has reacted. As a result, the system shifts from the region characterized by the fast explosion process to the region of the relatively slow reaction with the concentration of atoms at about 10^{10} cm^{-3} corresponding to the stretched tail of the kinetic curves in Figure 7. In accordance with the linear theory of BCP, a system with a stable rate constant of AC heterogeneous decay has the maximum reaction rate and maximum AC concentration at the instant it leaves the explosive region. The reaction of these AC leads to production of almost as much reagent after the system leaves the explosive region as during combustion before the system leaves the region. In the presence of the above-mentioned negative chain interaction, the withdrawal from an explosive region takes place at AC concentrations much lower than that predicted by the linear model. Hence, considerably smaller extents of conversion of the mixture could be observed than expected from the linear theory.

*The Evaluation of the Reaction Kinetics
with Negative Heterogeneous Chain Interaction*

To verify the suggested model, the calculation of the kinetics incorporating the heterogeneous negative chain interaction was undertaken.

As often done for these conditions, we may take the quasi-steady-state concentrations for atomic oxygen and hydroxyl and neglect the rate of chain initiation. Thus, the process may be approximately described by the following equations [2]:

$$(3) \quad \begin{aligned} \frac{d[\text{H}]}{dt} &= 2k_b[\text{O}_2][\text{H}] - a[\text{H}] + b[\text{H}]^2 \\ \frac{d[\text{O}_2]}{dt} &= -k_b[\text{O}_2][\text{H}] \end{aligned}$$

where a is the independent H-atom concentration part of the heterogeneous decay "rate constant" and b is the constant of heterogeneous chain interaction. When $b > 0$ there is a positive chain interaction and when $b < 0$ there is a negative chain interaction. It was shown in ref. 13 that at a negative chain interaction the use of quasi-steady-state approximation is allowable. At a strong positive chain interaction this approximation is not valid; therefore, extending the results presented below for the $b > 0$ region should be done discretely. The dependencies of $[\text{H}]$ and $[\text{O}_2]$ on time, obtained from (3), are inconvenient for analysis. Similar to the procedure used in ref. 2, we divide the

first equation by the second one and get:

$$(4) \quad \zeta = \frac{[H]}{[O_2]_0} = \left(\frac{[O_2]}{[O_2]_0} \right)^\beta \left(\frac{2}{\beta + 1} - \frac{A}{\beta [O_2]_0} \right) - \frac{2}{(\beta + 1)} \frac{[O_2]}{[O_2]_0} + \frac{A}{\beta [O_2]_0}$$

Here $A = a/k_b$, $\beta = b/k_b$, and $[O_2]_0$ is the initial concentration of molecular oxygen. Equation (4) is a generalization of the corresponding Semenov equation in the linear theory of BCP [2] for the case of $\beta \neq 0$. Equation (1) for the value of final conversion in the linear BCP theory could be easily obtained from expression (4) at $\zeta = 0$ and $\beta \rightarrow 0$, if we use the definition of extent of conversion, $\eta = 1 - [O_2]/[O_2]_0$ and the equality $P_1/P_0 = [O_2]_1/[O_2]_0 = A/2[O_2]_0$ derived from eq. (2).

At a heterogeneous negative chain interaction, the linear relation for the rate constant of heterogeneous decay on the concentration of H atoms $k_{het} = a + |b| [H] = a - b [H]$ may be accepted as the first approximation for a certain range. In this case the constant b should be formally negative because it is the constant of negative interaction of chains in the equations (3). According to our experimental estimations, a is equal to about several s^{-1} and b is equal to $10^{-13} \text{ cm}^3/\text{molecule s}$ [14–16].

The dependencies of ζ on $\eta = 1 - [O_2]/[O_2]_0$, calculated by using eq. (4) for various values of parameter β at the fixed ratio $P_1/P_0 = 0.8$, are shown in Figure 8. The final extent of conversion and maximum concentration of H atoms at explosion ζ_{max} diminishes with decreasing β and the conversion curve becomes essentially asymmetrical in relation to the point $[H]_{max}$. Because molecular oxygen is consumed in accordance with eq. (3), by the curves in Figure 8 it may be easily estimated that transition, say, from $\beta = 0$ to $\beta = -100$ increases the duration of explosion 3 to 4 times.

In Fig. 9 are presented the dependencies of ζ_{max} , η_f , and $\alpha = \eta_f/\eta_{max}$ on β when $P_1/P_0 = 0.8$. Here ζ_{max} and η_{max} are the values corresponding to $[H]_{max}$. These functions show that the final extent of conversion and asymmetry factor α are the most convenient values for experimental evaluation of negative chain interaction. Assuming ζ is equal to zero, we obtain the expression for final extent of conversion via parameters P_1/P_0 and β :

$$(5) \quad \frac{(1 - \eta_f)^{\beta+1} - 1}{\beta + 1} = \frac{(1 - \eta_f)^\beta - 1}{\beta} \frac{P_1}{P_0}$$

From this expression it can be seen that a fast increase of η_f up to 1 takes place at $P_0/P_1 = (\beta + 1)/\beta$ (Fig. 10). An abrupt rise of the extent of conversion at the lower explosion limit revealed previously

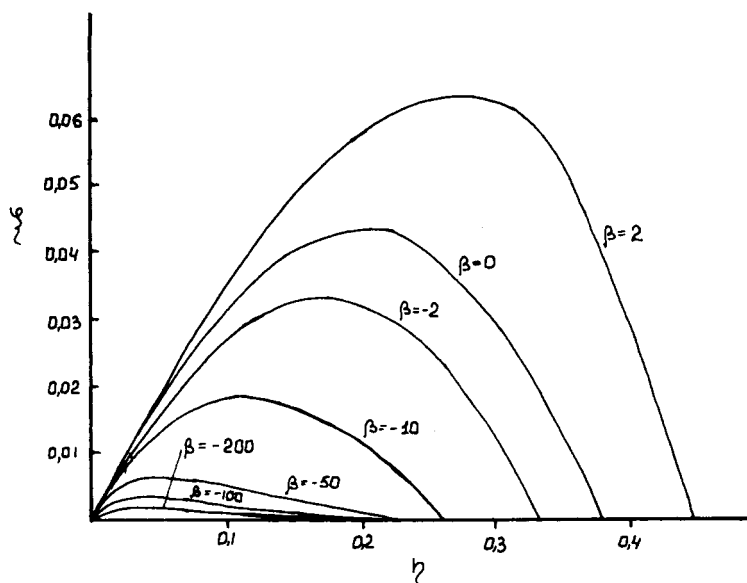


Figure 8. Dependence of $\zeta = [\text{H}]/[\text{O}_2]_0$ on $\eta = 1 - [\text{O}_2]/[\text{O}_2]_0$ calculated using eq. (4) for different values of $\beta = b/k_b$.

[7, 8] did not exceed 0.4 to 0.5 (Fig. 10) and could not be explained by the positive chain interaction with the constant parameter b .

According to Figure 8, the asymmetry factor α tends to 1 when $\beta \rightarrow \infty$, i.e., in the presence of an efficient positive chain interaction or branching via the surface. Therefore, the explosions having maximum intensity of chemiluminescence and maximum reaction rate considerably shifted to its end should be observed (Fig. 8). If the quasi-steady-state approximation is not valid, this trend would only increase. The absence of such phenomena indicates the domination at these conditions of the negative heterogeneous chain interaction. Indeed, the experimental

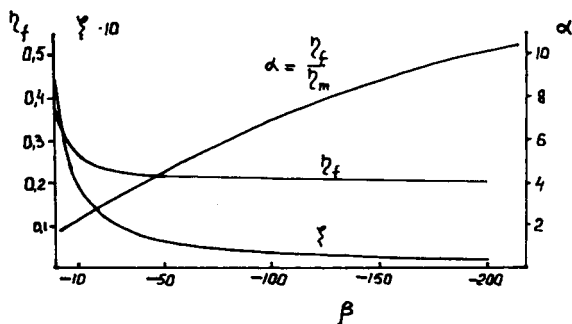


Figure 9. Calculated dependencies of ζ_{\max} , η_f , and asymmetry factor $\alpha = \eta_f/\eta_{\max}$ on β .

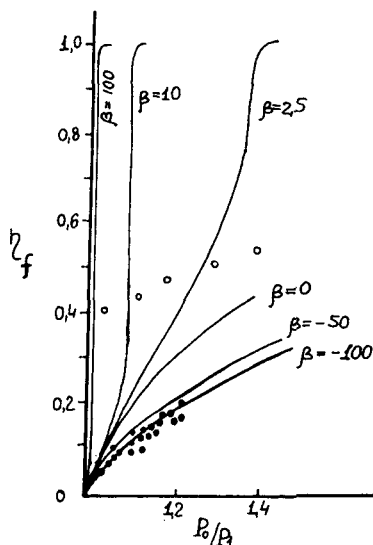


Figure 10. Final extent of conversion η_f as a function of P_0/P_1 : (○) ref. 8; (●) this work (Fig. 5). Curves were obtained using eq. (5) for different values of β .

values of final extents of conversion obtained after elimination of the inhibiting effects (Fig. 5) fit reasonably well the calculated curve with $\beta \approx -100$ (Fig. 10).

From eqs. (3), in accordance with refs. 2 and 13 and with our data, it follows that $d[H]/dt \approx 0$ for $[H] = 2k_b[O_2]/b \approx 10^{12} - 10^{13} \text{ cm}^{-3}$. Thus, the transition to almost a constant reaction rate is achieved in this case at very small concentrations of H atoms.

Note that the qualitative models of chain interaction via the surface considered here may be compared with the actual processes only for very small variations of $[H]$ because the linear approximation for $k_{\text{het}} = f(H)$ is applicable only within a certain range.

The above analysis allows one to obtain the macrokinetics criteria useful for identifying the presence of chain interaction in a system and its sign. The model used delivers qualitative and partly quantitative descriptions of all observed divergencies from linear theory of BCP in this region in an inhibitor-free system.

The Experimental Investigation of Hydrogen Oxidation in an Inhibitor-Free System

Below we present the experimental data on hydrogen oxidation used to assess the contribution of heterogeneous chain interaction in an inhibitor-free system.

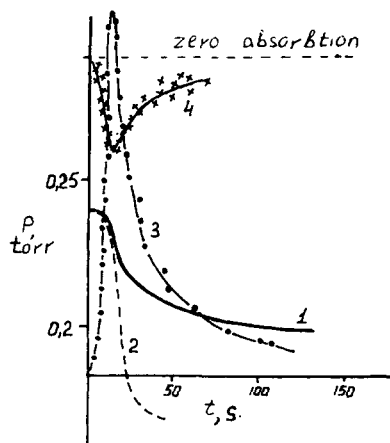


Figure 11. Parameters of the reacting $2\text{H}_2 + \text{O}_2$ mixture in the quartz reactor treated with hydrofluoric acid, $d = 36$ mm, $T = 390^\circ\text{C}$, $P_1 = 0.196$ torr. (1) Pressure (experiment), (2) pressure [calculation by eq. (1)], (3) O-atom resonance fluorescence signal, (4) light absorption by H-atoms on the H_α line.

The typical kinetic curves for hydrogen-oxygen mixture explosions are presented in Figure 11. The maximum concentrations $[\text{H}]_{\text{max}}$ and $[\text{O}]_{\text{max}}$ estimated for this experiment by the calibrations described in refs. 11 and 14 range from 4×10^{12} to $8 \times 10^{12} \text{ cm}^{-3}$ and from 4×10^{10} to $8 \times 10^{10} \text{ cm}^{-3}$, respectively. It can be seen from the figure that for this case the asymmetry factor $\alpha \sim 5\text{--}6$ corresponds to $\beta = -(80\text{--}100)$, i.e., $|b| \approx 5 \times 10^{-13} \text{ cm}^3/\text{molecule s}$. The combustion of the mixture in this case proceeds only up to the lower limit, and the explosion time is much longer than the time calculated by the linear approximation of Semenov's theory [1,2] (a dotted line in Fig. 11).

In accordance with data of refs. [6,10, and 11] and this work, it can be stated that stretched explosions are observed in different reactors. The asymmetry factor α is particularly high in reactors treated by potassium tetraborate. The quartz surface treated by hydrofluoric acid provides significantly smaller values of α , whereas coating the walls with boric acid accompanied by freezing out the reaction products sometimes leads to decreases in α up to 2 [14].

Using both the expression

$$(6) \quad \left(\frac{[\text{O}_2]_0}{[\text{O}_2]_{\text{max}}} \right)^{\beta+1} = \frac{P_0}{P_1 - \beta(P_0 - P_1)}$$

obtained from the solution of eq. (3) and the curves $\alpha = f(\beta)$ (Fig. 9), the change in the rate constant of H-atom heterogeneous decay

with increasing H-atom concentration in volume was derived (Fig. 12).

Estimations given above indicate that the rate constant of negative heterogeneous chain interaction in our experiments is 50–100 times higher than the rate constant of branching process and almost that much higher than the effective rate constant for negative chain interaction in volume [13]. On going deeper into the explosive region, the role of homogeneous (in volume) negative interaction should increase, whereas that of heterogeneous interaction should decrease. Because in our experiments, even for $P_0/P_1 \approx 1.8$, the latter is quite effective, the range of an appreciable influence of the negative homogeneous chain interaction on the kinetics of hydrogen combustion is shifted deeper into the explosive region than thought [13]. A similar negative heterogeneous chain interaction, caused by a change in recombination mechanism at surface saturation by atoms, should also be expected for other species, for instance, oxygen atoms. Such effects as considerable distortion of the symmetry of the kinetic curves in comparison with the calculations made by the linear theory are possible in other chemical systems, for example, during carbon monoxide oxidation and during combustion of lean hydrogen mixtures.

The upper boundary of possible contribution of heterogeneous positive chain interaction may be estimated by comparing the values derived from the linear theory of BCP [2,3] with the reaction kinetics at conditions when the effect of inhibition is eliminated but heterogeneous negative chain interaction is still small. In the reactor washed with hydrofluoric acid and equipped with nitrogen-cooled traps, such conditions are provided by conducting the reaction outside the explosion

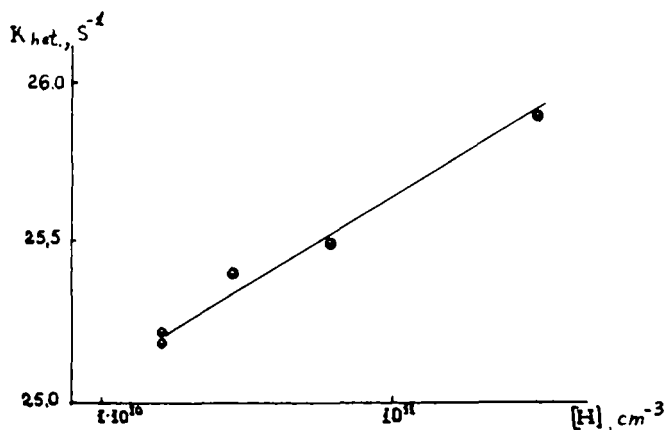


Figure 12. Dependence of k_{het} on $[H]$ calculated by eq. (6) on the basis of experimental data given in Fig. 7.

region or directly at the explosion limit until the H-atom concentration is $\leq 10^{10} \text{ cm}^{-3}$. At these concentrations, the heterogeneous decay still depends very slightly on the concentration, and the effect of negative heterogeneous interaction is not significant [14]. These conditions correspond to the kinetic curves presented at Figure 7. The change of AC concentration for the below-limit curves with $P_0 < P_1$, as well as for the initial steps of reaction development for the curves with initial pressure $P_0 > P_1$, occurs in accordance with the linear theory of BCP and is described by the following expression [2,3]:

$$(7) \quad n = \frac{w_0}{\varphi} (e^{\varphi t} - 1)$$

where

$$(8) \quad w = 2 k_b [\text{O}_2]_0 \left(1 - \frac{P_1}{P_0}\right)$$

Table I shows the chain branching rate constant k_b and the AC generation specific rate w_0 obtained using these equations. The mean value of $k_b = (4.8 \pm 2.0) \times 10^{-15} \text{ cm}^3/\text{molecule s}$ is in good agreement with the recommended value of rate constants for this reaction of $4.6 \times 10^{-15} \text{ cm}^3/\text{molecule s}$ ($T = 500^\circ\text{C}$) [17]. The mean value of AC generation specific rate $w_0 = 0.8 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$ exceeds by more than two orders of magnitude the experimentally determined rates of AC generation in volume [18]; hence, the generation of AC under these conditions proceeds on the reactor's surface (1.1×10^{10} particles/($\text{cm}^2 \text{ s}$)). These experiments indicate that for the quartz reactor washed with hydrofluoric acid, within the accuracy of our experiment (about 50%), it is practically impossible to detect the contribution of heterogeneous positive chain interaction.

Interesting results have been obtained using a reactor treated with boric acid. If such a reactor has no contact with vacuum grease (Teflon or metal valves), the probability of H-atom heterogeneous decay occurring is very small (ca. 10^{-6} at room temperature) and only slightly depends on temperature [14]. If such a reactor is equipped with nitrogen-cooled traps (Fig. 1), then with our apparatus geometry and dimensions the major part (ca. 90%) of the H-atom decay is accounted for not by their interaction with the side surface of the reactor but by their diffusion over a relatively large distance ($l \approx 25 \text{ cm}$ to the cooled traps). Therefore, although in such a reactor the lower explosion limit decreases on the average by an order of magnitude compared with the reactor treated with hydrofluoric acid (Tables I and II), the H-atom decay occurs not in the kinetic but in the diffusion region. In this case, a relatively small change in the probability of H-atom heterogeneous decay on the side surface of the reactor should affect only

TABLE I. Experimental values for the branching rate constants k_b and for the chain generation specific rate w_0 , during combustion of a mixture of $2\text{H}_2 + \text{O}_2$ in a quartz reactor treated with hydrofluoric acid ($d = 55$ mm, $T = 500 \pm 4^\circ\text{C}$, $P_1 = 0.663$ torr).

Run no.	P_0 (torr)	P_0/P_1	φ_{exp} (s^{-1})	$k_b(10^{-15})$ ($\text{cm}^3/\text{molecule s}$)	H stat ^a (pulse/s)	w_0^b (pulse/ s^2)
25	0.698	1.053	1.13	4.1		34
30	0.702	1.059	0.98	3.2		78
31	0.676	1.020	0.74	6.8		132
32	0.674	1.017	0.31	3.3		86
33	0.655	0.988			360	111
34	0.688	1.038	1.06	5.2		48
39	0.633	1.000				78
48	0.681	1.027	0.51	3.5		114
49	0.670	1.011	0.40	6.6		78
50	0.668	1.008	0.185	4.2		46
51	0.663	1.000				—
52	0.663	1.000				94
53	0.648	0.98			100	52
54	0.642	0.97			70	55
55	0.642	0.97			80	63
56	0.603	0.91			35	88
57	0.572	0.86			24	100
Average				4.8		79
						$(0.79 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1})$

^a For $\varphi < 0$.

^b For $\varphi = 0$, $w_0 = H(t)/t$. 1 pulse/s corresponds to $\approx 10^8 \text{ cm}^{-3}$.

slightly the reaction kinetics. If there is no positive chain interaction in the system, the kinetic curves should have approximately the same shape, as predicted by the linear theory of BCP. (Examples of such curves are presented in Figure 4(b), and their shape is almost symmetrical in relation to the pressure at the lower explosion limit.) Treatment of the curves with the equations for the conversion extent

TABLE II. Experimental values for the branching rate constant k_b for the chain generation specific rate w_0 during combustion of a mixture of $2\text{H}_2 + \text{O}_2$ in a quartz reactor treated with boric acid ($d = 55$ mm, $T = 490, \pm 4^\circ\text{C}$, $P_1 = 0.075$ torr).

Run no.	P_0 (torr)	P_0/P_1	φ_{exp} (s^{-1})	$k_b(10^{-15})$ ($\text{cm}^3/\text{molecule s}$)	$w_0(10^{10})$ ($\text{cm}^{-3} \text{ s}^{-1}$)
15	0.082	1.093	0.53	4.7	7.5
16 ^a	0.076	1.013	—	—	—
17	0.079	1.053	0.27	4.1	2.0
18	0.089	1.187	1.12	5.1	10.0

^a The accuracy of the pressure measurements was not sufficient for quantitative treatment of the curve 16.

$$(9) \quad \eta = \frac{w_0}{4 k_b [\text{O}_2]_0^2 (1 - P_1^2/P_0^2)} e^{\varphi_0 t}$$

where

$$(10) \quad \varphi_0 = 2 k_b [\text{O}_2]_0 \cdot (1 - P_1^2/P_0^2)$$

corresponding to the case of AC diffusion decay [3] allows one to obtain well-matching values of k_b (Table II) close to the value 4.0×10^{-15} cm³/molecule s [17] recommended for this temperature. The values of the AC generation specific rate w_0 are also in agreement with each other, although somewhat higher than those for a quartz surface treated with hydrofluoric acid. The high rates of heterogeneous AC generation, obtained using both surfaces, account for the absence of any considerable induction periods in those cases when special measures are taken to eliminate inhibiting impurities [Fig. 4(b) and Fig. 7].

Because the probability $P_1(T)$ of H-atom heterogeneous decay on the quartz surface treated with boric acid only slightly depends on temperature [14], the temperature dependence of the lower explosion limit in a greaseless reactor without cooling, treated with boric acid (Fig. 6, curve 2), described by eq. (2) must coincide with the temperature dependence of the branching rate constant k_b . The value of $E_b = 15.5 \pm 1$ kcal/mol obtained from Figure 6, curve 2 is in a good agreement with the value recommended by ref. [17]. Thus, within the accuracy of these experiments (50%), for the quartz surface treated with boric acid as well, it has not been possible to detect the contribution of the positive chain interaction at hydrogen oxidation.

Conclusion

The deviations observed in the kinetics of hydrogen oxidation near the lower explosion limit in the kinetic region of chain termination in quartz reactors treated with hydrofluoric or boric acid are caused by two effects:

The inhibition of the reacting mixture by the products of interaction of active centers with impurities (presumably vacuum grease or substances dissolved in it) and by the heterogeneous negative chain interaction accounted for by the relation of the probability of heterogeneous AC decay with the products' concentration in volume. The calculations made on the basis of suggested model, incorporating the heterogeneous negative chain interaction, are in good agreement with the available experimental data. As a result of calculations, some criteria have been suggested enabling one to establish by the shape of kinetic curves the presence of chain interaction in a system and the predominant sign of the interaction. The analysis of literature data and our results

indicate no traces of positive heterogeneous chain interaction under these conditions. However, from some recent data [19], it may be supposed that on some other surfaces (for instance, halogenated grease) this effect is more pronounced.

It was also shown that at 500°C and lower the AC generation in the hydrogen–oxygen reaction occurs mainly on the reactor's surface.

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