On the Possibility of a Thermal Explosion Initiated by a Heterogeneous Reaction between H$_2$ and O$_2$

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The challenge of the authors of the present paper is to respond to the arguments of the above-published critical review (in what follows, it is indicated by [CR]). In the paper presented, the authors consider surface-initiated ignition of the oxyhydrogen gas at the first and third limits; flame propagation, detonation, and combustion of hydrocarbons are not considered.

The authors [CR] develop a concept of initiation of the explosion of the oxyhydrogen gas at the third limit by branching chains and consider heat as a secondary factor, which accelerates combustion only at the second stage of the process. The authors of the present paper and [3] develop Semenov’s concept [1, 2], which implies that usually the primary factor acting at the third limit is heat. In this case, the explosion occurs as a result of decomposition of hydrogen peroxide whose main amount is formed above the second limit in the chain reaction with no branching chains [1, 2, 4, 5]. The branching factor $\varphi_0$ in this region is negative [1, 2], and the fraction of branching chains is smaller than unity.

Semenov considered that the chain-branching third limit is theoretically possible but is little probable in practice. Thus, in [6] (see also [2, p. 587]), Semenov criticized the paper of Akulov on the third limit in the hydrogen sulfide oxidation reaction and wrote about the oxyhydrogen gas explosion: “The third chain limit of ignition is sometimes possible, as was demonstrated by Voevodskii. We can see, however, that it arises only as an exception, under extremely specific conditions of the reaction, and only for the reaction of a rarely encountered chain mechanism. The reason for the widespread character of the third limit is the inevitability of the thermal explosion at sufficiently high pressures. The third limit usually has the thermal nature.”

Voevodskii’s concept about the chain third limit [7] was based on a hypothesis of existence of two forms of the H$_2$O$_2$ radicals with the bond energies of 44 and 10 kcal/mole and explained that the chain mechanism was responsible for the experimentally observed [5, 7] increase in pressure at the third limit in a pyrex reactor rinsed by the KCl solution. The hypothesis did not find further development, because the H$_2$O$_2$ radical with the low bond energy was not found and, apparently, does not exist.

The problem of interpretation of the elevated third limit in the KCl-treated vessel still remained unsolved. An alternative explanation of this fact by participation of catalytic reactions on the reactor walls in thermal explosion initiation [1, 8] was given in [3] and further below in the present paper.

1. Response to Comment Nos. 1 and 2 [CR] (Except for Comment No. 1.5). Comment Nos. 1 and 2 [CR] deal with the theoretical proof of a possible chain-branching third limit and dispute the results of [3] where the authors concluded that the higher value of the third limit in a KCl-treated vessel can be attributed to a lower reaction rate of heterogeneous chain initiation.

This important conclusion is based on the following facts and considerations [3].

It is known that chain-branching ignition of the oxyhydrogen gas in reactors 2.0 to 5.5 cm is noticeably accelerated by heat at low pressures ($\approx$1 torr) [1, p. 518]. At pressures of 7 to 10 torr, the heating of the reacting oxyhydrogen gas measured in the experiments [9] was higher by an order of magnitude than the expected pre-explosion heating due to the thermal explosion [1, 8]. In experiments at the first (chain-branching) limit at a pressure $p_1 = 10$ torr, therefore, complete burnout obtained in [10] was explained in [11] by the conversion of the chain explosion to the thermal explosion. In [3], we proposed a phenomenological criterion of participation

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of branching chains at the third limit:

\[ \tau_3 \approx \tau_1 \cdot p_1/p_3. \]  \hspace{1cm} (1)

Here \( \tau_3 \) and \( \tau_1 \) are the mean delays of the explosion at the third and first limits, respectively. Criterion (1) agrees with Semenov's theory [1, chapter X, § 2] validated by the experiment (see [1, Table 46]), where eight series of experiments, in accordance with the theory, displayed a decrease in the ignition induction period with increasing pressure of the oxyhydrogen gas fed into the reactor; this decrease was inversely proportional to pressure. Semenov estimated the difference between the theory and experiments as 10% [1, p. 510]). As other similar criteria, the criterion proposed should be considered as approximate. The inversely proportional dependence of \( \tau \) on \( p \) supported by calculations [25] and experiments [20, 22] is described below. The validity of the criterion for extrapolations in a wide range of pressures is also demonstrated below.

We compared [3] the mean ignition delays obtained at the first limit at a pressure \( p_1 = 10 \) torr (\( \tau = 0.4 \) sec [3, 10]), where the chain character of the explosion was definitely recognized, with the ignition delays in the experiments [7] at the third limit at \( p_3 = 760 \) torr, where the explosion character could not be unambiguously determined [1]. If the explosions at both limits had a chain character, the ignition delay at the third limit at atmospheric pressure should have been 76 times shorter than the delay at the first limit at \( p_1 = 10 \) torr [1, 3]. At the chain third limit, we could have expected \( \tau \approx 0.4 \) sec/76 \( \approx 0.005 \) sec. In the only experimental work [7] cited by Semenov in [6] as an extremely rare case, the values were \( \tau = 10-18 \) sec in pyrex reactors rinsed and not rinsed by KCl, which was greater than \( \tau \approx 0.005 \) sec by a factor of 2000–3000. This means that the reaction mechanisms at the first [10] and third [7] limits are principally different, and it was the thermal explosion and the thermal explosion only that occurred in reactors [7] rinsed and not rinsed by KCl.

An assumption was made [14] that the time of a complicated multistage process can be estimated by the characteristic time of the reaction of chain initiation in the gas

\[ \text{H}_2 + \text{O}_2 = 2\text{OH} \]

with the rate constant \( k_0 = 2 \cdot 10^{-22} \) cm\(^3\)·molecule\(^{-1}\)·sec\(^{-1}\). After obtaining the time of this reaction (\( t \approx 1800 \) sec) to be two orders greater than the ignition delays in the experiments [7], Azatyan [14] considered the hypothesis about the chain-branching third limit to be proved. A calculation with a more complete scheme consisting of 44 reactions was performed in [15]. The explosion delays in [15], \( \tau = 10-20 \) sec, are in good agreement with the experiments [7]. The calculation [15] directly indicated that the explosion had a thermal character, because the transition from \( \varphi < 0 \) to \( \varphi > 0 \) occurred after gas heating several times more intense than the pre-explosion heating in the thermal explosion [8]. Babushok et al. [15] used the gas-phase-heterogeneous value of \( k_0 [16] \) with the fraction of the heterogeneous reaction close to 0.8.

2. Response to the Criticism in Comment Nos. 3 and 4 [CR]. The authors of [CR] dispute the processes of chain initiation on the wall in comment Nos. 3 and 4, whereas the paper [17] and the criticized paper [3] involve a quantitative study of the heterogeneous reaction \( \text{H}_2 + \text{O}_2 = 2\text{OH} \) whose rate increases in the course of treatment (activation) of the reactor wall by the flame. At the same time, the authors [CR] admit that particles are issued from the quartz surface during hydrogen combustion. It is mentioned in comment No. 5 [CR] that heterogeneous ignition of the oxyhydrogen gas above the quartz surface observed in [18] is a chain process.

Alea and Haber [18] proved the possibility of surface-induced initiation of an explosion. In their experiments, the authors [18] ignited the oxyhydrogen gas by a quartz rod inserting the latter into the gas flow with the rod temperature being 20° lower than the gas temperature. In [18], the results of these experiments were explained by heterogeneous chain branching. It was found later [2, 13, 19] that the reason was the heterogeneous reaction of chain initiation, which was much faster on the wall than in the gas. Thus, admitting the realistic character of the heterogeneous ignition process in experiments [18], the authors [CR] believe that the heterogeneous reaction \( \text{H}_2 + \text{O}_2 = 2\text{OH} \) in [3, 16, 21] is unrealistic. Avoidance of the contribution of heterogeneous reactions to the global process contradicts the results of [1, 2, 12, 13, 17, 19, 21, 23] where such a contribution was taken into account as much as possible, based on the results of [1, 13, 18]. As our opponents have doubts about the quality of our experiments, we will use the experimental data in their publications to prove our concept.

Figure 1, which was borrowed from [20, 22], shows the changes in the oxyhydrogen gas ignition pattern after cleaning the reactor from vacuum lubrication. Figure 1a shows the kinetic curves obtained for ignition of the oxyhydrogen gas fed into a quartz reactor treated in the heated state with vacuum lubrication vapors. Figure 1b shows the time evolution of pressure in the case of ignition of the oxyhydrogen gas in a reactor with a metallic "lubrication-free" gate; the reactor surface was not subjected to treatment by vacuum lubrication vapors. The ignition induction period (time before the signs of the reaction appear) near the limit in the reactor.