

The Thermal Explosion of the Detonating Mixture Is Impossible without a Chain Avalanche

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Abstract—The fundamental regularities of hydrogen/oxygen combustion are considered, which unambiguously indicate the branched chain character of the process at atmospheric pressure. It is noted that, in the general case, the ignition conditions are determined by the competition between chain termination and both chain branching and chain propagation reactions. Some publications ignoring this important point are considered.

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Hydrogen is finding increasing use in various technical applications, including power engineering. The high value of hydrogen as a fuel is due to the branched chain mechanism of its oxidation, which makes possible hydrogen combustion in a wide concentration range and at a high rate. The process exhibits all specific features of branched chain reactions: the formation of atoms and radicals at concentrations comparable with the concentrations of the initial reactants; the existence of two different kinetic regimes of developed chain combustion, one of which is thermal explosion caused by a chain avalanche; and the inhibitability of combustion in all of its regimes (see, e.g., [1–9]). These facts are used in the chemical control of combustion, explosion, and detonation (see, e.g., [6–9]).

However, Aleksandrov et al. [10] deny the branched chain character of H₂ combustion at atmospheric pressure (including under flame propagation conditions) and state that the explosion is caused by the joint action of a hypothetical “autocatalytic reaction on the reactor wall and gas-phase processes not involving branched chains.” This hypothetical reaction is assigned a rate constant with an unreal dimension and value [10]. The authors ignore the fact that, in nearly all of the studies on gas combustion, explosion, and detonation at atmospheric and elevated pressures, including our works, the process is carried out in reactors whose walls are at room temperature and cannot cause H₂ combustion. Moreover, combustion is most often initiated in the center of the reactor, the flame reaches the walls only

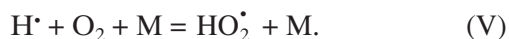
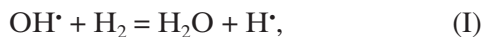
upon the completion of the process, and there are no heterogeneous reactions capable of stimulating combustion. Depending on the initial conditions, combustion takes place either in the pure chain avalanche regime, in which self-heating does not result in a thermal explosion, or in the simultaneous chain avalanche and thermal explosion regime [4–6]. Even without a chain thermal explosion, the concentrations of atoms and radicals in the flame become comparable with the concentrations of the initial reactants [1–3], so the latter react mainly with these reactive species, resulting in chain branching (including at 1 bar). Small amounts of certain admixtures either inhibit both combustion regimes or inhibit only the thermal explosion regime with a chain avalanche, without affecting nonexplosive chain combustion [11].

Note that the inhibition of combustion is unambiguous evidence of the chain character of the process since it involves atoms and radicals, including OH radicals and H atoms. The presence of H atoms at these temperatures means the occurrence of a chain branching reaction involving O₂.

Thus, even if Aleksandrov et al. [10] merely denied the branched chain character of hydrogen combustion at atmospheric pressure, ignoring the above well-known features of the process, this denial alone would make their article fundamentally erroneous. However, along with the above false statement, other statements inconsistent with experimental data and chemical

kinetic theory can be found in their article [10]. Below, we will consider some of these statements.

One of the specific features of hydrogen combustion is the existence of three self-ignition limits in a comparatively narrow temperature range below 850 K [1, 12]. The first two limits are quantitatively explained by the occurrence of the following reactions, including chain branching and termination steps:



Aleksandrov et al. [10] try to substantiate their denial of the existence of branched chains in H_2 combustion at atmospheric pressure by identifying chain termination under these conditions with reaction (V) and by stating that, at 830 K (third-limit temperature at 1 atm), the termination rate is much higher than the branching rate. All facts that are in conflict with these considerations are held back by the authors. Furthermore, referring to some publications, Aleksandrov et al. [10] permit themselves to “quote” ideas and statements that are exactly the converse of what was actually written. Here are some examples:

I.1. The evolution of the second limit into the third limit is explained by Semenov [1, pp. 545, 546] as follows: as the pressure and temperature are raised, the termolecular formation of HO_2^\bullet radicals (reaction (V)) progressively rarely ends in chain termination because “the rate of the reaction $\text{HO}_2^\bullet + \text{H}_2 = \text{H}_2\text{O}_2 + \text{H}$ becomes noticeable and HO_2^\bullet formation stops causing chain termination.” Aleksandrov et al. [10] deny this explanation and claim that “this reaction cannot be responsible for the existence of an ignition limit.” Instead of providing any arguments, the authors refer to the same monograph [1], ignoring the fact that the words *the third limit appears* are immediately followed there by the statement that this limit arises from the reaction between HO_2^\bullet and H_2 . In addition, contrary to Aleksandrov et al. [10], Semenov [1] states that the third limit in hydrogen combustion over KCl has a chain character.

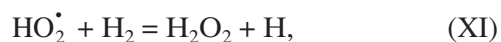
2. Aleksandrov et al. [10] state, with reference to Semenov [1], that the competition between chain branching and termination “does not make any significant contribution to hydrogen combustion” near the third limit. However, just the reverse is stated about the third limit in Semenov’s monograph [1, p. 437]: “Ignition in vessels treated with KCl is of chain, not thermal, nature.” Nearly the same is stated after the explanation

of the role of the reaction between HO_2^\bullet and H_2 in the appearance of the third limit [1, p. 546].

3. Denying Semenov’s view of the role of the reaction between HO_2^\bullet and H_2 [1], Aleksandrov et al. [10] refer to a monograph by Lewis and Elbe [12]. In fact, Lewis and Elbe [12] wrote that, owing to this reaction, the chain termination rate is lower than the rate of the termolecular reaction (V). The fraction of HO_2^\bullet radicals resulting from reaction (V) that lead to chain termination is expressed as follows [12]:

$$k_{12}/\{k_{12} + k_{11}[\text{H}_2]\}. \quad (1)$$

Here, k_{11} and k_{12} are, respectively, the rate constants of H atom regeneration and the disappearance of HO_2^\bullet radicals (numbered as in [12]):



In addition, Lewis and Elbe [12] state that, as the temperature and pressure are raised near the third limit, reaction (XI) begins to dominate over HO_2^\bullet disappearance and, accordingly, chain termination slows down.

4. Aleksandrov et al. [10] hold back Semenov’s work [13] in which, based on a mechanism involving reactions (I)–(V) and the competing reactions (XI) and (XII), he set up an equation for the three chain ignition limits. This equation is readily representable in the form such that the above fraction is a multiplier standing before the rate constant of the termolecular reaction (V). Therefore, only part of the reaction (V) events results in chain termination and this part decreases with an increasing rate of the reaction between HO_2^\bullet and H_2 .

The same fraction (1), which takes into account the decrease in the chain termination rate as a result of reaction (XI), appears in the expressions for the chain ignition condition reported in our earlier works [14, 15], in which we explain the role of the competition between reactions (XI) and (XII). Aleksandrov et al. [10] ignore these explanations as well. However, these explanations and formulas presented in [1, 13–15] make clear that not any reaction (V) event leads to chain termination, contrary to what is stated in [10]. The reaction between HO_2^\bullet and H_2 , which regenerates hydrogen atoms, compensates significantly for chain termination via reaction (V). Taking into account the well-known values of k_{11} and k_{12} , one can readily see that, for the stoichiometric $\text{H}_2 + \text{O}_2$ mixture at 830 K and 1 bar, fraction (1) is smaller than 0.1. Therefore, the chain termination rate is by no means lower than the chain branching rate.

Aleksandrov et al. [10] pass by some other publications demonstrating the branched-chain character of H_2 combustion at atmospheric pressure, including [16–

18]. In these works, by numerically solving the set of kinetic equations for a branched chain mechanism involving reactions (XI) and (XII) and the decomposition of H_2O_2 into 2OH^\bullet , it was shown that H_2 self-ignition near the third limit is possible even without self-heating. Analytical solution of a set of kinetic equations additionally taking into account the reactions between H and HO_2^\bullet yielded an equation for the three chain ignition limits [17], and this equation is in agreement with experimental data. The transition from chain combustion to chain thermal explosion was also simulated.

5. It can readily be seen that, near the third limit, reaction (XI) competes efficiently with reaction (XII). Obviously, if a radical, in addition to participating in a chain propagation reaction, is involved in a termination reaction occurring at a comparable rate, the regularities of the chain process, including the critical condition of ignition, will be determined by the rates of both competing reactions. This is one of the fundamental laws of the kinetics of complex reactions, and it is described and explained in a number of monographs [1, pp. 497–499, 12, 19], textbooks of chemical kinetics, and articles (see, e.g., [13, 20]). Ignoring all of the above explanations, Aleksandrov et al. [10] deny this law and refer to nonexistent works instead of presenting any arguments.

The mistake of Aleksandrov et al. [10], who state that “the rate of chain termination in the gas phase is higher than the chain branching rate almost by one order of magnitude,” is not only that they deny the decrease in the rate of termolecular termination as a result of reaction (XI), but also that they ignore self-heating. Indeed, stating that combustion is caused by the temperature rise and that there is no chain branching, the authors compare the chain branching and termination rates only at the initial temperature (830 K). They do not take into account that, even at the earliest stages of combustion (after the burnout of 2–3% of the H_2), the rate of the branching reaction (whose activation energy is 70 kJ/mol [21]), increases with increasing temperature and exceeds the rate of reaction (V), which decreases slightly with increasing temperature. Therefore, after the beginning of H_2 combustion, chain branching would dominate over termolecular chain termination even if reaction (XI) did not occur.

II. Having chosen the particular case of a hot reactor, Aleksandrov et al. [10] hypothesize that the thermal explosion is caused by the heterogeneous generation of reactive species and by gas-phase reactions of these species without chain branching. Let us consider this case.

1. When there is no contact with the walls, H_2 combustion, with the above characteristic features of its branched chain mechanism, certainly takes place. It is, therefore, quite obvious that, other conditions being equal, chain combustion in the hot reactor can be prevented only by heterogeneous chain termination provided that this process is more rapid than chain branch-

ing. In the opposite case, the developing chain combustion can evolve into a chain thermal explosion [4–6, 11].

2. Semenov, who considered the third limit of hydrogen ignition to be thermal in the general case, nevertheless demonstrated [13] that, if the heterogeneous chain branching in H_2 combustion is limited by the diffusion of reactive species, the equation of chain ignition limits is cubic and all of its three roots are positive under certain conditions. Accordingly, one of these roots was assigned to the chain third limit. The example of a chain third limit provided by Semenov is the third ignition limit for a reactor washed with a KCl solution [22]. This treatment of the walls reduces the rate of the reaction $\text{H}_2 + \text{O}_2$ under the third limit by a large factor [12, 13, 19, 22]. Aleksandrov et al. [10] not only ignore the results of this study by Semenov [13], but, in their other publication [23], denying the chain character of the third limit, they dare refer to the same study and ascribe, to Semenov, just the reverse of what he actually wrote. Furthermore, Aleksandrov et al. [10] refer incorrectly to a monograph by Kondrat'ev and Nikitin [25]: conversely, it is stated by these authors (p. 432) that reaction (V) is not a termination reaction to the extent to which the HO_2^\bullet radical is involved in the regeneration of reactive species. The branched chain character of the third limit of $\text{H}_2 + \text{O}_2$ ignition over KCl is also accepted in other monographs [19, 24, 26].

3. Aleksandrov et al. [10] deny branched chains in H_2 oxidation at atmospheric pressure not only in hot reactors with any type of surface (including KCl), but also in nonheated-wall reactors, as well as chain branching in flame propagation and detonation. When doing this, the authors refer to the monograph by Lewis and Elbe [12]. However, in this monograph, the reaction between H_2 and O_2 under the third limit is considered exceptionally in terms of the branched chain mechanism. It is also demonstrated that, in the reaction over KCl, chain initiation takes place in the bulk, contrary to what is hypothesized in [10], and is, therefore, characterized by a very small rate constant [12].

In addition, Aleksandrov et al. [10] misrepresent our works. For example, the obviously wrong statement that the inhibitor is equally effective at very low and high pressure is ascribed to us. In none of our works did we make this statement of a similar one. Without any reason, Aleksandrov et al. [10] regard our combustion and detonation inhibition data as being nonquantitative. Conversely, in all our publications relevant to the subject, we demonstrate the quantitative reproducibility of our measurements, which elucidate even the role of the isomerism of minor admixtures and allow the rate of the detonation way to be determined with a high degree of accuracy.

III. The quantity $k_0 = 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [10], which is suggested as the rate constant of the heterogeneous generation of reactive species in order to justify the hypothesis that combustion takes place without

chain branching, is in conflict with all known experimental data.

1. As measured by Hinshelwood and Thomson [27], the maximum water formation rate and, accordingly, the rate of H_2 consumption in the $2\text{H}_2 + \text{O}_2$ mixture in a quartz reactor at 822 K and 615 Torr is 0.6 Torr/s. This value is three orders of magnitude lower than the value implied by the above k_0 value [10]. Lewis and Elbe [12], like a number of other authors [15–18, 22, 28], consider measured third-limit values and reaction rates near the third limit for reactor washed with a KCl solution and report, by way of example, that the reaction rate at 625 Torr is 9.0 Torr/min. This value is 3300 times smaller than would be observed with the k_0 value suggested in [10]. So, this k_0 value is implausible. It is in conflict with all induction period data measured near the third limit, including the induction period considered by the authors themselves (>10 s). It can readily be seen that, with this k_0 value, over 80% of the $\text{H}_2 + \text{O}_2$ mixture would react within a fraction of a second and there would be no induction period.

2. Criticizing Azatyan [15] for discarding the value of $k_0 = 7 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [29], Aleksandrov et al. [10] hold back the fact that, in the dissertation that they mention [30, pp. 301, 302], Azatyan notes that this value and the method of its determination are inaccurate. In addition, in a number of works that appeared after [29], coauthored with Semenov and other researchers, including Aleksandrov [31, 32], Azatyan reported a k_0 value that is one order of magnitude smaller than the value reported in [29].

3. Suggesting the use of the $k_0 = 7 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ value [29], obtained as early as 1972, Aleksandrov et al. [10] forget that, very recently, they themselves have obtained a value that is three orders of magnitude smaller ($k_0 = 5.6 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 773 K) [33]. They do not refer to another work in which a research team including one of them determined k_0 for the process taking place over different surfaces [34]. The k_0 value at 830 K again appeared to be three orders of magnitude smaller than the value suggested in [10]. Contrary to the hypothesis of Aleksandrov et al. [10], it was demonstrated that the reactive species are generated in the bulk [34]. These data were included in Aleksandrov's dissertation [35].

Arguing against the k_0 value taken by Azatyan [15] from handbooks, Aleksandrov et al. [10] ignore the statement made in [15] that, in the absence of chains, the self-heating calculated using the k_0 value from Semenov's monograph [1] is as low as with k_0 determined by the shock wave method.

4. It is still more important that the self-ignition limit and most characteristics of H_2 combustion after the induction period are independent of the chain initiation rate [1, 19, 25, 29, 36]. For this reason, when considering combustion that has started, Semenov et al. [1, 19, 25, 29, 31, 36], including Aleksandrov, do not take into account the chain initiation rate in calculations and

data processing. For the same reason, the use of the $k_0 = 7 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ value, even though it was demonstrated to be incorrect [30], had no effect on the results reported in [29].

5. The k_0 value suggested by Aleksandrov et al. [10] is disproved by data from the same article. Indeed, using the data presented in [10, Fig. 1] and a familiar formula for the H atom concentration under the first limit (see, e.g., [1, p. 499]) and assuming that the rate constant of reaction (II) is $1.9 \times 10^{14} \times \exp(-8300 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [21], we obtain a k_0 value smaller than $10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Thus, suggesting the value of $k_0 = 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Aleksandrov et al. [10] ignore the fact that, as follows from all of their data and from data reported by other authors, this constant is actually three orders of magnitude smaller even for the quartz surface. It is, therefore, clear that the problem of k_0 in [10] is far-fetched and is raised only to justify the false hypothesis.

It is also clear from the above that the use of the k_0 value in [15], where the values reported in [1, 32, 37–39] were taken into account, was fully justified and that the conclusions made in [14, 15] are quite right.

IV. The role of the chain avalanche will be illustrated by the example of the real combustion of the $7.5 \text{ H}_2 + \text{air}$ mixture. Combustion initiated in the reactor center takes place only in the bulk. The adiabatic temperature is close to 850 K. Using the rate constants of the molecular reaction between H_2 and O_2 from, e.g., [1, 32–34, 37–40], we can see that the characteristic time of this reaction is longer than 100 s. Therefore, the molecular reaction itself cannot be responsible for the observed combustion. At the same time, taking into account chain branching and step (XI) provides a natural explanation for combustion.

V. The thermal explosion in the $\text{H}_2 + \text{O}_2$ mixture and in many other gases is known to be brought about only by developed branched-chain combustion [4–6, 41]. This is also true for heterogeneous self-ignition and chain thermal explosion of silane, discovered and investigated in [6, 42, 43]. The heterogeneous ignition of hydrogen over quartz is also a branched chain process [44]. In this connection, note that the statement of Aleksandrov et al. [10] that the chain-to-thermal explosion transition was studied in [4, 5] (according to the numbering used in [10]) is also false. In the studies quoted by Aleksandrov et al. [10], this phenomenon was not observed and, therefore, could not be studied. Combustion in those works was studied in the immediate proximity of the first limit. It is quite natural that, in the first of these works, we can read that “the observed self-heating values are far below the values characteristic of thermal explosions” [10, p. 63]. Furthermore, conclusion no. 7 in this dissertation [10, p. 123] reads that the role played by self-heating is insignificant.

The statement of Aleksandrov et al. [10] as to the distorting effect of vacuum grease on chain combustion data applies to their own work [45], which was carried

out using an improperly pumped installation (as is clear from the data they presented). This was also noted in earlier publications (see, e.g., [46]). The attempt to ascribe this error to the standard procedure is in conflict with data of other authors, including the data confirming the main point of N.N. Semenov's theory [1]. Heterogeneous chain propagation was predicted in [29] and was proved by direct experiments using advanced kinetic and spectroscopic techniques, including isotopic methods [47].

Thus, the denial of the branched chain mechanism of H_2 combustion at atmospheric pressure and the hypothesis that there are heterogeneous reactions capable of causing a thermal explosion without chain branching ignore the conventional methods and results of the investigation of combustion, explosions, and detonation in gases and are in conflict with the above-listed, well-known features of hydrogen combustion that are typical of the branched chain mechanism. Another mistake of Aleksandrov et al. [10] is that they deny the decrease in the chain termination rate as a result of reaction (XI), ignoring the explanations presented in [1, 13–16, 19]. Aleksandrov et al. [10] hold back the facts that contradict their statements, including their own data. It is particularly unacceptable that Aleksandrov et al. [10] knowingly make incorrect references, distorting the contents of publications by other authors, including monographs [1, 12], and ascribing, to these authors, false statements with opposite meanings.

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