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On the Chain Nature of the Third Self-Ignition Limit of the Detonating Mixture

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Abstract—It is demonstrated by numerical simulation that neglect of branched chains at the third self-ignition limit of the detonating mixture is in conflict with actual observations.

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The elucidation of the laws and mechanism of hydrogen combustion with oxygen has made a significant, well-documented contribution to chemical kinetic theory. The experimental data available on hydrogen combustion at low pressures are in good agreement with the theory of branched chain reactions [1, 2]. Nevertheless, some authors are still attempting to revise the mechanism of hydrogen combustion at atmospheric pressure. In a recent publication [3], it is claimed that hydrogen combustion at atmospheric pressure takes place without chain branching, possibly via a nonbranched chain reaction, and is purely thermal in character. This hypothesis is based on the groundless assumption that the rate constant of chain initiation is three orders of magnitude larger than the hitherto reported values, including the data obtained by the authors themselves [4]. Ignoring the multiply verified estimates based on known rate constants, Aleksandrov et al. [3] deny that the chain branching rate exceeds the chain termination rate at elevated pressures. The incorrectness of the above statements was demonstrated in a number of works [5–7]. It was noted in these works that the false statement that the chain termination rate is independent of the $HO_2^{\bullet} + H_2$ reaction at elevated pressures is ascribed by Aleksandrov et al. [3] to monographs by N.N. Semenov [1] and Lewis and Elbe [2]. In fact, these authors expressed and substantiated an opinion quite opposite to what was stated by Aleksandrov et al. [3].

It was demonstrated by Azatyan [8] that, at elevated pressures outside the ignition region, even in the immediate vicinity of the critical condition, the hydrogen oxidation rate and the degree of self-heating are so low that no thermal explosion takes place. Note that it was established [9, 10] that the Frank–Kamenetskii formula [11], which determines the possibility of steady-state temperature distribution occurring in an exothermic single-step reaction (gives the thermal explosion condition), is equally applicable to the case of a thermal explosion caused by a branched chain reaction (chain thermal explosion, discovered by Azatyan and Merzhanov [12, 13]). Therefore, the Frank–Kamenetskii formula does not distinguish between the chain and thermal mechanisms of the process.

A specific feature of the self-ignition region of the detonating mixture is that, as the temperature is raised to 820 K, the second limit begins to rise rapidly with temperature and then disappears [1, 2, 14, 15]. The third self-ignition limit, P_3, appears here, which rises as the temperature decreases. It was demonstrated [1, 2, 14, 15] that the disappearance of the second limit with increasing temperature is due to the reaction $H_2 + HO_2^{\bullet} \longrightarrow H_2O_2 + H$ (or $H_2O + OH^{\bullet}$ [15]), which begins to proceed at an appreciable rate at these temperatures and pressures on the order of 10^2 Torr. As a consequence, the formation of $HO_2^{\bullet}$ radicals stops causing chain termination. At the same time, it is claimed that P_3 over the Pyrex surface is of thermal nature, while P_3 in the case of the reactor walls washed with a KCl solution is of chain nature [1, 14]. This statement is based on the fact that the temperature dependence of P_3 over the Pyrex surface obeys the Frank–Kamenetskii formula. However, in view of the above, this is not a forcible argument.

According to the P_3 data reported by Poltorak and Voevodskii [14], the P_3 versus temperature curve in the pressure range of 550–750 Torr for the Pyrex surface lies at lower temperatures than the same curve for the surface coated with potassium chloride [14, Fig. 1]. Thus, according to Poltorak and Voevodskii [14], thermal ignition, which can be due only to the strongly activated $H_2 + O_2$ reaction, takes place at lower temperatures than chain self-ignition. However, the highest activation energy in a chain unit, which is that of the chain branching reaction, is ~2.5 times lower than the activation energy of the $H_2 + O_2$ reaction [1, 2].

Therefore, chain ignition should occur at a lower temperature. This contradiction rules out the pure thermal ignition of the detonating mixture near P_3. Note also that, when considering thermal self-ignition at the third limit P_3, one should take into account the activated homogeneous reaction in all cases since the heat released in a heterogeneous reaction will be immediately removed by the reactor walls because the Lewis number under these conditions is close to unity.

There is evidence of the chain nature of P_3 in the literature. This evidence is based on an analysis of the cubic equation for the three chain ignition limits. This equation can be derived from the abridged kinetic scheme of hydrogen combustion. It was demonstrated that this cubic equation can have three real roots corresponding to three limits [16], and use of plausible values of kinetic constants provides a quantitative description for the shortening of the induction period with an increasing total pressure at the third limit [17]. There has been a numerical and approximate analytical investigation of the self-ignition of the detonating mixture in a perfectly mixed reactor [18]. That study indicated that the calculation is highly sensitive to the occurrence of the chain branching reaction $H + O_2 \longrightarrow O + OH^{\bullet}$ [18, Figs. 3, 4]. Using the analytical relationships established in that study, it can be demonstrated that neglect of the chain branching reaction eliminates the third limit. Thus, the results of this calculation show that chain branching at the third limit plays the determining role under the perfectly mixed reactor conditions.

The data available on the mechanism and rate constants of the hydrogen oxidation reaction make it possible to see whether thermal ignition at the third limit is possible in this reaction and, accordingly, whether it is necessary to take into consideration chain branching. The purpose of this work is to find out how adequately the hydrogen combustion mechanism ignoring the reactive intermediate multiplication reactions can explain the observed facts in hydrogen self-ignition near the third limit.

The chemical mechanism of hydrogen combustion near atmospheric pressure can be represented as follows [19–21]:

$H_2 + O_2 \longrightarrow OH^{\bullet}\ (H + HO_2^{\bullet})$,	$k_0 = 1.92 \times 10^{14}\exp(-21890/T)$ cm^3 mol^{-1} s^{-1} [22],	(0)
$OH^{\bullet} + H_2 \longrightarrow H_2O + H$,	$k_1 = 4.63 \times 10^{12}\exp(-2100/T)$ cm^3 mol^{-1} s^{-1} [23],	(I)
$H + O_2 \longrightarrow OH^{\bullet} + O$,	$k_2 = 1.99 \times 10^{14}\exp(-8460/T)$ cm^3 mol^{-1} s^{-1} [23],	(II)
$O + H_2 \longrightarrow OH^{\bullet} + H$,	$k_3 = 1.88 \times 10^{14}\exp(-6897/\mathrm{T})$ cm^3 mol^{-1} s^{-1} [24],	(III)
$H + O_2 + M \longrightarrow HO_2^{\bullet} + M$,	$k_4 = 6.47 \times 10^{15}(T/298)^{-0.8}$ cm^6 mol^{-2} s^{-1}) [25],	(IV)
$H + HO_2^{\bullet} \longrightarrow 2OH$,	$k_5 = 1.69 \times 10^{14}\exp(-440/T)$ cm^3 mol^{-1} s^{-1} [23],	(V)
$H_2 + HO_2^{\bullet} \longrightarrow H_2O_2 + H$,	$k_6 = 3.00 \times 10^{13}\exp(-14400/T)$ cm^3 mol^{-1} s^{-1}) [23],	(VI)
$OH^{\bullet} + O \longrightarrow H + O_2$,	$k_7 = 9.29 \times 10^{12}$ cm^3 mol^{-1} s^{-1}) [26],	(VII)
$O + HO_2^{\bullet} \longrightarrow OH^{\bullet} + O_2$,	$k_8 = 3.25 \times 10^{13}$ cm^3 mol^{-1} s^{-1}) [23],	(VIII)
$OH^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O + O_2$,	$k_9 = 2.89 \times 10^{13}\exp(250/T)$ cm^3 mol^{-1} s^{-1} [25],	(IX)
$2\,HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$,	$k_{10} = 2.00 \times 10^{12}$ cm^3 mol^{-1} s^{-1} [27],	(X)
$H_2O_2 + M \longrightarrow 2\,OH^{\bullet} + M$,	$k_{11} = 1.30 \times 10^{17}\exp(-22750/T)$ cm^3 mol^{-1} s^{-1}) [18],	(XI)
$H + H + M \longrightarrow H_2 + M$,	$k_{12} = 2.20 \times 10^{15}$ cm^6 mol^{-2} s^{-1} [25],	(XII)

$H, O, OH, HO_2^{\bullet} \longrightarrow$ chain termination on the wall in the diffusion-controlled region.

A one-dimensional Cauchy problem was considered. The characteristic time scale was chosen as follows: $t_0 = 1/(k_1^0[H_2]_0)$, where $k_1^0 = 4.63 \times 10^{12}$ cm^3 mol^{-1} s^{-1} is the preexponential factor of reaction (I). It can readily be seen that, with the dimensionless time scale chosen, 1 s is approximately equal to 10^6 units of dimensionless time on the τ axis in Figs. 1 and 2. Dimensionless variables and parameters were defined as follows: $\tau = t/t_0$, Y_i = [ith component concentration]/$[H_2]_0$, K_p is the dimensionless rate constant of the reaction. For a bimolecular reaction, $K_p = k_p/k_1^0$, where p is the reaction number ($p \neq 4, 12$). For a trimolecular reaction, $K_p = k_p[H_2]_0/k_1^0$, where $p = 4, 12$. The diffusion coefficients D_0, D_1, D_2, and D_6 for the hydrogen–air mix-

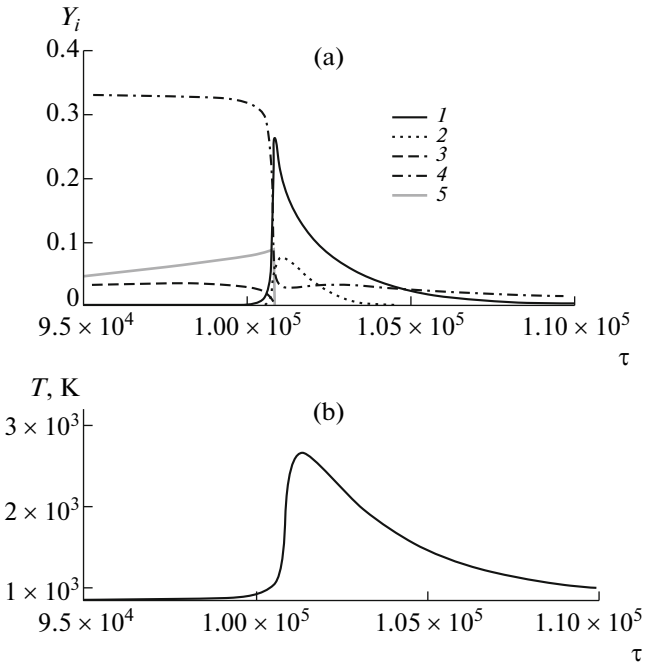

Fig. 1. Calculated profiles of the (a) reactants and intermediated ad (b) temperature for the self-ignition of the detonating mixture: (*1*) H, (*2*) O_3, (*3*) $HO_2^{\bullet} \times 500$, (*4*) O_2, and (*5*) $H_2O_2 \times 1000$. All of reactions (0)–(XI) are taken into consideration; β = 700 Torr; E_6 = 21000 cal/mol.

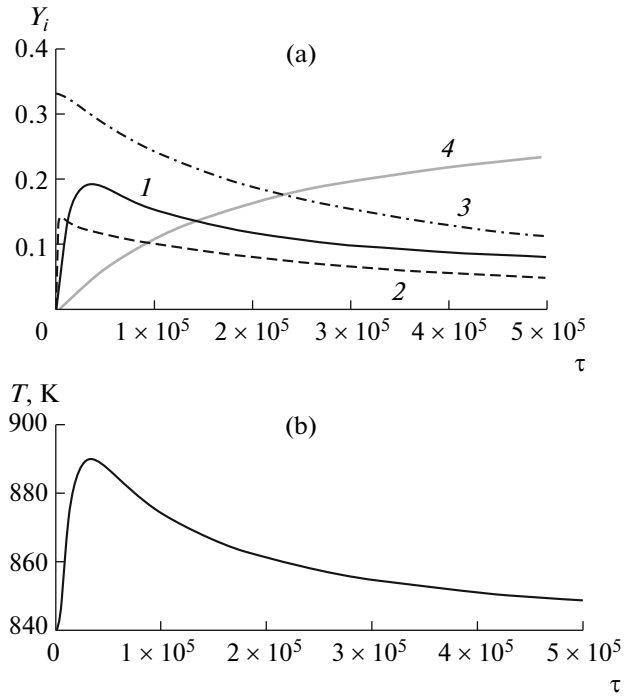

Fig. 2. Calculated profiles of the (a) reactants and intermediated ad (b) temperature for the self-ignition of the detonating mixture in the case of reaction (II) causing no chain branching: (*1*) H × 1000, (*2*) $HO_2^{\bullet} \times 2000$, (*3*) O_2, and (*4*) $H_2O_2 \times 200$. $k_0 = 10^{-18}$ cm^3 molecule^{-1} s^{-1}; β = 700 Torr; E_6 = 21000 cal/mol.

ture refer to H, $OH^{\bullet}$, O, and $HO_2^{\bullet}$, respectively. The heats of elementary reactions (Q_p) and diffusion coefficients were taken from [28, 29].

The set of kinetic equations in dimensionless variables for the above mechanism are as follows:

$$
\begin{aligned}
&dY_0/d\tau = K_0Y_3Y_4 + K_1Y_1Y_3 - K_2Y_0Y_4 + K_3Y_2Y_3\\
&- K_4Y_0Y_5M + K_8Y_2Y_6 - K_5Y_0Y_6 + K_6Y_3Y_6 + K_7Y_2Y_1\\
&- K_{12}Y_2{}^2M - 23.2\,D_0(T/273)^{1.7}/\beta^2d^2,\\
&dY_1/d\tau = -K_1Y_1Y_3 + K_2Y_0Y_4 + K_3Y_2Y_3 + 2K_5Y_0Y_6\\
&- K_7Y_2Y_1 + K_8Y_2Y_6 - K_9Y_1Y_6 + 2K_{11}Y_6M\\
&- 23.2\,D_1(T/273)^{1.7}/\beta^2d^2,\\
&dY_2/d\tau = K_2Y_0Y_4 - K_3Y_2Y_3 - K_7Y_2Y_1\\
&- K_8Y_2Y_6 - D_2(T/273)^{1.7}/\beta^2d^2,\\
&dY_3/d\tau = -K_1Y_1Y_3 - K_3Y_2Y_3 - K_6Y_3Y_6 + K_{12}Y_2{}^2M,\\
&dY_5/d\tau = -K_2Y_0Y_4 - K_4Y_2Y_5M + K_7Y_2Y_1\\
&+ K_8Y_2Y_6 + K_9Y_1Y_6 + K_{10}Y_6^2,\\
&dY_6/d\tau = K_4Y_2Y_5M - K_5Y_0Y_6 - + K_6Y_3Y_6\\
&- K_8Y_2Y_6 - K_9Y_1Y_6 - K_{10}Y_6^2 - D_6(T/273)^{1.7}/\beta^2d^2,\\
&dY_7/d\tau = K_6Y_3Y_6 + K_{10}Y_6^2 - K_{11}Y_7M,\\
&dT/d\tau = 1/C\sum_p\sum_{m,n}Q_pK_pY_mY_n - \alpha(L/C)(T - T_0).
\end{aligned}
\qquad (1)
$$

The set of equations (1) was integrated by the fourth-order Runge–Kutta method with an adaptive integration step. The initial conditions were $Y_0 = Y_1 = Y_2 = Y_6 = Y_7 = 0$, $Y_3 = 1$, $Y_5 = 0.5$, T_0 = 840 K, d = 4 cm (reactor diameter), and β = total pressure (Torr). Calculations were performed for β = 700–1900 Torr.

The last of Eqs. (1), in combination with the other equations, allows the dynamics of temperature variation in the reacting gas to be calculated. Here, C is the weighted average heat capacity at constant pressure, which is 0.25 cal g^{-1} K^{-1} [30]; T is temperature (K); $\rho = 10^{-3}$ is the density of the gas mixture (g/cm^3); and $M = 760 \times 10^{19}/T$.

In these calculations, the units of T are degrees. The value of α was estimated using the following relationship [11]: $\alpha = (L/r^2)\delta\lambda e$, where r is the radius of the cylindrical reactor (cm), L is the length of the reactor (cm), e is the base of natural logarithm, δ is the critical parameter (2.00 [11]), and λ is the thermal conductivity of the stoichiometric mixture $2H_2 + O_2$ taken from [30].

The subscripts m and n at the dimensionless reactant concentrations, varying from 0 to 6, refer to the following reactants: $OH^{\bullet}$, O, H, H_2, O_2, $HO_2^{\bullet}$, and H_2O_2. The subscript p at the dimensionless rate constants $K_p = k_p/k_1^0$ varies from 0 to 12, and its values are

consistent with the reaction numbering in the kinetic mechanism of hydrogen combustion.

It was found that, under the conditions chosen for calculations, heterogeneous chain termination in the diffusion-controlled region has only a slight effect on the results of the calculations. Therefore, the role of heterogeneous processes at atmospheric pressure is insignificant. It was also demonstrated that the calculations are weakly sensitive to the value of the rate constant of reaction (XI). Therefore, the reaction steps that include chain branching involving H_2O_2 are slow as compared to the chain branching reaction (II).

The calculations demonstrated that the inclusion of reaction (II) in the hydrogen combustion mechanism is necessary to reproduce the third ignition limit P_3 and to account for the observation that the self-ignition induction period τ_{ind} shortens with increasing total pressure. The calculated decrease in τ is ~20% for an increase in the total pressure from 700 to 1000 Torr. It was found that τ_{ind} decreases as the k_6 value is decreased (for $E_6 = 21\,000$ cal/mol [31], $\tau_{ind} \sim 0.1$ s; for $E_6 = 28\,800$ cal/mol [23], $\tau_{ind} \sim 2$ s). In addition, τ_{ind} increases with increasing k_8 and k_9. Because of the strong dependence of τ_{ind} on the rate constants of the reactions included in the kinetic scheme and because of the fairly wide confidence intervals of these rate constants, the decrease in τ_{ind} with an increase in β can be described only qualitatively.

Typical calculated kinetic curves of self-ignition above P_3 in Figs. 1a and 1b. The calculations, as well as available experimental data, indicate an abrupt flash accompanied by considerable heating. Not that reducing the heat evolution by a factor of 4 (dividing all terms of the sum on the right-hand side of the last equation of (1) by 4) leads to an approximately fourfold decrease in the degree of self-heating, but does not have any significant effect on τ_{ind}. This is direct evidence in favor of the branched chain character of combustion near P_3.

Independent computational verification of this inference was carried out by "switching off" the chain branching reaction (II). The absence of chain branching in the bulk at the given rate constants of elementary reactions (see the kinetic scheme) was simulated as follows. It was assumed that, in the linear branching reaction $H + O_2 \longrightarrow OH^{\cdot} + O$ (reaction (II)), the number of free valences does not change. For this reason, the reactions of the oxygen atoms resulting from reaction (II) were ignored in subsequent calculations. Accordingly, the first term on the right-hand side of the third equation in (1) was taken to be zero. The chain initiation rate constant was varied by setting it to be 10^{-22}, 10^{-18}, and 10^{-14} cm^3 molecule^{-1} s^{-1} in three different calculations. For $k_0 = 10^{-22}$ cm^3 molecule^{-1} s^{-1}, slow linear-law hydrogen peroxide accumulation takes place without any significant self-heating of the mixture. For $k_0 = 10^{-18}$ cm^3 molecule^{-1} s^{-1} (Figs. 2a, 2b), a rapid reaction accompanied by self-heating occurs. The maximum self-heating values is 50 K, and the initial compounds are completely reacted within 1 s. A comparison between Figs. 1 and 2 shows that neglect of the linear law chain branching via reaction (II) leads to a slow hydrogen oxidation mode that does not compare even qualitatively with the observed abrupt ignition after a well-defined induction period [14].

Note that the k_0 values of 10^{-18} and 10^{-14} cm^3 molecule^{-1} s^{-1} are obviously overrated. Indeed, the maximum water formation rate in the $2H_2 + O_2$ mixture measured by Hinshelwood and Thomson [32] in a quartz reactor at 773 K at 615 Torr is 0.6 Torr/s. This value is three orders of magnitude smaller than would be observed at $k_0 = 10^{-18}$ cm^3 molecule^{-1} s^{-1}. Data presented in the monograph by Lewis and Elbe [2], who considered experimental P_3 values and reaction rates under the third limit in a reactor with KCl-coated walls, lead to a still greater discrepancy. For example, the reaction rate at 625 Torr is 9.0 Torr/min [2, p. 42]. This value is 3300 times smaller than would be observed at $k_0 = 10^{-18}$ cm^3 molecule^{-1} s^{-1}.

A thermal explosion accompanied by self-heating of up to 800 deg is deduced only for an obviously unrealistic rate constant value of $k_0 = 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

These results demonstrate that the above mechanism of hydrogen oxidation at elevated pressure and the recommended values of kinetic constants lead to the conclusion that chain branching plays the determining role at the third self-ignition limit and that the reaction does not proceed in the thermal explosion mode. This is due to the following circumstance: thermal ignition, which can be brought about only by highly activated reaction (0), will immediately effect a unit of the reaction chain because the highest activation energy in the unit, which is that of the chain branching reaction (II), is ~2.5 times lower than E_0.

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