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The Contribution from Quadratic Reactions to the Thermal Regime of Branched Chain Combustion

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Abstract—A mathematical model was developed for the dependence of maximal self-heating in the course of the combustion of a hydrogen–oxygen mixture inside the ignition peninsula. The specific features of the thermal regime, which are related to a dual role of quadratic termination reaction, are discussed.

INTRODUCTION

Currently, it is known that branched chain combustion is characterized by the presence of two kinetic regimes, which differ strongly in their kinetic parameters [1–4]. One of these regimes is only due to the chain avalanche, which is accompanied and strengthened by the self-heating of the reacting mixture. This is chain combustion. The other regime is much more intensive. It is characterized by both the multiplication of active centers and avalanche-like heat accumulation in the system due to the feedback from self-heating and chain-branching as a result of reaching high rates of reaction and temperatures higher than a certain critical value. The second kinetic regime was called chain–thermal explosion (CTE). The possibility for the transition of combustion to the CTE regime and conditions for this transition depend on the type of branched chain process. The initial conditions that distinguish these two kinetic regimes have a critical nature. However, since once combustion starts the transition to CTE is very fast, it is possible to register this transition in a physical experiment in the course of the combustion development only if it occurs at very low pressures (e.g., in the combustion of silane and its derivatives) [4].

To study the transition of chain combustion to CTE and the development of this intensive kinetic regime is of interest for both the practice and theory of combustion. Valuable information can be obtained by combining experimental studies with qualitative analysis and finding numerical solutions to rate equations corresponding to the reaction system and the heat balance equations. It has been shown by calculations [5] that there are two kinetic regimes of chain combustion and critical conditions that separate these regimes. In that work, only the abstract generalized scheme was considered. This scheme contained the steps of branching, quadratic termination, the interaction of active and inactive radicals, and the termolecular reaction of transforming active sites into inactive. Correspondingly, the kinetic parameters were rather general. A dimensionless value that was the ratio of evolved heat and heat removal (Semenov's parameter) was used as a variable. This prevents the monitoring of separate parameters (e.g., the pressure). In a more recent paper [6], which dealt with the real scheme of the branched chain reaction of hydrogen oxidation, critical conditions for thermal explosion were not found in the numerical modeling of the nonisothermal process inside the region of chain ignition. Of course, the process of heat accumulation occurred with self-acceleration. There were inflection points on the plots of the maximal self-heating versus parameters like the pressure of Semenov's parameter, but there were no critical conditions for the reaction transition from one regime to another as observed in experiments and found using the abstract scheme [5]. In [7], the experimental data on CTE are reviewed and the effect is considered as a result of two simultaneous processes that enhance each other: chain and thermal avalanches.

The goal of this work was to determine the role of heat evolution from radical recombination in the heat balance of the reaction system and in the transition of chain combustion to CTE. This goal is achieved by numerical modeling.

The Second Limit of Ignition under Nonisothermal Conditions (Linear Approximation)

At the first stage, we considered the steps of hydrogen oxidation that are linear with respect to the concentrations of radicals. These are steps 1–3 and 5 of scheme (I) below, the reactions of heterogeneous radical (H, O, and $HO_2^{\bullet}$) decay. Since we considered the region inside the chain ignition peninsula, the cycles that include the formation and decomposition of hydrogen peroxide, which are important at higher pressures, were not considered. For the corresponding set of rate equations and the heat-balance equations, the critical condition means the appearance of the positive eigenvalue of the Jacobian matrix for this system assuming that the concentrations of initial reactants are constant.

	ΔH, kJ/mol
0. $H_2 + O_2 \longrightarrow 2OH^\bullet$	78.2
1. $O_2 + H \rightleftharpoons OH^\bullet + O$	69.2
2. $H_2 + O \longrightarrow OH^\bullet + H$	8.4
3. $H_2 + OH^\bullet \longrightarrow H_2O + H$	–58.8
4. $2H + M \longrightarrow H_2 + M$	–431.8
5. $H + O_2 + M \longrightarrow HO_2^\bullet + M$	–200.8
6. $H + HO_2^\bullet \longrightarrow 2OH^\bullet$	–147.3
7. $H + HO_2^\bullet \longrightarrow H_2 + O_2$	–216.0

(I)

The cited condition formulated so that it takes into account only steps that are linear with respect to radical concentrations provide the expression for the critical condition in the form of the equality $A = B$, where

$$\begin{aligned} A = {} & \alpha\{k_2[H_2]k_3[H_2](k_5[O_2][M] - 2k_1[O_2]) \\ & + (k_g^{O}k_5[O_2][M] + k_g^{H}k_2[H_2])(k_g^{OH} + k_3[H_2]) \\ & + k_g^{O}k_g^{OH}(k_1[O_2] + k_g^{H})\}, \end{aligned} \tag{1}$$

$$\begin{aligned} B = {} & E_0/RT^2W_0[k_5[O_2][M]k_3[H_2](k_2[H_2] + k_g^{O}) \\ & \times(2Q_3 + 2Q_5 + Q_0) + Q_0(k_g^{H}(k_g^{OH} + k_3[H_2]) \\ & \times(k_g^{O} + k_2[H_2]) + k_g^{O}k_g^{OH}(k_1[O_2] + k_5[O_2][M]) \\ & + Q_3k_g^{H}k_3[H_2](k_g^{O} + k_2[H_2]) \\ & + (Q_1 + Q_3)k_1[O_2]k_3[H_2]k_g^{O}]. \end{aligned} \tag{2}$$

Here, Q_i is the enthalpies of the corresponding reactions shown in scheme (I); k_g is the rate constant of the heterogeneous radical decay shown in the superscripts of the corresponding constants; α is the parameter of heat removal; and w_0 is the rate of chain initiation. The range of parameters where the condition $A < B$ is fulfilled is the region of chain nonisothermal ignition and combustion. The condition $A < 0$ determines the region of isothermic ignition. Under conditions when the rates of heterogeneous radical decay are low compared to the rates of chain propagation, the above critical condition transforms into the well-known relation $2k_1 = k_5[M]$.

When the role of heterogeneous chain termination is minor, the expression for the critical value of pressure (the second limit) that accounts for self-heating is as follows:

$$p^* = \frac{2k_1}{k_5[1 - E_0/RTw_0\alpha(2Q_3 + 2Q_5 + Q_0)]}. \tag{3}$$

This formula shows an increase in the upper critical pressure of ignition under nonisothermal conditions. If the parameter of heat removal α is expressed in terms of pressure, then we arrive at the formula for the critical value of this parameter:

$$\alpha = \frac{k_5PE_0/RT^2w_0(2Q_3 + 2Q_5 + Q_0)}{(k_5P - 2k_1)}. \tag{4}$$

It can be seen from this formula that the critical value of the heat-removal rate in the region of chain ignition cannot be described in the framework of this set of equations, because the denominator is negative and the numerator is positive. An attempt to describe the CTE phenomenon by the accumulation of heat in the bulk failed even when heat removal, which accompanies heterogeneous chain termination, was neglected. The results of our calculations show that self-heating accelerates with an increase in pressure, but there is no jump-like increase in self-heating over the whole interval that we considered, although it was observed in the experiment. The table shows the results of calculation of the maximal values of system self-heating and the hydrogen atom concentration at 728 K, $\alpha = 0.001$ cal K^{-1} s^{-1} according to scheme (I) without bimolecular reactions and with heat formation due to the reaction $H \longrightarrow 1/2H_2$.

2. Critical Conditions in Nonlinear Approximation

Obviously, most of the heat is evolved in radical recombination reactions. In the cited work [5], where the value of Semenov's parameter (which determines thermal explosion inside chain ignition) was found by calculations, the abstract scheme contained the reaction of quadratic chain termination. In the scheme used in this work, this is step 4.

To determine what was the reason for the existence of the critical value of Semenov's parameter within the framework of the abstract scheme used in [5], we repeated those calculations. It was found that, in the developed chain reaction, the rates of recombination reactions are comparable to the rates of active center multiplication. Therefore, these steps are responsible for most heat evolved in the reaction since they have a higher thermal effect. The rate constant adopted in [5] for the reaction of quadratic termination after recalculating it for the termolecular reaction is three orders of magnitude higher than the rate constant of reaction $H + O_2 + M = HO_2^\bullet + M$. With a decrease in the value adopted in [5] by an order of magnitude, the effect of criticality is diminished. We carried out many calculations of the nonisothermal problem according to the reaction scheme from [5] using the kinetic parameters that refer to the specific reactions of H_2 oxidation [7, 8].

Results of the calculation of the maximal values of self-heating $(\Delta T)_{max}$ and hydrogen concentration $[H]_{max}$ on the critical pressure P^* ($T = 728$ K, $\alpha = 0.001$ cal K^{-1} s^{-1})

P^*, torr	$[H]_{max}$, mol/cm^3	$(\Delta T)_{max}$, K
1	0.84×10^{-8}	0.37
2	0.16×10^{-7}	1.89
3	0.22×10^{-7}	5.03
4	0.28×10^{-7}	10.3
5	0.33×10^{-7}	18.2
6	0.39×10^{-7}	30.2
7	0.45×10^{-7}	48.5
8	0.54×10^{-7}	77.9
9	0.64×10^{-7}	123
10	0.78×10^{-7}	194
11	0.92×10^{-7}	268
12	0.10×10^{-6}	330
13	0.11×10^{-6}	379
14	0.12×10^{-6}	418
15	0.13×10^{-6}	449
17	0.15×10^{-6}	495
20	0.17×10^{-6}	542
23	0.20×10^{-6}	574
24	0.20×10^{-6}	583
25	0.21×10^{-6}	584
25.1	0.21×10^{-6}	581
25.2	0	0

All termolecular reactions with a third body were written separately for hydrogen, oxygen, and water as third bodies according to the scheme described in [9] and taking into account their different activities. However, this did not lead to the desired result, the curves of the maximal heating vs. pressure inside the region of chain ignition at a constant value of the heat removal parameter did not show jumps. In numerical calculation, we did not obtain the dependence of the critical value of this parameter on α for the pressure inside the region of chain ignition.

To determine the role of various nonlinear reactions in the formation of CTE, we varied the rate constants of the recombination of radicals k_i within the limits of two orders of magnitude. Of course, the cited values were considered as conventional calculation parameters. Only for strongly increased rate constants of exothermic reactions did numeric calculations give the critical value of pressure inside the region of chain ignition when a jump-like change in the maximal value of self-heating takes place. In one series of calculations, the value of the parameter of heat removal were kept constant. In another series of calculations, the value of pressure was kept constant, and the heat-removal parameter was a variable. So, we managed to register its critical value corresponding to a drastic change in the intensity of combustion (Fig. 1). With a decrease in the high values of the rate constants of exothermic reactions, the jump of an increase in maximal self-heating decreases. With a decrease in these calculated parameters by a factor of 10, a jump-like fashion of a change in the reaction kinetics disappears in the framework of the scheme proposed in [5] (Fig. 2).

To determine the role of heat evolution in the reaction of the quadratic decay of radicals when the regimes of combustion change in a critical manner, we considered a simplified scheme, given in this work, that accounts for all quadratic reactions. In this case, the characteristic polynomial is of the fifth order and its absolute term is the determinant of the Jacobian matrix. The formula shown below does not account for the reactions of heterogeneous radical decay, because the role of these steps is insignificant at pressures that we considered.

$$J = \Pi \left\{ \begin{array}{l} k_1[O_2]_0(\partial k_3/\partial T[OH][H_2](|Q_1 + Q_2|) - 2\alpha) + 4k_4[H]\begin{pmatrix} -Q_0E_0/(RT^2)w_0 + \alpha + |Q_1 + Q_2|\partial k_1/\partial T[H][O_2] \\ -(2Q_3 + Q_4)Dw \end{pmatrix} \\ -2Pk_5[O_2](Q_5 + 2Q_3 + Q_6)Dw \end{array} \right\} \quad (5)$$

Here, $\Pi = [H][H_2]_0^2 k_2k_3k_6P^3$ and $Dw = (1/2\partial k_3/\partial T\,[OH][H_2] + \partial k_1/\partial T\,[O_2][H] + E_0/(RT^2)w_0)$.

It is seen from formula (5) that $J = 0$ at the initial moment, and at the beginning of the induction period this term is of the order of the hydrogen atom concentration, which has a very small absolute value and a negative sign. The existence of a positive eigenvalue in the region of chain ignition is determined by the sign of the coefficient a_4 of the first exponent of the spectral parameter λ. This coefficient takes the following form:

$$a_4 = k_2k_3P^3[O_2][H_2]^2(-k_5PE/(RT^2 \times (Q_0 + 2Q_5 + 2Q_3) - \alpha(2k_1 - k_5P)). \quad (6)$$

It can be seen that a_4 is negative in the region of chain ignition. Therefore, an eigenvalue that is close to zero at the beginning of the induction period is also negative. However, there is also one positive eigenvalue (which is not close to zero) responsible for chain propagation in the region where a_4 is negative. Consequently, at the beginning of the process, no other positive eigenvalue appears. If we consider changes in the concentrations of initial reactants, then there are two positive eigenvalues, as can be seen from the corresponding formulas: one is close to zero and the other is close to the value that appears in the model that neglects changes in the concentrations of initial components. However, this takes place both under isothermic conditions and when temperature changes are taken into account. Therefore, it cannot determine the appearance of thermal explosion as should be expected. Thus, the above formulas do not determine the critical conditions for CTE, because they neglect changes in either initial reactant concentrations or temperature. If both these factors are taken into account, then the formulas become very complex and can be used only if one knows the changes in temperature and reactant concentrations in the course of combustion. Therefore, we obtained quantitative information on the process by calculating the eigenvalues in the course of the reaction. In both regimes, the system has two positive eigenvalues at the beginning of the process (for parameters inside the region of chain ignition). One eigenvalue is very small, and the other is determined by the criterion of chain branching (this fact agrees with formulas (5) and (6)). However, changes in the positive eigenvalues in the CTE regime differ radically from those for the nonisothermal regime of branched chain reaction. Figure 3 shows the results of calculations (in the framework of the simplified scheme (I)) for the dependence of the maximal heating on pressure for different values of the rate constant of hydrogen atom recombination. It is seen that these curves are qualitatively the same as the corresponding curves calculated in the framework of the complete scheme borrowed from [9] (see Fig. 2). We also calculated kinetics according to scheme (I), which neglects the step of quadratic branching (step 6). This scheme preserves the phenomenon of the critical pressure, but the values of critical values (the pressure and the heat loss coefficient) change. Figures 4 and 5 compare the subcritical and supercritical processes taking into account quadratic branching and neglecting it. Because the eigenvalues of the Jacobian matrix calculated in the course of the process are the generalized characteristics of both the qualitative behavior and the rate of parameter changes, the eigenvalues were calculated at each moment of time when solving the rate

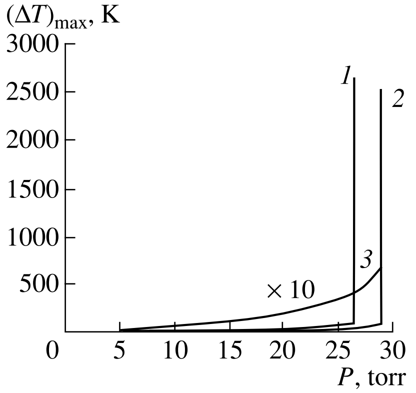

Fig. 1. Dependence of the maximal self-heating on pressure for various values of the heat-removal parameter α, cal K^{-1} s^{-1}: (*1*) 0.00795, (*2*) 0.0088, and (*3*) 0.0089.

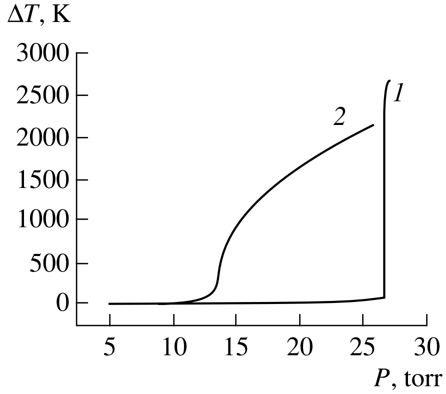

Fig. 2. Dependence of the maximal self-heating on pressure for two values of the radical recombination constant k_i: (*1*) 10^2 and (*2*) 10, $\alpha = 0.008$ cal K^{-1} s^{-1}, and $T = 728$ K.

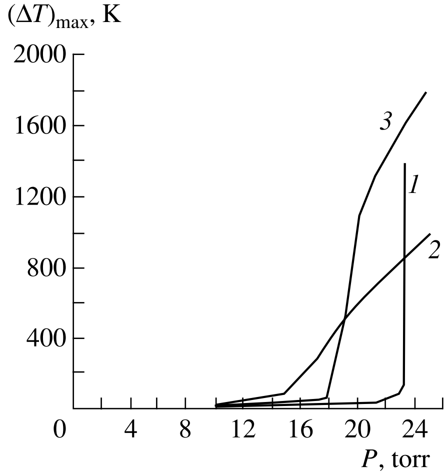

Fig. 3. Dependence of the maximal self-heating on pressure for various values of the hydrogen atom recombination constant k, cm^6 mol^{-1} s^{-1}: (*1*) 7.76×10^{18}, (*2*) 7.76×10^{17}, and (*3*) 3.88×10^{18}. $\alpha = 0.121 \times 10^{-1}$ cal K^{-1} s^{-1}, $T = 728$ K, and $[H_2] : [O_2] = 2 : 1$.

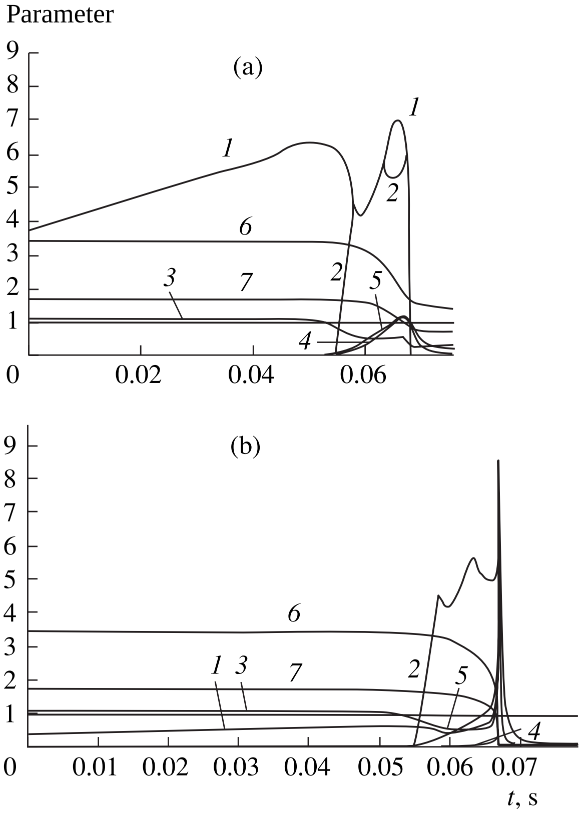

Fig. 4. Calculated changes in the process parameters using scheme (I) taking into account quadratic branching (step 6): (*1*) $\ln\lambda_1$; (*2*) $\ln\lambda_2$; (*3*) the criterion of chain branching; (*4*) $(\Delta T) \times 10^m$, K; (*5*) $[H] \times 10^n$, mol/cm^3; (*6*) $[H_2] \times 10^6$, mol/cm^3; and (*7*) $[O_2] \times 10^6$, mol/cm^3. $\alpha = 0.0121$ cal K^{-1} s^{-1}, $k_4 = 7.76 \times 10^{18}$ cm^6 mol^{-2} s^{-1}; (a) $P = 23.3$ torr, $m = -2$, $n = 8$; (b) $P = 23.4$ torr, $m = -3$, $n = 6$.

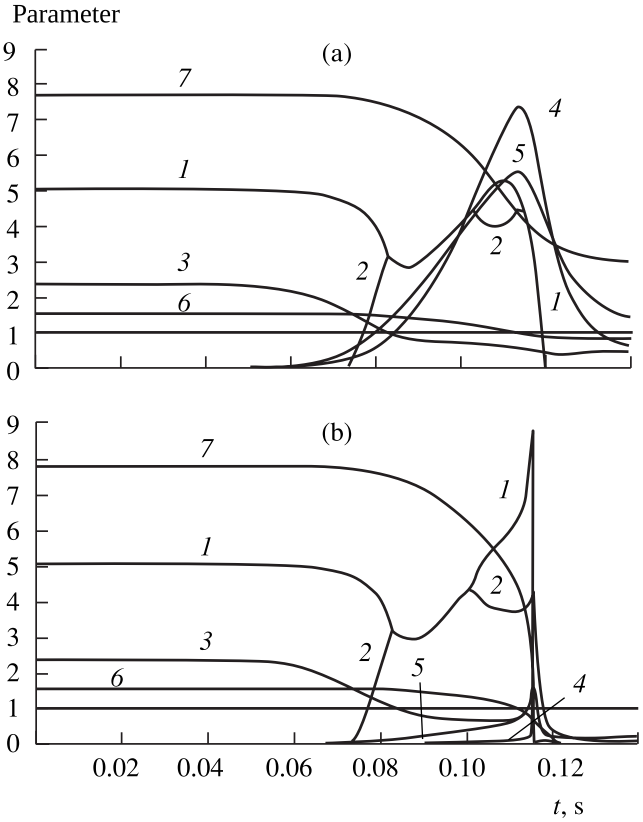

Fig. 5. Calculated changes in the process parameters using scheme (I) without taking into account quadratic branching (step 6): (*1*) $\ln\lambda_1$; (*2*) $\ln\lambda_2$; (*3*) the criterion of chain branching; (*4*) $(\Delta T) \times 10^m$, K; (*5*) $[H] \times 10^n$, mol/cm^3; (*6*) $[H_2] \times 10^6$, mol/cm^3; and (*7*) $[O_2] \times 10^7$, mol/cm^3. $\alpha = 0.0018$ cal K^{-1} s^{-1}, $k_4 = 7.76 \times 10^{18}$ cm^6 mol^{-2} s^{-1}; (a) $P = 10.5$ torr, $m = -2$, $n = 7$; (b) $P = 10.6$ torr, $m = -3$, $n = 6$.

equations numerically. Simultaneously, we traced the criterion of chain branching

$$2w_1 > w_5 + w_4, \tag{7}$$

which takes into account the main terms in a slightly simplified form.

Figure 4 and the subsequent figures show the ratios of the left-hand and right-hand sides of inequality (7).

Changes in this criterion during the reaction in the case of simple nonisothermic combustion (at a subcritical pressure) and in the case of CTE are very different. In the first case, the criterion starts to be violated as the initial reactants are consumed and then is never fulfilled again. In the case of explosion, the criterion only becomes violated when reactants are consumed to a substantial degree (~50%) and with an increase in the concentrations radicals that determine the rate of their recombination. This, in turn, leads to an accumulation of a large amount of heat and an increase in temperature. Accordingly, the rate constants of branching increase and the sign of inequality (7) changes. As a result the system returns to the region of chain branching under these new conditions. Figures 6a and 6b refer to subcritical and supercritical pressures, respectively, and illustrate this effect. These figures illustrate changes in two positive eigenvalues λ_1 and λ_2 of the Jacobian matrix in the course of the process (their natural logarithms are shown), the branching criterion, system self-heating, and changes in the concentrations of H_2, O_2, and H calculated according to the complete scheme taken from [9]. The violation of the criterion corresponds to the intersection of these curves with the line at the unity level. It is seen that, in the subcritical case, the maximal eigenvalue that characterizes variations in the process rate in the course of the reaction does not itself change considerably, whereas it increases stepwise by more than an order of magnitude in the supercritical case. Note that, in the former case, reactants are not consumed completely by the end of

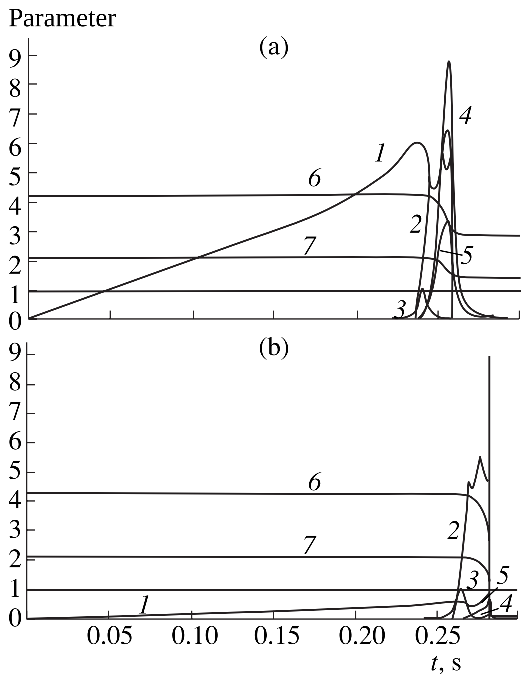

Fig. 6. Calculated changes in the process parameters using the complete scheme for (a) subcritical and (b) supercritical pressures: (*1*) $\ln\lambda_1$; (*2*) $\ln\lambda_2$; (*3*) the criterion of chain branching; (*4*) $(\Delta T) \times 10^{-2}$, K; (*5*) $[H] \times 10^7$, mol/cm^3; (*6*) $[H_2] \times 10^6$, mol/cm^3; and (*7*) $[O_2] \times 10^6$, mol/cm^3. P = 28.9 torr, T = 728 K, α = 0.008 cal K^{-1} s^{-1}.

reaction (the conversion is lower than 50%), whereas in the CTE regime, the conversion is complete.

CONCLUSION

The results of calculations carried out in this work point to the fact that the main role in the appearance of CTE belongs to heat formation in radical recombination reactions and branching processes. These interactions do not take place at the beginning of the process when the concentrations of radicals are small; they occur when reactants are consumed and radicals are accumulated and strengthen in the course of the process.

We would like to note that we restricted ourselves to considering only the nondistributed system in our calculations. Under real conditions, the distribution of temperature over the reactor is not uniform: in the center of the reactor, the temperature is much higher. Possibly, this is due to the fact that we had to raise the values of the rate constants of radical recombination (that contribute most to heat formation) too high. That is why the formulas of linear approximation without reactant consumption do not reflect the effect of CTE. Under the conditions of CTE, one of the two positive Jacobian matrix eigenvalues of the kinetic scheme increases sharply (by an order of magnitude), and this increase reflects an avalanche-like nature of self-heating.

Note also that the CTE regime is one of the indicators of the determinative role of the chain avalanche in combustion processes both during the induction period and in the course of developed combustion. In a number of studies, many reactions between the components of a reacting system are included in the kinetic scheme for modeling. These include unimportant steps. Usually, researchers seek agreement between one or another observed phenomenon and calculations. Usually, this is an ignition delay.

It is remarkable that, even after papers [1–5], the experimentally observed CTE regime has not been found by calculations. Moreover, if the pressure is noticeably higher than the second ignition limit, then some researchers assert that the ignition and combustion are of thermal rather than chain nature. The authors of such claims in their further publications restrict themselves to considering a one-step reaction and find that the calculation and experiment agree with each other, although they compare only a single value. Obviously, claiming that there is agreement between an experiment and calculation that neglects the chain mechanism is like denying the role of a chain mechanism in combustion.

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