

**INFLUENCE OF SMALL CHEMICAL ADDITIVES ON THE VELOCITY OF DETONATION WAVE AND THE DETONATION LIMIT IN RICH HYDROGEN MIXTURES****N.M.Rubtsov**

Moscow region, Chernogolovka, Institute for Structural Macrokinetics and Materials Science of Russian Academy of Sciences

**Keywords:** detonation, limit, "chemical" losses, chain mechanism, inhibitor, rich, hydrogen**ABSTRACT**

On the basis of Zel'dovich–von Neumann–Doering detonation theory with allowance for the theory of chain processes by the example of the oxidation of hydrogen-rich mixtures in the presence of an inhibitor, it is shown that taking into account inhibition reactions leads to the occurrence of "chemical" losses in addition to heat losses. "Chemical" losses alone can provide the occurrence of concentration limit of detonation; the velocity of the combustion wave near the limit is supersonic. Theoretical estimates agree qualitatively with the experimental data on the inhibition of a developing detonation wave in H<sub>2</sub>–air mixtures with additives of propane–butane mixture (0.5–4%) at 1 atm.

**I. INTRODUCTION**

The suppression of gas detonation occurring in explosions of combustible mixtures is a significant challenge in industrial plant operation. Physical methods for suppressing detonation (grids, nozzles, etc.) are generally ineffective [1]. However, the overwhelming majority of works aimed at calculating the characteristics of the detonation wave and the detonation limits are devoted to physical aspects of detonation wave propagation (e.g., [2, 3]), whereas the chemical reaction kinetics is described by the simple Arrhenius law. It is incorrect for a branched-chain process (BCP) in the presence of small amount of chemically active additive [4].

Indeed in [5] the sharp dependence of detonation limits of 2H<sub>2</sub> + O<sub>2</sub> mixture on the small amount of chemically active additive (up to 3%) was revealed for the first time. It was shown that isopropene iso-C<sub>3</sub>H<sub>6</sub> and isobutene iso-C<sub>4</sub>H<sub>8</sub> were the most effective inhibiting additives. It is evident that the description of the inhibiting effect requires either the formal selection of acceptable value of activation energy in Arrhenius law or the consideration of chemical inhibition mechanism. It points to necessity of taking into account of detailed combustion kinetics in the presence of active additives near detonation limits. Unfortunately, the consideration of detailed kinetic mechanism introduces additional uncertainty into calculations. The vast majority of kinetic parameters is not accurate enough to draw reliable conclusions based on numerical modeling. The question of completeness of the kinetic mechanism used is always open, i.e. whether any important reaction is overlooked. However, practical importance of prevention of detonation with chemical methods demands the development of the simplified models, which will allow making adequate recommendations on the problems of explosion safety.

It is known that chlorofluorocarbons (halons) are also applied as inhibitors of hydrogen combustion. Borisov et al. [6] showed that addition of ~30% C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> decreases the detonation ability of a stoichiometric hydrogen–air mixture but it was noted that the additive content was too high to judge whether or not the nature of inhibition is purely chemical.

Agafonov and Frolov [7] analyzed the detonation limits on the basis of one-dimensional Zel'dovich-von Neumann-Doering theory by the example of hydrogen-containing mixtures using a detailed kinetic scheme of hydrogen oxidation. However, the numerical calculation with consideration for a large number of elementary reactions did not reveal any decisive role of chemical factors. For example it was pointed to an important role of the termolecular termination reaction between H, O<sub>2</sub>, and M, but for M = Ar, He, and N<sub>2</sub>, equal rate constants were taken, which is contrary to the fact [8]. Hence, it was concluded [7] that the main contribution to narrowing the detonation range at dilution of combustible mixtures with nitrogen is determined by the ratio of specific heats for diluents, so chemical features of reaction mechanism controlling the detonation wave propagation were not considered.

The aim of this work is to reveal the governing factors responsible for the occurrence of a detonation limit in the presence of inhibitor based on both the theory of chain processes and Zel'dovich–von Neumann–Doering detonation theory by the example of the oxidation of hydrogen-rich mixtures.

**II. RESULTS AND DISCUSSION**

Since one-dimensional pattern becomes unstable and transforms to spin detonation near the limit, one-dimensional theory of

the detonation limit is generally of theoretical interest as an internally consistent method for calculating detonation ability [9]. Because the experiment [5] showed a clear concentration limit of detonation on inhibitor content, it is first necessary to consider the detonation wave propagation with losses. In this work, one-dimensional detonation wave propagation with losses is studied and reaction kinetics is described by the model scheme of hydrogen oxidation according to Semenov [10]. Notice that, by the Reynolds analogy, such a consideration is qualitative one [9]. Here, the study follows the logic of considering this subject by Zel'dovich and Kompaneets [9] and retains their notation [9]. The gas-dynamic equations with allowance for heat losses have the form

$$D/v_0 = \frac{D-w}{v}; p - p_0 = -\frac{D^2(v-v_0)}{v_0^2}; H' - H_0 + \frac{(p-p_0)(v_0+v)}{2} = -\int L dx \quad (1)$$

$v$  is volume of mass unit,  $D - w$  is the detonation wave velocity in a coordinate system fixed with the leading front of the detonation wave ( $D$  is the detonation velocity,  $w$  is the velocity of reaction products),  $p$  is pressure,  $H'$  is the enthalpy behind the detonation wave front,  $L$  is the function describing the heat losses,  $x$  is the coordinate, and the subscript '0' refers to the initial state. In the case, the quantities  $p$  and  $v$  are linearly related and this significantly simplifies the analysis.

Separating out the chemical part of the enthalpy  $H' = k/(k-1)v + \beta Q$ , where  $\beta$  is the fraction of unreacted oxidizer molecules, assuming  $k = C_p/C_v$  to be the same behind and ahead of the front, and ignoring the temperature dependence of the specific heat and the initial pressure  $p_0$  one can obtain the following expression ([9], Eq. (14.19)):

$$R \left( \frac{dT'(x)}{dx} \right) = \frac{Q(k-1)(v_0-2v(x))(\psi-L/Q)}{k(v_1-v(x))} \quad (2)$$

where  $v_1 = k/(k+1)/v_0$ ,  $T'(x)$  is temperature,  $R$  is the gas constant,  $\psi = d\beta/dx$  is the rate of chemical reaction taken with the opposite sign (in the classical consideration [9],  $\psi$  is described by the Arrhenius equation  $\psi = Ae^{-E/RT}$ ). Let the origin of coordinates be directly behind the shock wave front, and let the initial values at this point be  $v = (k-1)/(k+1)v_0$  and  $\beta=1$ . Let us study the behavior of  $T'(x)$  near the front, taking  $v = (k-1)/(k+1)v_0$ .

Let us calculate the rate  $\psi$  of the chemical reaction, which is a BCP and, therefore, as noted above, cannot be described by the simple Arrhenius law. On the basis of the simplest hydrogen oxidation mechanism [10], taking into consideration the termolecular chain termination as well as termination *via* inhibitor, and neglecting the chain initiation rate, one can obtain:

$$\begin{aligned} \frac{dn(t)}{dt} &= n(t)(2k_2 [O_2(t)][O_{20}] - k_6 [O_2(t)][O_{20}] M - k_1 [In]) \\ \frac{dO_2(t)}{dt} &= -k_2 n(t)[O_2(t)] \cdot [O_{20}] - k_6 [O_2(t)][O_{20}] M \end{aligned}$$

where  $n(t)$ ,  $O_2(t)$  are the ratios of the concentrations of hydrogen atoms and  $O_2$  molecules, respectively, to the initial concentration  $[O_2]_0$  of molecular oxygen;  $[In]$  is the inhibitor concentration; and  $k_1$ ,  $k_2$ , and  $k_6$  are the rate constants of the elementary reactions of hydrogen atoms with the inhibitor, molecular oxygen and the termolecular chain termination reaction, respectively.  $M$  is total pressure. The inhibitor consumption is neglected. Let us divide the first equation by the second to eliminate  $t$  and denote (by definition)  $[O_2] = \beta$ . Further, the behavior of all the parameters is considered only near the shock wave front where the extent to which the reaction proceeds is considerably small. Therefore, the result should be integrated with allowance for  $n(\beta) = 1) = 0$  at constant temperature within a narrow zone near the front:

$$n(\beta) = (1 - \beta)(2k_2 - k_6 M)/(k_2 + k_6 M) + k_1 [In] \ln(\beta)/((k_2 + k_6 M) [O_{20}]) \quad (3)$$

This approach is comparatively rough, since it ignores the quadratic termination of reaction chains [11]. However, as is shown below, this approximation allows qualitative considering of the branched-chain nature of the combustion reaction and determining the possibility of detonation wave suppression by the chemically active additive.

Let us write  $O_2$  consumption rate as  $-k_2\beta[O_{20}] n(\beta)$  and use Eq (3); by dividing both parts of the equation by  $c$ , where  $c = D - w$  is the speed of sound in reaction products [9] and evaluating  $k_0$  in  $k_2 = k_0 e^{-E/RT}$  we pass to dimensionless coordinate. We ignore temperature dependence of the rate constant of inhibition reaction, because activation energies of H atoms interaction with halons or hydrocarbons are  $\ll E$ , see below. Assuming  $\ln(\beta) \approx -\beta^{-1/3}$  and redefining  $[O_{20}] = P$  we get



## International Journal OF Engineering Sciences & Management Research

$$W = - \frac{\beta(2(1-\beta)Pk_0 e^{-\frac{E}{RT}} - k_1[In]/\beta^{1/3} - k_6MP(1-\beta))}{c(1 + k_6M / k_0 e^{-\frac{E}{RT}})} \tag{4}$$

It is easy to estimate that at  $T > 1500K$   $k_6M / k_0 e^{-\frac{E}{RT}} \ll 1$  using e.g.  $k_2$  и  $k_6$  from [10]. In addition at higher temperatures radicals  $HO_2$  arising in reaction of termolecular chain termination enter into reaction  $H + HO_2 \rightarrow 2 OH$  [10] leading to chain propagation.

Let us substitute Eq.(4) into Eq.(2) and use the expansion  $1/(1+x) \approx 1-x$  for small  $x$  in the denominator. We put also  $k_6M / k_0 = \gamma$ ,  $\Omega = -\beta(2(1-\beta)Pk_0 e^{-\frac{E}{RT}} - k_1[In]/\beta^{1/3} - k_6MP(1-\beta))$  then

$$R \frac{dT'(x)}{dx} = \frac{Q(k-1)(v_0 - 2(k-1)v_0/(k+1))\Omega / c(1 - \gamma/e^{-\frac{E}{RT}}) - Lc/(k_0P)/Q}{(kv_0/(k+1) - (k-1)v_0/(k+1))} \tag{5}$$

The behavior of the function  $W$  is also considered near the shock wave front. The multiplier  $e^{-\frac{E}{RT'(x)}}$  changes most rapidly. It varies by an order of magnitude when  $T'(x)$  increases by a small fraction in comparison with the temperature  $T_0$  determined for the wave front itself. Consequently, the change in the exponential function can be represented by expanding the exponent in a series, by making the following change of variables:

$$E/(RT'(x)) = E/(RT_0) - E((T'(x) - T_0)/(RT_0^2)) \tag{6}$$

Let us make this change of variables in Eq.(5) taking  $T'(x) - T_0 = T(x)$ ,  $\delta = \beta(1-\beta)$ ,  $\alpha = k^{-1}(k-1)(3-k)$  and  $f_0 = e^{-E/RT_0}$ :

$$R \frac{dT'(x)}{dx} = \alpha(Pk_0/c) \left( 2f_0 Q \delta e^{\frac{ET(x)}{RT_0^2}} - \beta^{2/3} Q k_1 [In]/(k_0P) - k_6 \delta Q M / k_0 (1 - \frac{\gamma}{e^{-\frac{E}{RT}}} ) - Lc/(k_0P) \right) \tag{7}$$

The equation is integrated by making the change of variable  $T(x) = \ln(t(x))R/ET_0^2$ .

As is seen from Eq.(7) the only difference from the classical consideration [9] is the appearance in (3.7) a new term:  $-\beta^{2/3} Q k_1 [In]/(k_0P) - k_6 \delta Q M / k_0 (1 - \gamma/e^{-\frac{E}{RT}})$  which is responsible for "chemical" losses along with heat losses  $L$ . This implies that if in the classical consideration the temperature change near the front is proportional to the difference  $Ae^{-E/RT} - L/Q$ , then with allowance for the branched-chain nature of combustion, the temperature change is proportional to  $-Lc/(k_0P)/Q$ ; ( $\phi$  is the branching factor, which is the difference of the chain branching rate and the chain termination rate).

To understand the term "chemical" losses, the termination of H atoms *via* In molecules must be considered in more detail. The termination is made possible by the low activation energy of the reaction, which amounts to e.g.  $< 1$  kcal/mole for iso-C<sub>4</sub>H<sub>8</sub> [12]. It is evident that the act of termination of H atoms *via* a molecule of inhibitor cannot give rise to a reaction chain as well as to energy release corresponding to the thermal effect  $Q$ . This means that the termination of H atom *via* inhibitor approximately corresponds to energy loss, which would release if the branching step occurred. Therefore, the process qualitatively comprises the heat losses.

Let us define the sum of the heat and "chemical" losses by  $H = \beta^{2/3} Q k_1 \frac{[In]}{k_0P} + \frac{k_6 \delta M Q}{k_0} + \frac{Lc}{k_0P}$ , denote  $\eta = 2f_0 Q \beta$  and integrate with allowance for  $t(0) = 1$ :

$$t(x) = - \frac{(-H - 2\eta\gamma + (2\eta\gamma - H))}{4\eta} \tanh\left(\frac{x\alpha E(-2\eta\gamma + H)}{2T_0^2 R^2}\right) + \left(\frac{1}{2}\right) \ln \frac{2\eta(1-\gamma)}{H-2\eta}$$

After simplification, with allowance for  $t(0) \ll 1$ , the solution is obtained in the form:

$$e^{(ET(x)/RT_0^2)} = \frac{H}{4f_0 Q \delta (2f_0 Q \delta / H - (2f_0 Q \delta / H - 1) e^\xi)} \quad \text{where} \tag{8}$$

$$\xi = EHk_0P(k^2 - 4k + 3)x/(cT_0^2 R^2 k)$$

According to [9], for detonation to occur, at least the following inequality should be satisfied (the loss rate should be lower than the heat generation rate):

$$H/(2Q\delta f_0) < 1 \text{ or } \beta^{2/3} Q k_1 [In]/(k_0P) + k_6 \delta Q M / k_0 + Lc/(k_0P) < 2Q\delta f_0^{-1} < 1 \tag{9}$$



## International Journal OF Engineering Sciences & Management Research

Note that taking into account the branched-chain character of combustion (ignoring the quadratic chain termination) at  $Lc/(k_0P) \ll \beta^{2/3} Q k_1 [In]/(k_0P) + k_6 \delta Q M/k_0$  enables to obtain, from Eq. (9), the chain auto-ignition condition [10] :

$$2\delta k_0 e^{-E/RT_0} P > \beta^{2/3} Q k_1 [In] + k_6 \delta M P$$

The set of Eqs. (1) is easy to transform into the relation [9]:

$$h(v1, D) = Q(1 - \beta_{00}) - \int_0^{x1} H(x) dx \tag{10}$$

where  $h(v1, D) = D^2/2(k^2 - 1)$  is a function that describes detonation without losses [9],  $H(x)$  is the sum of the "chemical" and heat losses, where, at the point  $x1$   $v(x) = v1$  (the heat release is equal to the heat removal);  $\beta_{00}$  is the fraction of unreacted  $O_2$  at the point of tangency of the Hugoniot's adiabat curve and the Michelson's straight line. At this point, the fact that the numerator and denominator of the fraction on the right-hand side of Eq. (2) are simultaneously equal to zero makes a detonation mode possible. Thus, at the temperature  $T_{00}$ , corresponding to the tangent point,

$$\psi = L/Q \text{ or } \beta(1 - \beta)(2e^{-\frac{E}{RT_{00}}} - \beta^{2/3} k_1 [In]/(k_0 P(1 - \beta)) - k_6 M/k_0) = Lc/(k_0 P)/Q \tag{11}$$

Suppose that, at this point, the inhibitor has already been consumed; then

$$Lc/(2Qf_0 k_0 P) = \beta_{00}(1 - \beta_{00}) \tag{12}$$

From Eq.(9), it follows that  $1/2 L/(Qf_0) < 1$ . Let us write the identity:  $1/2 L/(Qf_0) = 1/2 L/(Qf_0) f_0/f_{00}$ :

$$\frac{L}{2Qf_0} = \frac{L e^{-\frac{E}{RT_0}}}{2Qf_0 e^{-\frac{E}{RT_{00}}}} \tag{13}$$

Hence, with allowance for Eq. (11) and the relation  $f_0/f_{00} \ll 1$  derived earlier [9] , one can obtain:

$1/2 L/(Qf_{00}) \ll 1$  and, finally,  $\beta_{00} \ll 1$  This means that, in Eq. (12)  $\beta_{00}$  can be ignored.

Let us estimate  $\int H(x) dx$ . From Eq. (8) it is evident that:

$$2f_0 \delta Q/H - (2f_0 \delta Q/H - 1)e^\alpha < 1 \text{ then } (1 - H/(2f_0 \delta Q))e^\alpha \text{ and } \alpha < -\ln(1 - H/(2f_0 \delta Q))$$

If the value of  $H/(2Q\delta f_0)$  is not too close to 1, one can use the first term of the expansion into a series::

$$\alpha < H/(2Q\delta f_0) \tag{14}$$

Then, using the expression for  $\alpha$  from Eq. (8), expressing  $x$  from it, replacing  $\alpha$  by its estimated upper limit from Eq. (14) and substituting  $f_0 = e^{(-E/RT_0)}$ , one can obtain:

$$x = \frac{T_0^2 R^2 k c e^{\frac{E}{RT_0}}}{2\delta k_0 P Q E (k-1)(3-k)} \tag{15}$$

Let us put  $\int H(x) dx \approx H x$ , and take the value of  $x$  from Eq. (15). Next, let us substitute this estimated value of  $\int H(x) dx$  into Eq. (10) and take into account that that  $\beta_{00} \ll 1$ ,  $3 - k \sim 2$ ,  $k/(k+1) = Cp/R$ ,  $\delta \sim \delta_{max} \sim \beta^{2/3} \sim 1/4$ . Transformed Eq. (10) appears as follows:

$$\frac{D^2}{2(k^2-1)} = Q - \frac{2 Cp c R T_0^2 (Q k_1 [In]/(4 k_0 P) + k_6 M Q/4 k_0 + Lc/(k_0 P)) e^{E/RT_0}}{Q.E k_0 P} \tag{16}$$

An important consequence of Eq. (16) is that, at  $k_6 = 0$  or  $[In] = 0$  Eq.(16) appears as the classical equation of detonation with heat losses ([9], Eq. (14.24)). In this case, the slightly temperature dependent reactions of termolecular chain termination and chain termination *via* inhibitor cause "chemical" losses. It is of interest to reveal whether or not only "chemical" losses can provide a detonation limit, i.e., whether or not the occurrence of only heat losses (and, accordingly, friction losses) is a necessary condition for the existence of the limit. Let us take into account in Eq. (16) that, in the shock wave front, if the initial temperature is neglected  $T_0 = D^2(1 - (k - 1)^2/(k + 1)^2)/C_p$  [9] then  $h(v1, D_0) = \frac{D_0^2}{2(k^2-1)}$ .

Next, making the change of variable  $\mu = 2EC_p/(R(1 - (k - 1)^2/(k + 1)^2))$ ,  $g_1 = 4(k^2 - 1)C_p cRT_0^2/(EQk_0P)$  one can obtain:

$$D^2 - D_0^2 = -g_1(Qk_1[In]/(4k_0P) + k_6M/4(k_0P) + Lc/(k_0P))e^{\mu/D^2} \quad (17)$$

Further expansion of the exponent in a series yields:

$$\exp\left(\frac{\mu}{D^2}\right) = \exp\left(\frac{\mu}{D_0^2}\right) \exp\left(-\frac{(D^2 - D_0^2)\mu}{D_0^4}\right) \text{ then:}$$

$$\frac{(D^2 - D_0^2)\mu}{D_0^4} = -\frac{g_1(Qk_1[In]/(4k_0P) + k_6M/4k_0 + Lc/(k_0P))\mu e^{\mu/D^2} e^{-(D^2 - D_0^2)\mu/D_0^4}}{D_0^4} \quad (18)$$

Let us denote

$$s = -\frac{(D^2 - D_0^2)\mu}{D_0^4}, \quad g_2 = g_1(Qk_1[In]/(k_0P) + k_6M/4k_0 + Lc/(k_0P))\mu \exp(\mu/D_0^2)/D_0^4$$

and transform Eq. (18) as follows:

$$s = g_2 e^s \quad (19)$$

It is easy to see that, at  $g_2=0$ ,  $D = D_0$  ( $D_0$  - is the detonation velocity without losses). Differentiation of Eq. (19) with respect to  $g_2$  gives:

$$ds/dg_2 = e^s/(1 - s) \quad (20)$$

It is seen that  $s < 1$ , since, at  $s=1$   $\frac{ds}{dg_2} = \infty$ . It is also seen that the steady-state detonation mode is possible not at all  $g_2$  values: starting from a certain value of losses, detonation is impossible. At the maximal value  $s=1$  (see [9])

$$D^2 = D_0^2 - D_0^4/\mu, \quad D^2 \sim D_0^2(1 - RT/E), \quad D \sim D_0(1 - RT/2E) \quad (21)$$

Let us now take  $M = 0$ . All the above is also valid for this case, i.e., at a certain  $g_2$  value detonation is impossible. Thus, it is shown that the occurrence of only "chemical" losses can provide a detonation limit.

Let us illustrate this. Let, in Eq. (18)  $L = 0$ ,  $[In]/P = X_0$ . Then, substitution of  $g_1$  value yields:



## International Journal Of Engineering Sciences & Management Research

$$(D^2 - D_0^2) = \frac{\frac{1}{2}(k^2 - 1)cC_pRT_0^2 (Qk_1 X_0/4k_0 + k_6 M/4k_0)^2 \mu e^{\mu/D_0^2} e^{-(D^2 - D_0^2)\mu/D_0^4}}{(EQk_0 P)(\frac{1}{2} \exp(-\mu/D_0^2) e^{\mu/D_0^2} e^{-(D^2 - D_0^2)\mu/D_0^4}) \gamma Q \delta - Qk_1 X_0/4k_0 - k_6 M/4k_0} \quad (22)$$

Let us use the definition of  $\beta$  (see Eq.(17)). The following values for the mixture of 45%H<sub>2</sub> and air are used: D<sub>0</sub>=2110 m/s [13],  $\gamma = 0.01$ ,  $c = 10^5$  cm/s [14],  $C_p = 4R/m$  ( $m$  – is the average molecular weight of the gas mixture).  $R = 8.3 \cdot 10^7$  erg/mole.grad,  $E = 22400 \cdot 10^7$  erg/mole [10],  $k = 3/2$ ,  $k_1 = 5.7 \cdot 10^{-11}$  cm<sup>3</sup>/molec.s (for propene [15]),  $k_0 = 4 \cdot 10^{-11}$  cm<sup>3</sup>/molec.s [16],  $k_6 = 6.47 \cdot 10^{15} \cdot (T/298)^{-0.8}$  cm<sup>3</sup>/mole<sup>2</sup>.s [16]. The T<sub>0</sub> value on the front of the inhibited detonation wave is taken to be 1500K. The transcendental equation for D obtained after substitution of numerical values of parameters into (22) was solved.

Figure 1b shows the positive branches of the solution for three values of the parameter  $\beta$ , experimental values [17] are presented in Fig. 1a. Therefore, there is a qualitative agreement between the theory and the experiment, which allows one describing the existence both of modes with  $D < D_0$  and the occurrence of detonation limit. In addition, in agreement with the experiment, the combustion front velocity near the limit is supersonic.

Thus, it is shown that, for the existence of the detonation limit, "chemical" losses, which are caused by the competition between the reactions of branching and termination of active centers in BCP mechanism, are of marked importance. Notice that in [18] the same problem was solved by numerical modeling. The results and conclusions of [18] are in complete agreement with those in the present work. The experimental dependence of the upper concentration limit of detonation on the inhibitor content [17] is shown in Fig.2a. We attempted to interpret the results of [17] using the developed approach based on detonation theory [9] and chain processes theory [10]. For this purpose, the detonation limit (similarly to Fig. 1) was calculated by Eq. (8) for various H<sub>2</sub> - air ratios in rich mixtures with allowance for a change in the average molecular weight  $m$  of the combustible mixture. The change in D<sub>0</sub> was taken into consideration using the literature data (Fig.1a [13]) for the dependence of D<sub>0</sub> on the fraction  $\theta$  ( $\theta$  - equivalence ratio:  $\theta H_2 + 0.5(O_2 + 3.76N_2)$ ) of the combustible mixture. The results for three values of the parameter  $\beta$  are presented in Fig. 2b. The comparison of Figs 2a and 2b shows that the calculated curve is qualitatively the same as the experimental one. Notice that, in view of the qualitative character of the developed approach, any quantitative comparison of these calculated and experimental data cannot be quite correct. However, the calculations performed in [18] taking into account more detailed mechanism of the reaction lead to the same qualitative conclusions. The above consideration can be qualitatively extended to the promotion of detonation *via* small amounts of chemically active additive that increases the number of branching acts per time unit. As Eq. (17) shows, "chemical" losses are described by the expression  $(Qk_1[In]/(4k_0P) + k_6M/4k_0P)$ , containing the branching rate in the denominator. It is obvious that the increase in the branching rate because of, e.g., reactions involving the active additive, can lead, within a certain range of compositions of combustible mixtures, to decrease in "chemical" losses and, accordingly, to increase in the detonation wave velocity, i.e., promotion of detonation. This reasoning is only illustrative. Note in conclusion that calculation of the detonation velocities based on consideration of the full kinetic mechanism of hydrogen oxidation with allowance for the competition between the reactions of chain branching and chain termination in the presence of hydrocarbon additives can provide additional information on the mechanism of chain branching in branched-chain reactions of hydrocarbon oxidation.

### III. CONCLUSIONS

We summarize briefly the results obtained. On the basis of Zel'dovich–von Neumann–Doering detonation theory with allowance for the theory of chain processes by the example of the oxidation of hydrogen-rich mixtures in the presence of chemically active additive (inhibitor), it is shown that taking into account reactions of inhibitor with chain carrier leads to "chemical" losses in addition to heat losses. "Chemical" losses alone can provide the occurrence of concentration limit of detonation; the velocity of the combustion wave near the limit is supersonic. Theoretical estimates agree qualitatively with the experimental data and numerical calculations on the inhibition of a developing detonation wave in H<sub>2</sub> –air mixtures with additives of propane–butane mixture (0.5–4%) at a pressure of 1 atm.

### IV. REFERENCES

1. M. A. Nettleton, *Gaseous detonations—their nature, effects and control*, Chapman and Hall, London, 1987.
2. Lefebvre M.H.,Oran E.S, Kailasanath K.,Van Tiggelen P.J., The Influence of heat capacity and diluent on detonation structure, *Combustion Flame*, 1993, V.95, P.206.
3. D A Kessler, V N Gamezo, E S Oran, Gas-phase detonation propagation in mixture composition gradients , *Philosophical Transactions of The Royal Society A Mathematical Physical and Engineering Sciences* , 2012; V.370, P. 567.
4. Ya.B.Zel'dovich, *Selected works, Chemical physics and hydrodynamics*, Moscow, Nauka, 1984, (in Russian).

5. A. Macek. Effect of additives on formation of spherical detonation waves in hydrogen-oxygen-mixtures, 1963, AIAA J., V.1, P.1915.
6. A.A.Borisov, V.V.Kosenkov, A.E.Mailkov, V.N.Mikhalkin and S.V.Khomik, Effect of flame inhibitors on detonation characteristics of fuel-air mixtures, Proc. of AIAA, 1993, p.312-323.
7. Agafonov, G.L. and Frolov, S.M., Calculation of the Detonation Limits of Hydrogen-Containing Gas Mixtures, Fiz. Goreniya Vzryva, 1994, N. 1, P. 92 (in Russian).
8. D.L. Baulch, C.T. Bowman, C.J. Cobos, R.A. Cox, Th. Just, J.A. Kerr, M.J. Pilling, D. Stocker, J. Troe, W. Tsang, R.W. Walker, J. Warnatz. Evaluated Kinetic Data for Combustion Modelling: Supplement II, J. Phys. Chem. Ref. Data, 2005, V.34, P. 566.
9. Ya.B.Zel'dovich, A.S.Kompaneets, *Detonation Theory*, Moscow, Gostechizdat, 1955, (in Russian).
10. Semenov, N.N., *On Some Problems of Chemical Kinetics and Reactivity*, Moscow: Akad. Nauk SSSR, 1958 (in Russian).
11. Baulch,D.L.; Cobos,C.J.; Cox,R.A.; Esser,C.; Frank,P.; Just,Th.; Kerr,J.A.; Pilling,M.J.; Troe,J.; Walker,R.W.; Warnatz,J. Evaluated kinetic data for combustion modeling// J. Phys. Chem. Ref. Data, 1992, V.21, P.411-460.
12. G.W.Harris and J.N.Pitts, Rate constants of reactions of atoms with unsaturated hydrocarbons, J.Chem.Phys., 1982, V.77, P.3994.
13. E. Schultz, J. Shepherd, *Validation of Detailed Reaction Mechanisms for Detonation Simulation*, Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, CA 91125, Explosion Dynamics Laboratory Report FM99-5, February 8, 2000, 70 p.
14. *Tables of Physical Values*, ed. I. K. Kikoin, Moscow, Atomizdat, 1976, 1007 P. (in Russian).
15. T. Watanabe, T. Kyogoki, S. Tsunasima, S. Sato, S. Nagase, Kinetic isotope effects in the  $H + C_2H_6 = C_3H_7$  reaction, Bull. Chem. Soc. Jpn., 1982, V. 55, P.3720.
16. Baulch,D.L.; Cobos, C.J.; Cox, R.A.; Evaluated Kinetic data for combustion modeling, Supplement 1, J.Phys.Chem.Ref.Data,
17. Azatyan, V.V., Baklanov, D.I., Gvozdeva, L.G., Lagutov, Yu.P., Merzhanov, A.G., Rubtsov, N.M., Tsvetkov, G.I., Sharov, Yu.L., and Shcherbak, N.B., Inhibition of Developed Detonation of Hydrogen-Air Mixtures, Rus. Dokl. Phys. Chem., V. 376, N. 1-3, P. 19.
18. V.V.Azatyan, S.N.Medvedev, S.M.Frolov, Numerical modeling of chemical inhibition of detonation of hydrogen-air mixtures, Rus.J.Phys.Chem.B, 2010. V.29, №4, P.56.

## V. FIGURES

**Fig. 1. Detonation velocity versus inhibitor concentration: a – Experimental data [17], b - Calculation by Eq. (22) for a mixture of 45% $H_2$  and air: 1 -  $\beta^{2/3} = 1/3$ , 2 -  $\beta^{2/3} = 1/4$ , 3 -  $\beta^{2/3} = 1/5$ .**

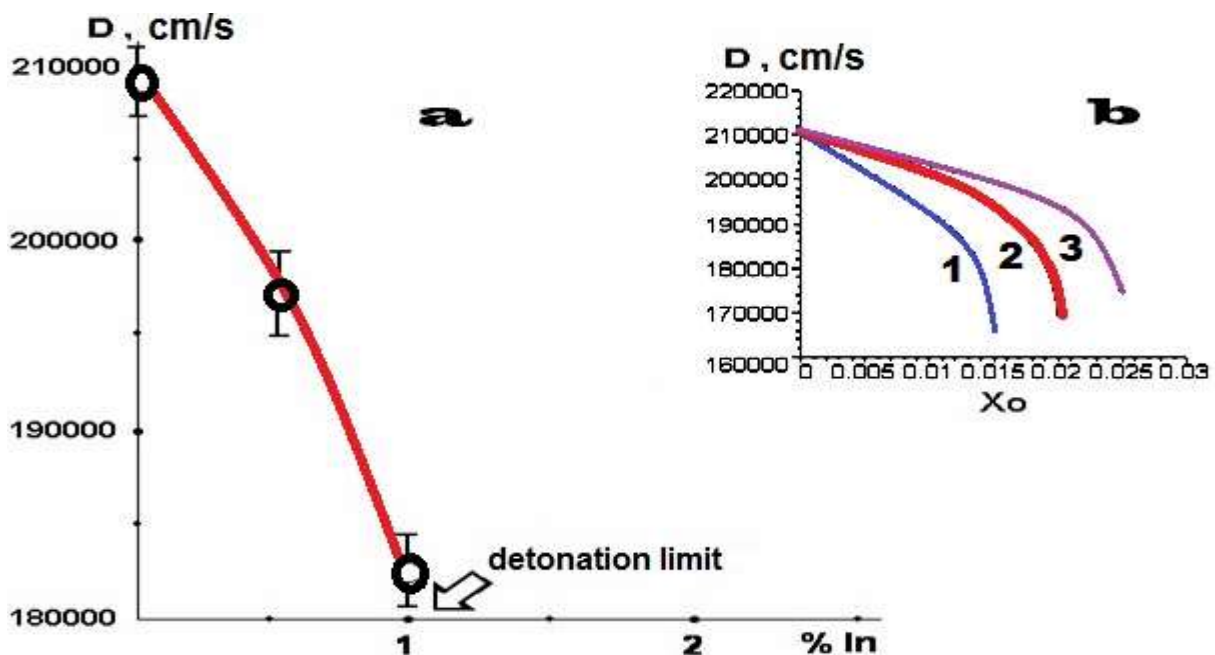


Fig. 2. Upper concentration limit of detonation versus inhibitor content. (a) Experimental data [17] in the cases where points designate detonation mode, circles designate the absence of detonation. b) – The results of qualitative calculations by Eq. (22) for a mixture of 45% $H_2$  and air;  $\beta^{2/3} = 1/4$  on the left of each line detonation occurs; on the right there is no detonation.

