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Flame propagation limits in H_2 + air mixtures in the presence of small inhibitor additives

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An approximate analytical approach to the estimation of the influence of inhibitor additives on flame velocity and flame propagation limits based on the method of a narrow reaction zone is exemplified by the branched chain combustion of rich H_2 + air mixtures.

The use of hydrogen as fuel holds promise for a decrease of air pollution. The modern means of providing safe conditions of production, transport and storage of H_2 is to use small chemically active additives (inhibitors).[1,2] In this connection, the revealing of main parameters responsible for the critical conditions of combustion and flame propagation (FP) in the presence of additives is of current interest. The majority of experimental data on the combustion and FP in H_2 + air mixtures in the presence of additives was analysed using numerical calculations including hundreds of elementary steps. However, the calculations do not contain any information on both physical meaning and uniqueness of a solution. In addition, the analysis of hundreds of reactions does not provide reliability of its results because the majority of rate constants and activation energies are not accurate enough to make plausible conclusions on the basis of calculations with such errors. For instance, in the kinetic modeling performed previously,[3] the mechanism of inhibition of combustion of rich H_2–air mixtures *via* propylene is represented as follows:

$$RH + H \rightarrow R + H_2, \quad R + H \rightarrow R^1H + H_2, \quad R^1H + H \rightarrow R^1 + H_2.$$

Here, the H atom addition to a double bond responsible for the specific action of propylene[4] (see below) is not taken into account. It means that the results[3] cannot be related to propylene. Therefore, the invalid consideration of the mechanism of inhibition reduces in value the calculations performed.[3]

This raises the question of whether both understanding the regularities of combustion and revealing the main parameters responsible for critical conditions of combustion and FP could be achieved without the use of numerical calculations. Actually, an analytical theory of thermal FP is adequately worked out;[5–8] the qualitative basis of the description of FP in branching-chain process (BCP) was given.[8] The analysis of FP can be performed analytically if the mechanism of BCP is known as with the model reaction $H_2 + O_2$. In the linear mechanism of H_2 oxidation, the only feedback factor responsible for the occurrence of stationary propagating flame is warming-up; therefore, the mathematical tools of thermal theory apply.

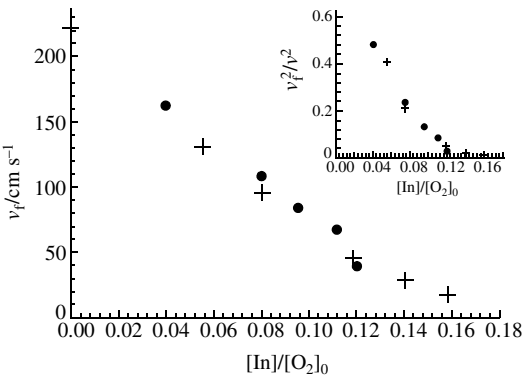

Figure 1 Dependence of normal flame velocity on the content of an inhibitor, $[O_{20}]$ – initial concentration of oxygen, $P_0 = 1$ atm, $T_0 = 298$ K, 40% H_2–air mixtures. Circles – additives of *iso*-C_4H_8, crosses – additives of C_3H_6.

The aim of the work is the establishment of the feasibility of the model of the narrow reaction zone (NRZ), proposed by Ya. B. Zel'dovich, for the description of the flame propagation limit (FPL) in the presence of chemically active additive by the example of combustion of 40% H_2–air mixtures in the presence of small (0–1.6%) isobutylene and propylene additives.†

Using initial parts of the curves of the pressure increase a value of normal velocity can be calculated by the equation[6]

$$r(t)/r_0 = \left[1 - \frac{P_b - P(t)}{P_b - P_0}\left(\frac{P(t)}{P_0}\right)^{-1/\gamma}\right]^{1/3},$$

where $r(t)$ is the radius of the sphere filled with products of combustion, r_0 is the radius of the reactor; P_b, P_0 and $P(t)$ are maximal, initial and current pressures, respectively; $\gamma = C_p/C_v = 1.4$.[9] The normal velocity of FP v is determined from the dependence of $r(t)$ on t. Our data on the pressure increase in initiated ignition of mixtures 40% H_2 + air + (0–2%) C_3H_6 are in good agreement with published data.[10] One can also calculate the adiabatic temperature of combustion T_b $[(P_b - P_0)/P_b = (T_b - T_0)/T_b]$ from P_b. The flame does not propagate at 1.6% *iso*-C_4H_8 (this value corresponds to the relation of amount of *iso*-C_4H_8 to O_2 in the mixture of 12.4%), and at 2% C_3H_6 (this value corresponds to the relation of amount of C_3H_6 to O_2 in the mixture of 16%) (Figure 1). As can be seen in Figure 1, v decreases by a factor of more than $e^{1/2}$ as it follows from data,[5–7] namely at the FPL $v_f^2/v^2 = 0.033$ for *iso*-C_4H_8, $v_f^2/v^2 = 0.018$ for C_3H_6; from this

† The experiments were carried out under static conditions at 293 K and atmospheric pressure. A stainless steel cylindrical reactor (10 cm in diameter, 16 cm in length) was equipped with inlets for gas evacuation and optical windows, as well as a pressure transducer. Ignition was provided with a spark (0.45 and 0.91 J) at the centre of the reactor. The reactor was evacuated to 10^{-3} Torr before each experiment. The mixtures of 30% H_2 + air (stoichiometric) were prepared prior to experiments. An additive was initially allowed to bleed into the evacuated reactor up to the necessary pressure. Then, the combustible mixture was admitted up to 1 atm. A signal from the pressure transducer was recorded by a C9-8 digital oscilloscope and stored in computer memory.

point on v_f is the normal flame velocity in the presence of an inhibitor. Note that the values of FPL and v_f at FPL do not depend on spark power.

To estimate the values of v and v_f, a simple mechanism of H_2 oxidation for stoichiometric and rich mixtures including both termolecular chain break and chain break *via* an inhibitor with no regard for the steps of chain origination was taken into account.[11] The specific heat Q of reaction chain

$$OH + H_2 \rightarrow H_2O + H\ (k_1),\ H + O_2 \rightarrow OH + O\ (k_2),\ O + H_2 \rightarrow OH + H\ (k_3)$$

is ≈ 0 kcal mol^{-1},[11] $Q > 0$ is in steps of recombination of active centres;[8] however, in rich mixtures at 1 atm both the step

$$H + O_2 + M \rightarrow HO_2 + M\ (k_6)$$

and steps including HO_2 reactions are of minor importance.[12–14] Thus, the rate of BCP is governed with branching step

$$H + O_2 \rightarrow OH + O\ [k_2 = k_2^0 \exp(-E/RT)].$$

We assume as previously[8] that heat release occurs in the step

$$H + H + M \rightarrow H_2 + M\ (k_4).$$

Let $\lambda = D_H = D_{O_2}$ (λ is thermal conductivity, and D is diffusivity). We obtain the system ($\Delta^2 = d^2/dx^2$, $\Delta = d/dx$):

$$\begin{aligned}
&\lambda\Delta^2 T_a(x) - v\rho C_p \Delta T_a(x) + Qk_4 H(x)^2(M) = 0;\\
&D_H\Delta^2 H(x) - v\rho\Delta H(x) + 2k_2 H(x)O_2(x) - k_5 H(x)In(x) - k_4 H(x)^2(M) = 0;\\
&D_{O_2}\Delta^2 O_2(x) - v\rho\Delta O_2(x) - k_2 H(x)O_2(x) = 0;\\
&D_{In}\Delta^2 In(x) - v\rho\Delta In(x) - k_5 H(x)In(x) = 0,
\end{aligned} \quad \text{(I)}$$

where ρ is density, C_p is heat capacity; $H(x)$, $O_2(x)$ and $In(x)$ are the concentrations of atoms H, O_2 and inhibitor, respectively, k_5 is rate constant of the step H + In → products, M is total pressure. The set (I) applies for rich mixtures; reactions of O atoms and OH radicals must be taken into account for poor mixtures, this markedly complicates the kinetics.[15] As assumed,[4] the action of alkenes can be represented by the following steps leading to reproduction of an inhibitor:

$$H + C_3H_6 \rightarrow C_3H_7;\quad C_3H_7 + O_2 \rightarrow C_3H_7O_2^*;\quad C_3H_7O_2^* \rightarrow C_3H_6 + HO_2.$$

Note that the results of this work and published data[3] could not be compared because the steps were not taken into account[3] (see above) even though this set of reactions was proved experimentally.[16] This gives grounds to neglect consumption of an inhibitor and correspondingly to ignore an inhibitor in the relation of enthalpy conservation.

Moreover, it follows from a simple estimation that the amount of an inhibitor is small enough (< 2%) to ignore its contribution to combustion, participation of an inhibitor in termolecular break and change in thermal properties of a combustible mixture, as well as dilution of the mixture at the expense of an inhibitor. The relation, following from (I) with regard to aforesaid takes the form

$$\begin{aligned}
&T(x) - T_0 + 2Q/C_p[O_2(x) - O_{20}] + Q/C_p H(x) = \text{const};\\
&T_b = T_0 + 2Q/C_p(O_{20})
\end{aligned} \quad (1)$$

T_b and T_0 are combustion and initial temperature, respectively, O_{20} is initial O_2 concentration.

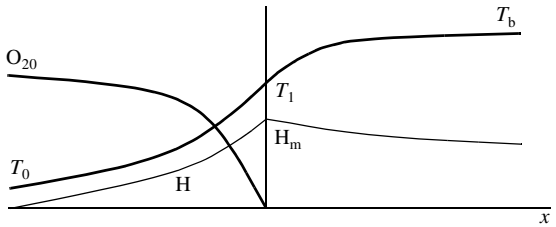

Figure 2 Distributions of temperature and concentrations in the vicinity of narrow reaction zone.

Therefore, the problem reduces to the one discussed previously.[8] Let us specify the distribution of concentration of O_2 consuming completely in a narrow branching zone in a branching step with substantial activation energy E. Therefore, the reaction occurs in a narrow zone. We place the zone at the origin of the coordinates. Let

$$O_2(x) = O_{20}[1 - \exp(ux/D_{O_2})],\quad x < 0,\quad O_2(x) = 0,\quad x > 0. \quad (2)$$

The consumption of O_2 leads to H atom formation. Outside of narrow branching zone H atoms consume only in termolecular recombination. In view of the fact that zones of branching and heat release are separated (Figure 2), the temperature in the branching zone is lower than T_b. We consider the second equation of set (I). Since the branching zone is narrow, the balance of O_2 gives $v\rho O_{20} = \int k_2 H(x)O_2(x)\,dx$.[8] According to published data,[8] in the narrow reaction zone (NRZ), approximation $v\rho O_{20}\delta(x) = k_2 H(x)O_2(x)$, where $\delta(x)$ is Dirac delta function. Let H_m be maximal concentration of $H(x)$ achievable at $x = 0$. We consider recombination in the vicinity of $x = 0$, where $H(x) \approx H_m$, then $k_4 H(x)^2(M) \approx k_4 H(x)H_m(M)$.[8] The equation for $H(x)$ takes the form

$$D_H\Delta^2 H(x) - v\rho\Delta H(x) + v\rho O_{20}\delta(x) - k_5 H(x)In_0 - k_4 H(x)H_m(M) = 0. \quad (3)$$

At $x \neq 0$, $\delta(x) = 0$, we have a homogeneous linear equation; its solution is sought in the form

$$H(x) = H_m \exp(sx). \quad (4)$$

The characteristic equation is $D_H s^2 - v\rho s - k_5 In_0 - k_4 H_m(M) = 0$, its solutions are

$$s_{1,2} = \frac{v\rho \pm \sqrt{(v\rho)^2 + 4D_H k_5 In_0 + 4D_H k_4 H_m(M)}}{2D_H} \quad (5)$$

In equation (5) s_1 is taken at $x < 0$, s_2 at $x > 0$. The first condition of joining solutions of equation (5) at $x = 0$ is the equality of concentrations provided by (4). The second condition implies that the sum of fluxes of H atoms to both directions from $x = 0$ must be equal to the amount of H atoms forming in a branching step.[8] To calculate the sum, we integrate equation (3) near NRS:

$$[D_H\Delta H(x)]_{x<0} - [D_H\Delta H(x)]_{x>0} = v\rho O_{20}. \quad (6)$$

Substituting (5) in equation (6) we obtain:

$$v\rho O_{20} = H_m\sqrt{(v\rho)^2 + 4D_H k_5 In_0 + 4D_H k_4 H_m(M)}. \quad (7)$$

T_1 is found from (1). We specify $T(x = 0) = T_1$ (Figure 2), $n = (T_b - T_0)/O_{20}$ then we have $T_1 = T_b - nH_m$ and values of $dT(x)/dx$ to the left and to the right of $x = 0$ identically equal to each other:

$$[\Delta T(x)]_{x=0} = 2O_{20}v\rho/D_H - nH_m s_1 = -nH_m s_2.$$

We add these values taking into account that $s_1 + s_2 = v\rho/D_H$, $n = T_b - T_0/O_{20}$, $T_1 = T_b - nH_m$:

$$T(x) = T_0 + \exp(v\rho x/2D_H)(T_1 - T_0) \text{ over the interval } -D_H/v\rho < x < 0. \quad (8)$$

We make up a balance equation of O_2 according to distributions of $O_2(x)$ (2) and $T(x)$ (8), and use Frank-Kamenetsky transform,[5–7] then:

$$\begin{aligned}
&v\rho O_{20} = \int k_2 H(x)O_2(x)\,dx = 4D_H H_m k_2^0 \exp(-E/RT_1)\alpha^2/v\rho,\\
&\alpha = RT_1^2/E(T_1 - T_0).
\end{aligned} \quad (9)$$

As a consequence we have three equations (7), (9) and $T_1 = T_b - nH_m$ and three unknowns H_m, T_1 and v. On can obtain from (7), (9):

$$M + Z = -(H_m^2 - O_{20}^2)k_2^0 \exp(-E/RT_1)\alpha^2/k_4 H_m^2 = k_2^0 \exp(-E/RT_1)\alpha^2 \frac{(T_b - T_0)^2 - (T_b - T_1)^2}{(T_b - T_1)^2}. \quad (10)$$

Here $Z = k_5\mathrm{In}_0/k_4\mathrm{H}_m$. Let T_1 be close to T_b: $T_b - T_1 = \theta << T_b - T_0$. This is called[8] the case of strong recombination. It is the case when all O atoms and OH radicals enter into branching, *i.e.* H atoms concentration is high; the role of termolecular break is therefore significant. Then we have:

$$M + Z = k_2^0\exp(-E/RT_b)R^2T_b^4/k_4T_0^2E^2\theta^2,$$

$$\theta = \pm\frac{\sqrt{k_4(M+Z)k_2^0\exp(-E/RT_b)}T_b^2R}{k_4(M+Z)E}.$$

For positive θ, which is only meaningful, we obtain for the velocity of inhibited flame v_f:

$$v_f^2\rho^2 = \frac{4D_Hk_2^0\exp(-E/RT_f)\sqrt{k_4(M+Z)k_2^0\exp(-E/RT_f)}T_f^6R^3}{k_4(M+Z)E^3(T_f-T_0)^3}. \quad (11)$$

In the absence of an inhibitor we have equation coincident with equation (70) from ref. 8:

$$v^2\rho^2 = \frac{4D_Hk_2^0\exp(-E/RT_b)\sqrt{k_4Mk_2^0\exp(-E/RT_b)}T_b^6R^3}{k_4ME^3(T_b-T_0)^3}. \quad (12)$$

To estimate FPL in the presence of an inhibitor let us consider thermal losses in planar stationary combustion wave using NRZ model:

$$\begin{aligned} &x<0 \quad \lambda\Delta^2T_a(x) - v_f\rho C_p\Delta T_a(x) - \delta_a[T_a(x)-T_0] = 0;\\ &x>0 \quad \lambda\Delta^2T_b(x) - v_f\rho C_p\Delta T_b(x) - \delta_b[T_b(x)-T_0] = 0;\\ &x=-\infty,\ T=T_0,\ x=0,\ T_a=T_b,\ T_b=T_f\\ &\lambda\Delta T_a(x) - \lambda\Delta T_b(x) = Q[O_2]_0v_f\rho. \end{aligned} \quad (II)$$

The subscript 'a' specifies quantities relating to preheating zone, and 'b' refers to products. The last equation expresses the heat balance on the reaction surface.[5–7] System (II) is closed by a kinetic equation obtained by dividing both right hand sides and left hand sides of equations (6) and (7) by each other. Considering that under our conditions ($T_f > 1450$ K, $T_b = 1800$ K[17]); $T_f^4(T_b-T_0)^3/T_b^4(T_f-T_0) \approx 1$:

$$v_f^2/v^2 = T_f^2/T_b^2[(M+Z)/M]^{-1/2}(e^{E(T_f-T_b)/RT_fT_b})^{3/2}. \quad (13)$$

Taking a logarithm of (13), expanding $\ln(T_f/T_b)$ in series since T_f/T_b is close to 1, we obtain:

$$T_f - T_b = \frac{-2RT_b^2[2\ln(v_f^2/v^2) + \ln[(M+Z)/M]}{3E+4RT_b}. \quad (14)$$

The solution of the set (II) gives[7]

$$T_f - T_b = \frac{-\lambda(T_b-T_0)(\delta_a+\delta_a)}{C_p^2v_f^2\rho^2}. \quad (15)$$

Setting equal right hand sides of equations (14) and (15), changing $v_f^2/v^2 = \zeta$ we get:

$$-\ln\zeta - 1/2\ln[(M+Z)/M] = \frac{1/4\lambda(T_b-T_0)(\delta_a+\delta_a)(3E+4RT_b)}{\zeta C_p^2v^2\rho^2RT_b^2}.$$

$$-\ln(\zeta\sqrt{1+Z/M}) = \beta/\zeta,\ \ \beta = \frac{1/4\lambda(T_b-T_0)(\delta_a+\delta_a)(3E+4RT_b)}{C_p^2v^2\rho^2RT_b^2}.$$

$$F(\zeta) = \zeta\sqrt{1+Z/M}\exp(\beta/\zeta) = 1. \quad (16)$$

Note that equation (16) differs from the equation $\zeta\exp(\beta/\zeta) = 1$, obtained[5–7] for only heat losses by a factor of $(1 + Z/M)^{1/2}$. Let us choose a value of β for which flame propagation occurs, *i.e.* equation (16) has two solutions at $Z/M = 0$. Then FPL will be attained with an increase in the value of Z/M, which corresponds to a rise of the amount of an inhibitor. Then equation (16) has no solutions. This is shown in Figure 3.

Therefore, equation (16) describes qualitatively the inhibition of FP with small amounts of an active additive. However, under our conditions FPL is observed at $r(t) << r_0$ when a spherical

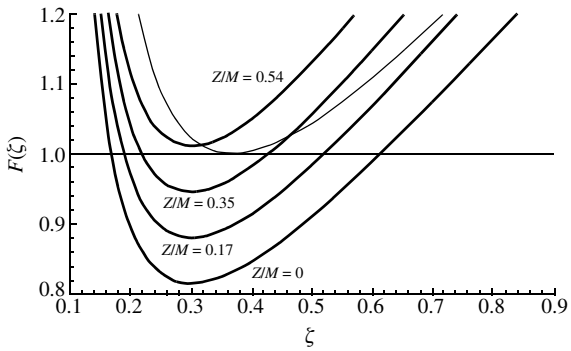

Figure 3 Dependence of $F(\zeta)$ on ζ by equation (16) at $\beta = 0.3$. Fine curve corresponds to the case of only heat losses:[5–7] $Z/M = 0$; $\beta = 1/e \approx 0.37$.

flame front does not touch reactor walls, *i.e.* heat losses into the wall are missing. Therefore, the FPL observed has chemical nature and it is caused by the termination of active centres of combustion *via* an inhibitor. Of particular interest is the estimation of chemical losses for the purpose of the *a priori* evaluation of the amount of an inhibitor and ζ at FPL on the basis of results obtained.

To understand the nature of FPL the peculiarities of the action of an inhibitor in preheating zone, namely H atoms termination *via* In molecules must be allowed for in more detail. The termination is made possible by the low activation energy which amounts to < 1 kcal mol^{-1} for *iso*-C_4H_8.[18] The act of termination of H atom *via* a molecule of an inhibitor cannot give rise to a reaction chain as well as to energy release corresponding to specific heat Q. The reaction of H atom drawn from reaction zone by diffusion, with an inhibitor makes up slightly active HO_2 radical and 44 kcal mol^{-1}.[17] This means that the break of H atom *via* inhibitor approximately corresponds to energy loss $q = (Q - 44)$ kcal mol^{-1}, which would release if the branching step occurred. The process qualitatively comprises heat losses discussed above. In accordance with our assumptions, heat losses are equal to $qk_5H(x)\mathrm{In}_0$. Based on equation (1) it can easily be shown that in preheating zone $H(x) \approx 2O_{20}[T(x) - T_0]/(T_b - T_0)$, *i.e.* the change in temperature profile at the expense of the reaction H + In is negligible. Then the set (II) if only chemical losses are allowed for (heat losses are neglected according to reasons given above) takes the form:

$$\begin{aligned} &x<0 \quad \lambda\Delta^2T_a(x) - v_f\rho C_pT_a(x) - 2qk_5O_{20}\mathrm{In}_0[T_a(x)-T_0]/N(T_b-T_0) = 0;\\ &x=-\infty,\ T=T_0,\ x=+\infty,\ T=T_b\\ &\lambda\Delta T_a(x) - \lambda\Delta T_b(x) = Q[O_2]_0v_f\rho. \end{aligned} \quad (III)$$

Here, N is the Avogadro number. Evidently, the first equations of sets (II) and (III) will coincide with each other if we take $2qk_5O_{20}\mathrm{In}_0/N(T_b - T_0) = \delta_a$, $\delta_b = 0$. With allowance made for this, the solution will coincide too. The solution of set (III) indeed gives the relation similar to equation (15):

$$T_f - T_b = \frac{-2\lambda(T_b-T_0)qk_5O_{20}\mathrm{In}_0}{N(T_b-T_0)C_p^2v_f^2\rho^2}. \quad (17)$$

Setting equal right hand sides of equations (14) and (17), changing $v_f^2/v^2 = \zeta$ we get the equation, coincident with equation (16) in which the value of β due to chemical losses is:

$$\beta = \frac{\lambda qk_5O_{20}\mathrm{In}_0(3E+4RT_b)}{2NC_p^2v^2\rho^2RT_b^2}.$$

Having regard to the relation $T_1 = T_b - n\mathrm{H}_m$ (see above) we get:

$$\mathrm{F}(\zeta) = \zeta\sqrt{1+\frac{k_5\mathrm{In}_0(T_b-T_0)}{2k_4(T_b-T_1)O_{20}M}}\exp\left(\frac{\lambda qk_5O_{20}\mathrm{In}_0(3E+4RT_b)}{2NC_p^2v^2\rho^2RT_b^2\zeta}\right) = 1. \quad (18)$$

The values of ζ and In_0 at FPL were estimated using the following parameters:

$k_4 = 0.14\times10^{-31}(T_b/T_0)^{-0.4}$ cm^6 s^{-2},[14]
$M = 760\times10^{19}/T_b$, $\rho = 10^{-3}$ g cm^{-3},[9]
$C_p = 2$ cal g^{-1} grad^{-1},[9] $\lambda = 150\times10^{-6}$ cal cm^{-1} s^{-1} grad^{-1},[9]
$k_2 = 0.30\times10^{-9}\exp(-16760/RT)$ cm^3 molec^{-1} s^{-1},[9]
$T_b = 1800$ K, $T_0 = 300$ K, $R = 2$ cal mol^{-1} grad^{-1},
$O_{20} = 0.21(1 - f_{H_2})\times760\times10^{19}/T_b$,
where f_{H_2} is a fraction of H_2 in the mixture,
$v \approx 250$ cm s^{-1},[17] $q = 40$ kcal mol^{-1},
$N = 6\times10^{23}$ molec mol^{-1},
$k_{5\ (C_3H_6)} = (0.92\pm0.2)\times10^{-11}\exp(1470\pm250/T)$ cm^3 molec^{-1} s^{-1},[19]
$k_{5\ (iso\text{-}C_4H_8)} = (0.73\pm0.2)\times10^{-11}\exp(533\pm200/T)$ cm^3 molec^{-1} s^{-1}.[19]

T_1 was taken equal to 1500 K in this qualitative consideration. The dependencies of $F(\zeta)$ on ζ and the content of an inhibitor equation (16) are shown in Figure 4(*a*),(*b*), which demonstrates qualitative agreement between equation (16) and experimental data: calculated values of $\zeta(iso\text{-}C_4H_8) = 0.045$ and $\zeta(C_3H_6) = 0.036$ correlate with experimental values 0.033 and 0.018, respectively; these values are less than $e^{1/2}$. Critical concentrations $[In_0]/[O_{20}]$ at FPL: ≈ 0.075 for *iso*-C_4H_8 and ≈ 0.135 for C_3H_6 correlate well with experimental values 0.12 and 0.16, respectively. It is seen that critical concentration of C_3H_6 at FPL is more than the one of *iso*-C_4H_8 because the former is a less active inhibitor.

Note that, in the immediate vicinity of FPL, a flame front does not propagate at all, so the amount of an inhibitor in the mixture is kept exactly constant. Therefore, at FPL neglect of the consumption of an inhibitor is always correct.

As is shown in the work, the consideration of the NRZ model with chemical losses *via* an inhibitor by the example of model reaction of hydrogen oxidation in rich mixtures allows qualitative description of experimentally observed regularities, namely: (a) occurrence of FPL in the presence of small amounts of an inhibitor, (b) a decrease in flame velocity at FPL more than by a factor of $e^{1/2}$, (c) the dependence of FPL on the chemical nature of an inhibitor.

In summary, the losses providing the occurrence of FPL as well as the occurrence of FPL with increasing amount of an active additive are of chemical nature and account for concurrence of chain branching and chain termination, though in the linear mechanism of H_2 oxidation the only feedback factor responsible for the occurrence of stationary propagating flame is warming-up.

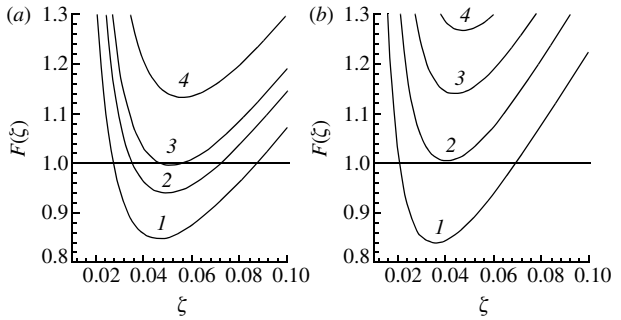

Figure 4 Dependences of $F(\zeta)$ on ζ by equation (18) for (*a*) *iso*-C_4H_8: (*1*) $[In]/[O_2]_0 = 0.07$, (*2*) 0.075, (*3*) 0.078, (*4*) 0.085; (*b*) C_3H_6: (*1*) $[In]/[O_2]_0 = 0.11$, (*2*) 0.124, (*3*) 0.135, (*4*) 0.145.

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