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Concentration limits of combustion in rich hydrogen–air mixtures in the presence of inhibitors

Nikolai M. Rubtsov* and Boris S. Seplyarskii

Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 495 962 8025;
e-mail: nmrubtss@mtu-net.ru

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An approximate analytical method is proposed for the analysis of data on the limits of flame propagation in hydrogen–air mixtures at atmospheric pressure in the presence of small quantities of active additives (inhibitors).

The use of hydrogen as fuel significantly reduces greenhouse emissions to the environment. However, the usage of hydrogen fuel is limited since hydrogen–air mixtures are explosive. One promising solution to such a problem is maintaining the safety of hydrogen production, storage and transportation through employing small quantities of chemically active additives (inhibitors).[1–3] Therefore, obtaining key parameters, which determine critical conditions of ignition and hydrogen flame propagation in the presence of these additives, is important.

We have previously proposed an approximate analytical method for the calculation of flame speeds and flame propagation limits (FPLs) in hydrogen–air mixtures at atmospheric pressure in the presence of small quantities of inhibitors.[4,5] Our method is based on a narrow reaction zone model[6] accounting for the termination of active centers (atoms and radicals) by an inhibitor in the pre-flame zone. Such an approach provides a qualitative description of the experimentally observed features associated with hydrogen combustion in the presence of an inhibitor. In particular, these include the occurrence of FPL in the absence of heat losses into the reactor walls and the dependence of FPL on the chemical nature of an inhibitor.

In the chemistry of gas-phase hydrogen combustion, the main factor enabling a steady propagation of the flame zone is the nonlinear temperature dependence of the chain-branching rate, as well as the burning rate. The occurrence of FPL with increasing inhibitor concentration is determined by the termination of active centers through the reaction with an inhibitor and a consequent decrease of combustion temperature. It is a reverse relationship between the combustion rate and the rate of active center termination by an inhibitor that leads to the formation of FPL at a small inhibitor content of the mixture.[4] An approximate analytical method[4] enabled one to formulate a formation mechanism of the upper FPL based on the account of effective heat losses in trimolecular chain-breaking steps.[5] The mechanism was presented for hydrogen oxidation in air and/or oxygen at atmospheric pressure. Using the model of a narrow reaction zone and considering specific features of the chain-branching mechanism in hydrogen oxidation, we have calculated the concentration of hydrogen at an upper FPL for both hydrogen–air and hydrogen–oxygen mixtures, and the calculation has shown an agreement with experimental results.[5]

The goal of this work was to examine the mechanism[4] of FPL formation in rich hydrogen–air mixtures in the presence of inhibitors at atmospheric pressure.

The narrow-reaction-zone method[4] applied to the problem of FPL formation in rich hydrogen–air mixtures in the presence of a small quantity of an inhibitor results in the following equation:

$$F(\zeta) = \zeta \exp(\beta/\zeta) = 1, \tag{1}$$

where $\zeta = v_\mathrm{f}^2/v^2$, v_f and v are the normal velocities of flame propagation (in the presence and in the absence of an inhibitor, respectively). Equation (1) is mathematically identical to the relation between the burning velocity and heat losses in a steady combustion wave.[7–9] However, in this case, heat losses arise from the difference between the heat release in the overall reaction (Q/kcal mol^{-1}), which would occur without an inhibitor, and heat release of active center (H atom) termination by an inhibitor (or chemical losses) Q_0 (~44 kcal mol^{-1})[10] for complete inhibitor regeneration. The value of β in equation (1) is defined as follows:[4]

$$\beta = \frac{\lambda q k_5 [\mathrm{O_2}]_0 [\mathrm{In}]_0 (3E + 4RT_\mathrm{b})}{2C_\mathrm{p}^2 v^2 \rho^2 R T_\mathrm{b}^2},$$

where λ is the thermal conductivity of the gas mixture; $q = (Q - Q_0)$ is the total heat loss in the reaction of H atom termination by an inhibitor; Q is the heat release of the $\mathrm{H_2 + O_2}$ reaction; k_5 is the effective reaction rate constant of H atom with the inhibitor molecule; $[\mathrm{O_2}]_0$ and $[\mathrm{In}]_0$ are the initial oxygen and inhibitor concentrations, respectively; E is the activation energy of the chain-branching step ($\mathrm{H + O_2 \rightarrow O + OH}$); R is the gas constant; T_b and v are the adiabatic flame temperature and normal burning velocity in a hydrogen–air mixture in the absence of an inhibitor, respectively; C_p is the thermal capacity at constant pressure; ρ is the density of a gas mixture at the initial temperature.

Taking into account that, at an FPL, $\beta = 1/\mathrm{e}$ (e = 2.718...)[7–9] and $E \gg RT_\mathrm{b}$, we obtain the following equation relating the inhibitor initial concentration and the initial oxygen content at FPL in rich hydrogen–air mixtures ($[\mathrm{In}]_{0,\mathrm{FPL}}$ and $[\mathrm{O_2}]_{0,\mathrm{FPL}}$, respectively):

$$\frac{1}{\mathrm{e}} = \frac{3\lambda q k_5 [\mathrm{O_2}]_{0,\mathrm{FPL}} [\mathrm{In}]_{0,\mathrm{FPL}} E}{2C_\mathrm{p}^2 v^2 \rho^2 R T_\mathrm{b}^2}. \tag{2}$$

From equation (2), the concentration of active chemical additive $[\mathrm{In}]_{0,\mathrm{FPL}}$ can be expressed as follows:

$$[\mathrm{In}]_{0,\mathrm{FPL}} = \frac{2}{3}\,\frac{C_\mathrm{p}^2 \rho^2 R}{\lambda k_5 \mathrm{e} E}\,\frac{v^2 T_\mathrm{b}^2}{[\mathrm{O_2}]_{0,\mathrm{FPL}}}. \tag{3}$$

The subscript FPL in equation (3) specifies that the value is taken at an FPL. According to the published approach,[6] the thermophysical and kinetic parameters involved in equations (2) and (3) are assumed constant. Therefore, from equation (3), it

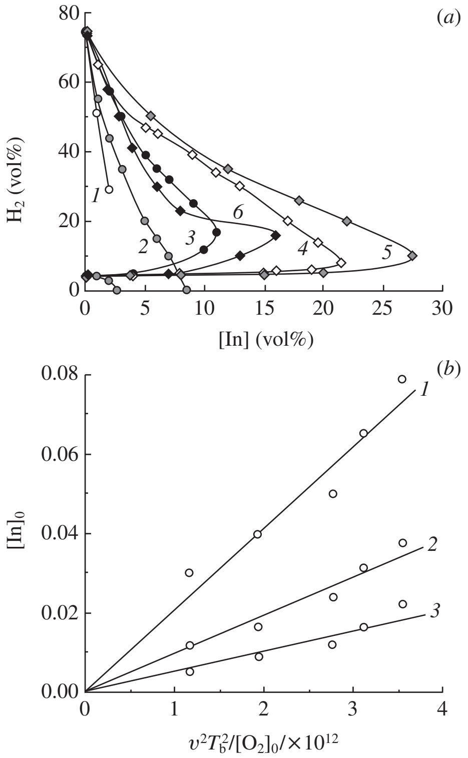

Figure 1 Influence of inhibitors on FPL in hydrogen–air mixtures at atmospheric pressure: (*a*) experimental data,[3] flame propagation does not occur to the right of each curve and occurs to the left of each curve; (*1*) octene, (*2*) hexene, (*3*) $C_2F_4Br_2$, (*4*) NAFS-III–perfluorobutane C_4F_{10}, (*5*) CHF_3 and (*6*) C_2F_5H; (*b*) the data from Figure 1(*a*) calculated using equation (3) for (*1*) CHF_3, (*2*) $C_2F_4Br_2$ and (*3*) hexene.

follows that the experimental values of $[\mathrm{In}]_{0,\mathrm{FPL}}$ and $[O_2]_{0,\mathrm{FPL}}$ taken at FPL in a rich hydrogen–air mixture for various concentrations of a given active additive should give a straight line (in the $[\mathrm{In}]_{0,\mathrm{FPL}}$–$v^2T_b^2/[O_2]_{0,\mathrm{FPL}}$ coordinates) with a positive slope passing through the origin of the coordinates.

To verify equation (3), published data[3,11,12] were analyzed. These studies were aimed at revealing the influence of various inhibitor additives (hydrocarbons and alcohols) on FPL values for hydrogen–air mixtures at atmospheric pressure [Figures 1(*a*) and 2(*a*)]. The experimental values of the normal velocities of flame propagation v for hydrogen–air flames were taken from ref. 13. For our calculations, we used the mean values while adiabatic combustion temperatures for various percentages of hydrogen in hydrogen–air mixtures were taken from ref. 14. Note that the values of T_b and the normal burning velocity v in equations (2) and (3) correspond to the combustion of hydrogen–air mixtures with the same oxygen content, but in the absence of an inhibitor.

The calculations based on equation (3) have been performed for the following parameters: $\rho = 10^{-3}$ g cm^{-3},[10] $C_p = 2$ cal g^{-1} K^{-1},[10] $\lambda = 10^{-3}$ cal cm^{-1} s^{-1} K^{-1},[10,15] $E = 16.7$ kcal mol^{-1},[16] $R = 2$ cal mol^{-1} K^{-1}, $[O_2]_0 = 0.21(1 - f_{H_2})\times 750\times 10^{19}/T_b$, where f_{H_2} is the H_2 mole fraction in the mixture and $q = 70$ kcal mol^{-1}.[4]

Experimental data[3,11,12] [Figures 1(*a*) and 2(*a*)] have been processed for a number of inhibitors, and the results are shown in Figures 1(*b*) and 2(*b*) in the $[\mathrm{In}]_{0,\mathrm{FPL}}$–$v^2T_b{}^2/[O_2]_{0,\mathrm{FPL}}$ coordinates. In order to construct straight lines for the corresponding inhibitors on the basis of equation (3), we used the following effective values of reaction rate constants for a hydrogen atom and an inhibitor molecule: for CHF_3, 0.1×10^{-11}; for $C_2F_4Br_2$, 0.23×10^{-11}; for hexene, 0.47×10^{-11} [Figure 1(*b*)], for ethanol, 0.93×10^{-12}; for *n*-butanol, 0.27×10^{-11}, for prop-2-en-1-ol, 0.45×10^{-11} cm^3 molec^{-1} s^{-1} [Figure 2(*b*)]. The rate constants for the reactions of a hydrogen atom with an inhibitor molecule were chosen to obtain the best fit between calculated and experimental relations.

As demonstrated in Figures 1(*b*) and 2(*b*), experimental data for small inhibitor concentrations in hydrogen–air mixtures are well described by straight line equations in the $[\mathrm{In}]_{0,\mathrm{FPL}}$–$v^2T_b^2/[O_2]_{0,\mathrm{FPL}}$ coordinates passing through the origin of the coordinates for each inhibitor. The obtained result implies that the main termination mechanism of a reaction chain by an inhibitor is the reaction of a hydrogen atom with the molecule of an inhibitor.[1] These results generally confirm the statements[4,5] regarding the mechanism of FPL formation in rich hydrogen–air mixtures in the presence of small quantities of inhibitors at atmospheric pressure.

Since equation (3) is applicable to a wide variety of inhibitors in hydrogen–air mixtures, it can be used for evaluating effective rate constants for the reactions of hydrogen atoms with the molecules of active additives, directly from experiments on flame propagation. These data can be used for the numerical modelling of flame propagation phenomena in hydrogen–air mixtures in the presence of inhibitors.

The effective rate constants (k_5) obtained using data given in Figures 1(*b*) and 2(*b*) for the reactions of hydrogen atoms with the molecules of active additives, correlate well with the literature data. We take into account that experimental data for hexene [Figure 1(*a*), curve *2*] closely match the data for propene as an additive[4] for rich H_2–air mixtures. Thus, the effective rate constant k_5 for hexene, obtained from the slope of a corresponding straight line in Figure 1(*b*) ($k_5 = 0.47\times 10^{-11}$ cm^3 molec^{-1} s^{-1}), corresponds to the value of k_5 for propene obtained by the method of self-ignition limits,[17] where the value was $(1.0\pm 0.3)\times 10^{-11}\,e^{-1500/T}$ cm^3 molec^{-1} s^{-1}. The narrow-reaction-zone model used in this work implies that the action of a chemically active additive is determined by the reaction-chain termination by the molecules of the additive in a pre-flame zone. Thus, the effective

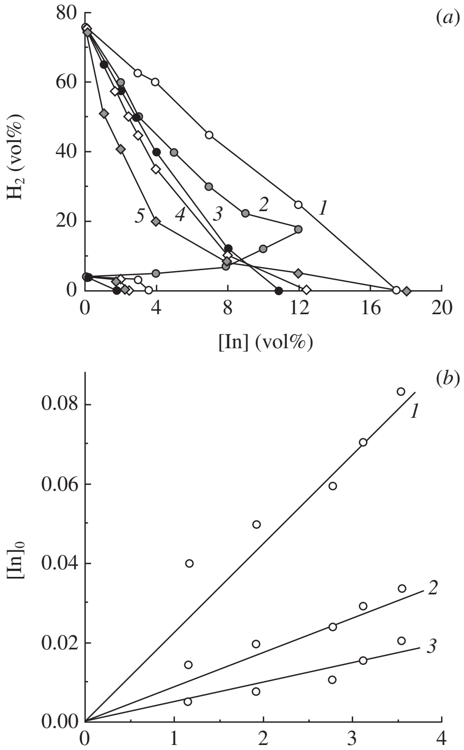

Figure 2 Influence of alcohols and $C_2F_4Br_2$ on FPL in hydrogen–air mixtures at atmospheric pressure: (*a*) experimental data,[11,12] flame propagation does not occur to the right of each curve and occurs to the left of each curve; (*1*) ethanol, (*2*) $C_2F_4Br_2$, (*3*) *n*-butanol, (4) isopropanol and (*5*) prop-2-en-1-ol; (*b*) the data from Figure 2(*a*) calculated using equation (3) for ethanol, *n*-butanol and prop-2-en-1-ol.

rate constants determined in this work correspond to a temperature close to $(T_0 + T_b)/2$. We note that the rate constants of the reaction $H + C_3H_6$ available in the literature are rather diverse, and they cover a range from $2.17\times10^{-11}e^{-820/T}$ to $7.67\times10^{-10}e^{-2568/T}$ cm^3 molec^{-1} s^{-1}.[18,19] The effective rate constant k_5 obtained in this work is actually closer to a reported value from ref. 18.

Note that, according to published data,[3,11,12] the activation energy of the reaction of hydrogen atoms with the molecules of active additives is much lower than that corresponding to the chain-branching step $H + O_2 \rightarrow O + OH$.[4] Thus, utilizing the narrow-reaction-zone model, one may consider a termination reaction by an inhibitor as temperature independent. The validity of such an approximation is confirmed by flattening of experimental data expressed in the $[In]_{0,FPL}–v^2T_b^2/[O_2]_{0,FPL}$ coordinates; the efficiency of an inhibitor is determined only by the rate constant k_5 [see equation (3)].

Thus, the method of a narrow reaction zone[4–6] applied to hydrogen flames is in a good qualitative agreement with the experimental data. The analytical expression for flame propagation limits in hydrogen–air mixtures in the presence of small quantities of active additives obtained in this work allows us to evaluate the efficiency of an inhibitor through the use of both experimental and published data.

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