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Effect of propylene additives on rich hydrogen–air flames

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In rich hydrogen–air flames, a chemical reaction is shown (by numerical methods) to have two stages, *i.e.*, a low-temperature stage with quadratic branching and a high-temperature stage with linear branching; changes in the chemical flame structure due to propylene additives are more effective in the first stage.

A decrease in the fire and explosion hazards of gaseous mixtures containing hydrogen is of crucial importance. One of the most significant characteristics of fire and explosion hazards and a measure of the reactivity of gaseous mixtures is the burning velocity S_u. There are two methods to reduce S_u. The chemical method is aimed at decreasing the concentration of active atoms and radicals in a flame zone; the physical method decreases the flame temperature. In the first case, combustion is retarded by adding small amounts of active agents (inhibitors) to an initial mixture. In the second case, inert substances in relatively large concentrations (flegmatizers) are usually employed. Although this viewpoint is commonly accepted, a concrete mechanism of the action of additives is open to argument.[1]

Any additives change, in one way or another, the thermodynamic parameters of a flame including its temperature. A negligible decrease in flame temperature is reached by adding active inhibitors in small concentrations. On the other hand, a great decrease in temperature is reached by means of flegmatizers used in large concentrations. The latter, in particular, include either excess fuel or an oxidizer in rich and lean mixtures, respectively. However, in the flame zone, the flegmatizers play not only the role of inert diluents. Introducing various definitions, measures, and criteria for estimating the efficiency of inhibitors and flegmatizers[1–4] is rather useful but phenomenological to some extent.

In terms of the inhibition of an H_2 flame, two facts are important. First, the mechanism of hydrogen oxidation is known to vary substantially with the initial temperature. During spontaneous ignition at high temperatures, a part of the $H \rightarrow OH$, $O \rightarrow 3H$ (in the reactions $H + O_2 \rightarrow OH + O$, $O + H_2 \rightarrow OH + H$, $OH + H_2 \rightarrow H_2O + H$) chain occurs, whereas at low temperatures ($T_0 < 900$ K) the link including the HO_2 radical is dominant, *i.e.*, $H \rightarrow HO_2 \rightarrow H_2O_2 \rightarrow OH \rightarrow H$[5,6] (in the reactions $H + O_2 + M \rightarrow HO_2 + M$, $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, $H_2O_2 \rightarrow 2OH$, $OH + H_2 \rightarrow H_2O + H$). Second, as H_2 flames are typical diffusion-thermal flames, they have rapidly changing properties in the flame zone, with diffusive flows of active particles into the preheating zone. Thus, some peculiarities can be observed in the course of chemical reaction and its retardation by inhibitors in rich H_2 flames. To elucidate this problem, we studied the effect of small (up to 1 vol%) additives of a model hydrocarbon (propylene, C_3H_6) on the macro characteristics of rich hydrogen–air flames, *i.e.*, the combustion rate, concentrations and the thermal structure of the flame zone.

The studies were performed by numerical methods using previously published programs[7,8] and a kinetic scheme.[9] In all calculations, we assumed that, initially, $T_0 = 298$ K and $p_0 = 0.1$ MPa. In the flame zone, a temperature of 400 K was observed at $x = 0.05$ cm. The calculation area began on the side of the fresh mixture at $x = -5$ cm and ended on the side of combustion products at $x = +40$ cm.

Figure 1(*a*) plots the OH concentration *versus* temperature in the zone of rich hydrogen–air flames. The OH dependence displays two maxima, $[OH]_{max}$. Clearly, the addition of more H_2 decreases [OH] over the entire flame zone. In this case, the decrease in the second peak is stronger. Figure 1(*b*) shows the dependence of the OH concentration for a 55% hydrogen–air mixture with propylene added. Adding C_3H_6 reduces substantially the concentration of OH and the decrease in $[OH]_{max}$ for the first peak is stronger than that of the second. After adding of the first 0.5% C_3H_6, the average decrease in burning velocity per 1% propylene is 310 cm s^{-1}; for the next 0.5% C_3H_6, the drop is 124 cm s^{-1}, *i.e.*, the first additive is 2.5 times more efficient in reducing S_u than the second. The existence of two [OH] peaks indicates two different stages of chemical transformations. Our analysis shows that the second $[OH]_{max}$ peak is typical of the high-temperature flame zone and can be assigned to the chain-thermal ignition due to the basic processes of linear branching

$$O + H_2 \rightarrow OH + H, \qquad (1)$$

$$H + O_2 \rightarrow OH + O. \qquad (2)$$

The first, low-temperature $(OH)_{max}$ peak is caused by two main factors, *i.e.*, the diffusion of H atoms from the high-temperature zone and the quadratic branching in the low-temperature zone *via*

$$H + HO_2 \rightarrow 2OH. \qquad (3)$$

The branching factor φ has the form

$$\varphi = 2K_2[O_2] - K_4[M][O_2] + K_3[HO_2],$$

where K_4 is the rate constant of chain termination in

$$H + O_2 + M \rightarrow OH_2 + M. \qquad (4)$$

According to the calculations, φ exceeds zero at 343 K, whereas the high-temperature branching factor φ, in which the third term can be neglected, exceeds zero at 680 K. The low-temperature area also contains sharp peaks in $[HO_2]$ and $[H_2O_2]$ at $T = 420$ and 612 K, respectively. The concentrations $[HO_2]$ and $[H_2O_2]$

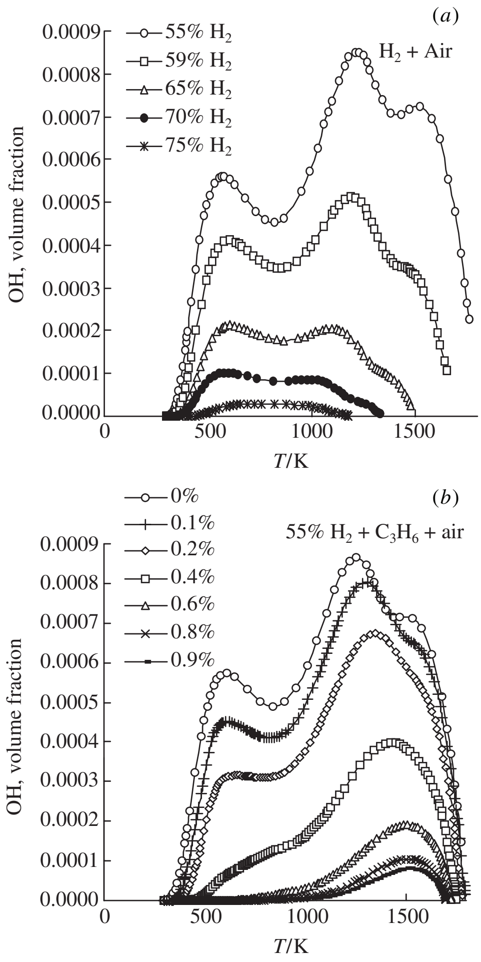

Figure 1 Temperature dependence of OH concentration (*a*) in the zone of an air–hydrogen flame in mixtures with different hydrogen contents; (*b*) in the zone of a 55% air–hydrogen flame with various amounts of propylene added.

decrease rapidly with increasing temperature. Note that a diffusive flow of H atoms is of particular importance for the case under study because it plays the role of initiation, which is involved in the critical condition for chain self-ignition with quadratic branching in (3). An additional argument in favour of the diffusive flow of H atoms to the low-temperature zone is a comparison between the temperatures at which $\varphi > 0$ under flame and self-ignition conditions. On the self-ignition of rich hydrogen–air mixtures at $p_0 = 0.1$ MPa, $\varphi > 0$ at 850–950 K,[5,6] and in the flame itself this holds for 340 K.

As regards the mechanism of retardating an H$_2$ flame with a C$_3$H$_6$ additive, small additions manifest inhibition characteristics, *i.e.*, they decrease S_u more effectively and have an effective action in the low-temperature area by decreasing strongly both [OH]$_{max}$ in the first peak and [HO$_2$]$_{max}$ and [H$_2$O$_2$]$_{max}$ with additives amounting to 0.5%. The most realistic inhibition scheme is the Panfilov–Voevodsky scheme,[10] in which a decrease in the concentration of H atoms is due to the reactions

$$\mathrm{H + RH \rightarrow H_2 + R,} \tag{5}$$

$$\mathrm{R + O_2 \rightarrow RO_2 \rightarrow oxidation\ products,} \tag{6}$$

and the fact that, prior to reaction (6), the radical R can be involved in another reaction with H atoms in

$\mathrm{R + H \rightarrow RH}$, then $\mathrm{RH + H \rightarrow R + H_2}$ or, alternatively
$\mathrm{R + H \rightarrow R_1H + H_2}$, then $\mathrm{R_1H + H \rightarrow R_1 + H_2}$.

Thus, the hydrocarbon molecule RH catalyses the recombination of excess H atoms. The intermediates CH$_4$, C$_2$H$_2$, and C$_2$H$_4$ also contribute to the catalytic recombination of radicals. At the same time, when the concentration of C$_3$H$_6$ exceeds 0.5%, a further decrease in S_u is caused by C$_3$H$_6$ acting as an excess fuel, which, like hydrogen, is effectively oxidised in the flame zone. The calculations indicate that, at the highest flame temperature, the molecules of CO and CO$_2$ contain more than 90% carbon added initially as propylene molecules.

Thus, in rich hydrogen–air flames, the chemical transformation runs in two stages. The chain process due to both H atoms diffusing from the high-temperature flame zone and the quadratic branching develops in the low-temperature stage. In this case, the temperature is of minor importance. Reactions with linear branching occur in the high-temperature stage and the temperature, in this case, is of decisive importance. Propylene additives retard chemical reaction and decrease the flame velocity. When propylene is added in small amounts, it thus acts as an inhibitor, but it acts as an excess fuel when it is used in large amounts.

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