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Role of Chain Termination in the Suppressing Effect of Hydrocarbons on the Combustion of Hydrogen–Air Mixtures

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Abstract—In the inhibition of the combustion of hydrogen–oxygen mixtures, the consumption of O_2 by the inhibitor is only due to preliminary reactions between the inhibitor and active intermediates of H_2 combustion. These reactions result in chain termination. The inhibiting effect of an admixture is determined by its chain-terminating capacity. The denial of the inhibiting effect by some authors is, in essence, the denial of the chain nature of combustion.

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A characteristic feature of chain processes is that they are inhibited by certain types of compounds, the inhibiting effect being due to extra chain termination reactions involving the inhibitor [1–12]. In particular, the branching-chain combustion of hydrogen–oxygen mixtures is inhibited by hydrocarbons (RH). This effect may be manifested as ignition suppression, a narrowing of the concentration range of flame propagation, and a decrease in the combustion rate (see, e.g., [4–11, 13]). The inhibiting effect of RH admixtures is known to be due to fast reactions between these admixtures and reactive intermediates of H_2 combustion, primarily hydrogen atoms:

$$H + R_1H = H_2 + R_1^{\bullet}, \tag{I}$$

$$H + R_2H = R_1^{\bullet}, \tag{II}$$

where R_1H and R_2H are the molecules of saturated and unsaturated hydrocarbons, respectively [5–11].

The alkyl radicals resulting from these reactions ($R_1^{\bullet}$) react readily with O_2:

$$R_1^{\bullet} + O_2 = R_1O_2^{\bullet} \longrightarrow \text{chain termination.} \tag{III}$$

This reaction is not accompanied by any considerable regeneration of H or O atoms or $OH^{\bullet}$ radicals [5–11, 14]. Thus, the reactions between RH and the reactive intermediates of H_2 combustion result in the replacement of these intermediates by inactive alkyl radicals, causing chain termination. These reactions compete with the following chain branching and propagation reactions:

$$H + O_2 = OH^{\bullet} + O, \tag{IV}$$

$$O + H_2 = OH^{\bullet} + H, \tag{V}$$

$$OH^{\bullet} + H_2 = H_2O + H. \tag{VI}$$

Since the rate constants of reactions (I) and (II) are much higher than the rate constant of the chain branching reaction (IV), even minor RH admixtures substantially increase the chain termination rate and thereby suppress hydrogen oxidation and combustion.

The familiar mechanism of the inhibiting effect of hydrocarbons on H_2 ignition provides a basis for the determination of the rate constants of reactions involving H atoms [5–10]. The development of chain combustion theory has demonstrated that, by introducing some hydrocarbons, it is possible to prevent the deflagration–detonation transition in hydrogen–air mixtures and to break the stationary detonation wave [11, 15, 16]. Experiments on the inhibition of developed detonation (in which RH was in that section of the reactor tube into which the detonation wave came) have shown that, above a certain inhibitor concentration, the combustion front lags behind the shock wave and, as a consequence, the latter decays (i.e., the detonation wave breaks).

The suppressing effect of RH on H_2 combustion is called inhibition [16] for the reason that the mechanism

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† Deceased.

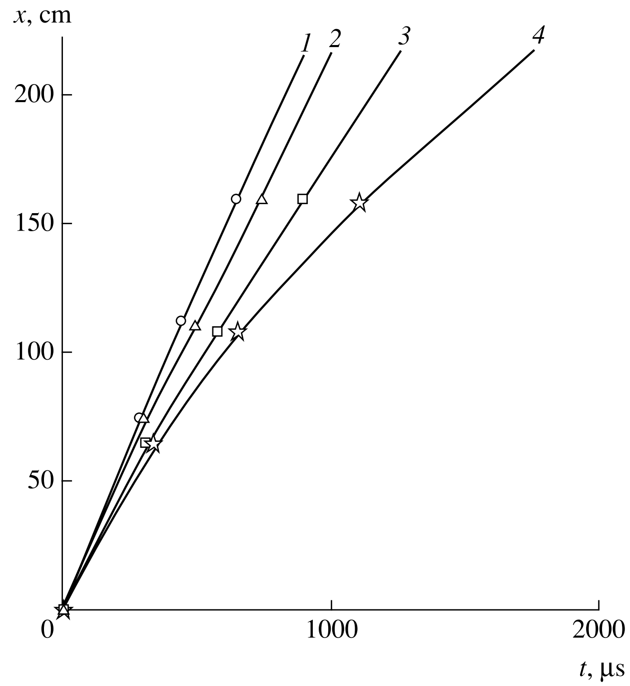

Fig. 1. *x*–*t* diagram for the 33.8% H_2 + 66.2% air mixture containing various amounts of the inhibitor AKAM-3 (vol %): (*1*) 2.3, (*2*) 3.0, and (*3*, *4*) 3.5 [16].

of this effect and the definition of the term *inhibition* are known from textbooks, monographs, and articles on chemical kinetics (see, e.g., [4–11]) and have become a matter of common knowledge. However, Gel'fand [17] considers it to be incorrect to explain the suppressing effect of RH on H_2 detonation in terms of inhibition [17]. He states that this effect is unrelated to inhibition and is simply due to a change in the mixture composition since the admixture causes significant changes in the excess air factor α. He explains the retardation of H_2 combustion by the rapid consumption of O_2 in the independent RH oxidation reaction [17]. Gel'fand's only argument in favor of this interpretation [17] is that the detonation limits calculated for propylene-containing hydrogen–air mixtures using Le Chatelier's empirical rule of concentration limits coincide with the observed detonation limits [16]. Although Gel'fand recognizes that this rule is nonrigorous and is rarely valid for the upper limit, he nevertheless suggests that this unreliable empirical rule rather than experimental data should be used in the determination of the H_2 concentration limits as a function of admixture concentration.

Since the correct interpretation of the effects of admixtures is of fundamental importance for combustion theory and practice and some of Gel'fand's statements [17] are in conflict with numerous experimental data and theoretical principles, we consider it to be necessary to draw attention to the following:

(1) Contrary to his statement, Gel'fand [17] could not compare the results of his calculations to our experimental data concerning the effect of propylene on detonation, because our data for propylene had not been published yet. The data reported in [16] refer to another inhibitor, namely, a mixture of propane, butane, and propylene. It was only noted that the efficiency of propylene differs from the efficiency of this hydrocarbon mixture.

(2) It can readily be seen that, contrary to Gel'fand's statement [17], all of our data [16] are in conflict with Le Chatelier's principle. For example, all experimental upper concentration limits fall below the values calculated according to this principle, the deviation being 32%.

(3) The validity or invalidity of a hypothesis cannot be judged from the agreement or disagreement of data with some empirical rule, particularly if this rule is nonrigorous. This is all the more true for Le Chatelier's rule of the ignition of RH mixtures, which was formulated late in the 19th century and is based on lower flame propagation limits for some alkane mixtures. Hydrogen does not belong to alkanes, and the upper detonation limit differs radically in nature from the lower ignition limit—these are but two of the reasons why our and other data deviate from Le Chatelier's rule. Furthermore, this rule ignores the specific features of chain combustion.

(4) The hypothesis that H_2 combustion is accompanied by an independent reaction between oxygen and RH that depletes the mixture of oxidizer [17] is demolished by many familiar facts (some of them are considered below), including experimental data concerning the decrease in the H_2 combustion rate under the action of RH [16]. Indeed, if the reaction between O_2 and H_2 were accompanied by a rapid consumption of oxygen in an independent RH oxidation reaction (i.e., in a reaction involving no hydrogen oxidation intermediates), RH admixtures would intensify combustion by giving rise to a parallel O_2 consumption route. In fact, RH slows down combustion from its very onset, as is clear from Fig. 1 [16].

(5) Gel'fand's hypothesis [17] is in conflict with the fact that minor amounts of RH [5–11, 18] or alcohol vapor [19] prevent H_2 combustion. If combustion has not begun and, accordingly, there is no oxygen consumption, then the prevention of combustion is obviously unrelated to oxygen depletion. The reactions involving RH that prevent hydrogen ignition (i.e., exert an inhibiting effect) do take place in developing combustion and affect this process.

The above arguments might seem sufficient to reply to Gel'fand's denial of the inhibition of H_2 combustion by hydrocarbons [17]. However, some of Gel'fand's statements can mislead those readers who are not closely acquainted with the phenomenon of inhibition and associated problems. For this reason, we will proceed with a brief discussion of these statements.

ON THE HYPOTHESIS THAT HYDROCARBON ADMIXTURES DEPLETE THE AMOUNT OF OXYGEN IN HYDROGEN–AIR MIXTURES

The hypothesis that the inhibiting effect is due to a change in the excess air factor ignores the following facts: when there is no hydrogen combustion, the reaction between oxygen and the hydrocarbon is slower than the reaction between oxygen and hydrogen by a factor of several tens, and the alkyl radical $R^\bullet$ reacting with O_2 (reaction (III)) results only from reactions between RH and reactive intermediates of H_2 combustion (i.e., inhibition reactions). This is proved by all data relevant to hydrocarbon and hydrogen combustion (see, e.g., [4, 20]), including the data presented below. The consumption of O_2 by hydrocarbon radicals is a consequence of inhibition. Asserting that an RH admixture can change α in spite of its apparently small concentration, Gel'fand is based only on the obvious difference in overall oxidation stoichiometry between RH and H_2 [17]. However, it is even more obvious that the ratio between the consumption rates of a given reactant in competing parallel reactions is primarily determined by the mechanisms of these reactions and by the rate constants of their rate-limiting steps rather than by their overall stoichiometric coefficients. This is a basic principle of reaction rate theory (see any textbook of chemical kinetics).

Unlike H_2 combustion, in which all reaction chains are branched and the rate-limiting step (reaction (IV)) is characterized by a high rate constant, RH combustion is characterized by rare chain branching and by a low rate constant of the rate-limiting step [4, 21]. As a consequence, under equal conditions, the reaction between O_2 and H_2 is much more rapid than the reaction between O_2 and RH. A manifestation of this difference is that the flame velocity (U) in hydrogen–air mixtures is higher than U in RH–air mixtures by a factor greater than 5 [4, 20]. Accordingly, since the reaction rate is proportional to squared U [22, 23], RH combustion involving no H_2 oxidation intermediates is slower than H_2 combustion by a factor of several tens. The combustion of RH in a burning hydrogen–air mixture is initiated and sustained by reactions between RH and H_2 oxidation intermediates, namely, H and O atoms and $OH^\bullet$ radicals. These reactions cause chain termination and thus inhibit the combustion process.

The fact that the reaction between O_2 and RH in the absence of H_2 combustion intermediates is much slower than the reaction between O_2 and H_2 is illustrated by our data concerning the effect of C_3H_6 on the combustion rate of H_2–air mixtures.

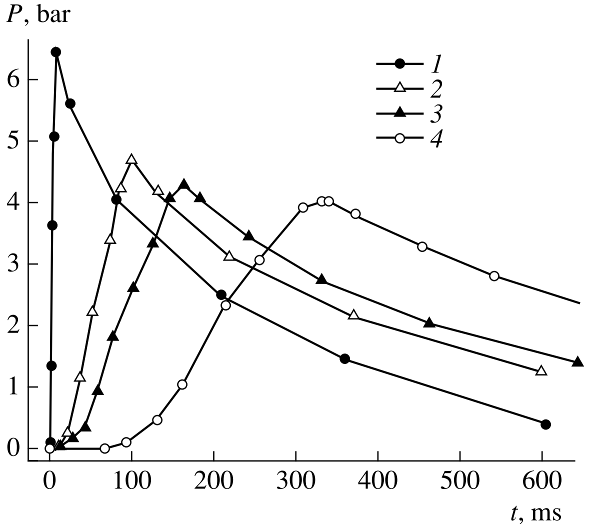

Fig. 2. Variation of pressure during combustion: (*1*) 30% H_2 + 70% air, (*2*) 30% H_2 + 3% C_3H_6 + 67% air, (*3*) 3% C_3H_6 + 97% air, and (*4*) 30% N_2 + 3% C_3H_6 + 67% air.

The mixtures to be examined were prepared in a stainless steel reactor of volume 3.15 l by mixing the components at appropriate partial pressures. The mixtures were ignited with a spark after a time necessary for perfect mixing (20 min). Pressure and chemiluminescence were measured starting at the ignition instant. The signal from the piezoelectric pressure sensor was amplified and was then recorded with an S9-8 double-beam memory oscilloscope. Chemiluminescence between 300 and 600 nm was recorded on the same oscilloscope with the use of an FEU-39 photomultiplier. Between combustion runs, the reactor was pumped down to ~2 Pa.

Since the number of moles of the gas mixture decreases steadily during H_2 oxidation, the increase in pressure (ΔP) observed in the reactor during developing combustion is only due to an increasing temperature. The temperature grows nonuniformly in the reactor volume. Therefore, the increase in pressure during developing combustion is a measure of the average temperature rise in the reactor volume. The temperature rise is determined by the ratio between the rate of heat generation due to combustion and the rate of heat dissipation. The shorter the characteristic time of the reaction in comparison with the characteristic time of heat dissipation, the higher the volume-average temperature and the closer it is to the combustion temperature. Therefore, ΔP is a measure of the heat generation rate and, accordingly, the combustion rate. This is the reason why chemiluminescence and pressure, which grow at an increasing rate, peak almost simultaneously (Fig. 2). The lagging of ΔP behind chemiluminescence at the early stages of combustion is due to the fact that a significant self-heating takes place only after a certain rate of chain combustion is reached [11].

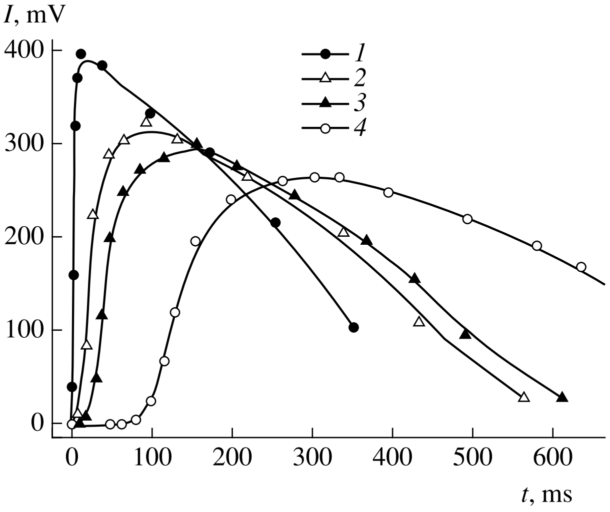

Fig. 3. Chemiluminescence intensity during combustion: (*1*) 30% H_2 + 70% air, (*2*) 30% H_2 + 3% C_3H_6 + 67% air, (*3*) 3% C_3H_6 + 97% air, and (*4*) 30% N_2 + 3% C_3H_6 + 67% air.

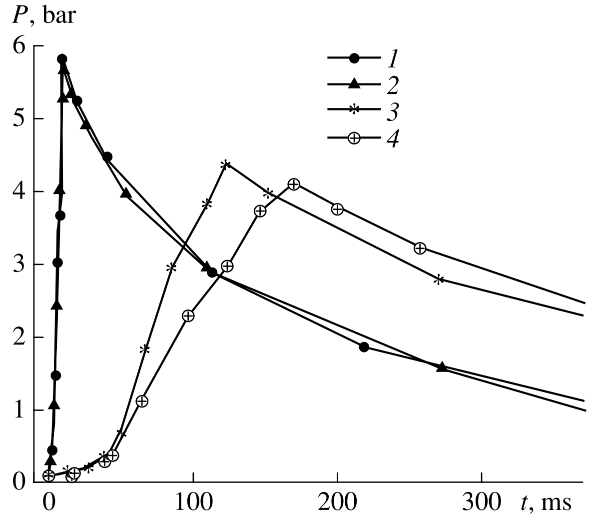

Fig. 4. Variation of maximum pressure in the course of the combustion of 30% H_2 + air mixtures containing various additions: (*1*) 30% H_2 + 70% air, (*2*) 30% H_2 + 3% N_2 + 67% air, (*3*) 30% H_2 + 3% C_3H_7OH + 67% air, and (*4*) 30% H_2 + 3% C_3H_6 + 67% air.

It is clear from Figs. 2 and 3 that RH reduces the combustion self-acceleration rate. Note that this effect is observed starting at the very onset of combustion, when no O_2 has been consumed. If O_2 were consumed in an independent reaction involving propylene, the hydrocarbon would enhance the acceleration of the process. Moreover, RH brings about a considerable induction period exceeding the pressure and chemiluminescence peak times for the RH-free mixture with the same H_2 concentration. At a fixed O_2 content, the combustion of the C_3H_6 mixture begins after an induction period so long that the H_2 combustion rate has time to pass through a maximum and to decrease to some extent (Figs. 2, 3, curves *4*). Even after this period, C_3H_6 combustion is still substantially slower than H_2 combustion.

Therefore, in hydrogen–air mixtures that are not very poor in hydrogen, RH admixtures have no time to react with O_2 before reacting with chain-propagating intermediates of hydrogen combustion. An additional O_2 consumption due to the presence of RH takes place only in reactions involving hydrocarbon radicals that have resulted from reactions between the hydrocarbon and chain-propagating intermediates of H_2 combustion (i.e., inhibition reactions).

The fact that the additive acts by initiating extra chain termination reactions rather than by changing the excess air factor is further illustrated by the effect of isopropanol and propylene vapors on the combustion of a hydrogen–air mixture (Fig. 4). These admixtures have the same stoichiometric number in their complete oxidation reactions and are characterized by very similar heats of combustion, concentration limits of ignition, and flame velocities [4, 20]. However, they have very different chain-terminating capacities. Owing to its π-bond, the C_3H_6 molecule readily adds a hydrogen atom (reaction (II)), thereby terminating the reaction chain. By contrast, the reaction between an H atom and an isopropanol molecule results in the detachment of an H atom from the molecule (reaction (I)). This reaction is much slower than reaction (II) because of a higher activation energy. In good agreement with this difference in chain-terminating capacity, propylene exerts a much stronger suppressing effect on H_2 combustion than isopropanol (Fig. 4). The mechanistic difference between the effects of these admixtures on H_2 combustion is detailed elsewhere [19, 24].

Contrary to Gel'fand's statement [17], it is not because of the small amount of the RH admixture that we ignore the depletion of oxygen in the hydrogen–air mixture. We do so based on numerous experimental data indicating that, if there is no preliminary reaction between RH and reactive H_2 combustion intermediates, O_2 is much more slowly consumed by the hydrocarbon than by hydrogen. This is also evident from Fig. 4.

The prevention of H_2 combustion by small hydrocarbon admixtures is explained by the fact that, owing to RH reacting with H atoms and, to a lesser extent, with O atoms and $OH^•$ radicals, the chain termination rate exceeds the chain branching rate starting at the very onset of the process. This prevents the mixture from ignition. Furthermore, since the H and O atoms and $OH^•$ radicals are few before ignition, RH prevents H_2 ignition without being consumed or causing O_2 consumption. Obviously, the chain termination reactions (I) and (II) compete with the branching reaction (IV) during flame propagation, inevitably reducing the combustion rate.

Thus, from both the mechanistic and kinetic standpoints, the suppressing effect of RH on H_2 combustion is fully consistent with the conventional definition of inhibition given in textbooks, encyclopedias, monographs, and articles (see, e.g., [1–10]), contrary to Gel'fand's statements [17]. The suppression of H_2 combustion by hydrocarbons was termed inhibition long before our publication on this issue [16] appeared (see, e.g., [4]).

Note that the narrowing of the concentration range of hydrogen detonation under the action of inhibitors [11, 16] allows spin detonation conditions to be modified as well.

Furthermore, as is demonstrated in an earlier work [25], the statement that experimental concentration limits for the ignition of CO–H_2 mixtures in air are in agreement with Le Chatelier's rule is also incorrect. Since it is well known that CO does not burn in air in the absence of hydrogen-containing compounds, the question of whether these experimental data are in agreement with Le Chatelier's rule makes no sense. At the same time, taking into consideration the branched-chain mechanism of CO combustion in the presence of hydrogen-containing compounds provides an understanding of this process, including the fact that the ignition limits and the combustion rate as a function of the admixture concentration pass through an extremum [26–28]. Taking into account the branched-chain mechanism of combustion in the CO–O_2 system in the presence of hydrogen-containing compounds allowed, for the first time, the rate constant to be determined for a number of key reactions involving H and O atoms [5, 6, 29]. These data were later confirmed by other methods.

Thus, the denial of the inhibition of H_2 oxidation by hydrocarbons is the denial of the chain character of the process. This denial stems from the illusion that the combustion process can be explained in formal terms of a purely empirical and nonrigorous rule, without taking into account the chain nature and the mechanism of the reaction. This illusion will disappear if well-known experimental findings and the fundamentals of reaction rate theory, including the theory of chain reactions, are not ignored. Some of these findings and fundamentals are quoted above.

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