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Inhibition of the Combustion and Detonation of Hydrogen–Air Mixtures behind the Shock Front

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Abstract—The chain avalanche plays the determining role in all regimes of combustion in the hydrogen–oxygen system in the initiating shock wave near atmospheric pressure in a wide range of high initial temperatures. The characteristics of combustion and detonation can be effectively controlled by varying the rates of the competing chain-branching and chain-termination reactions with the use of small amounts of admixtures. The reactivity of the combustible mixture is correlated with the chemical structure of the admixture. This correlation is manifested in the fact that changing a single functional group in the admixture molecule produces a strong effect on the kinetics, macrokinetics, and gas dynamics of the overall process.

Understanding combustion, explosion, and detonation processes that are due to a chain avalanche is a challenging problem of chemical kinetics and explosion theory. Research in this field is all the more important in view of the problem of controlling these processes by chemical means, specifically, by affecting the rates of the competing multiplication and loss of reactive intermediates.

This work is devoted to the role of the chain avalanche in the combustion of hydrogen–oxygen mixtures in various macrokinetic regimes under shock wave conditions. Furthermore, we report the chemical control of this process with chemically different small admixtures under various initial conditions and the control of combustion–detonation transition.

It has long been believed that, in gas-phase combustion processes, the branched-chain mechanism plays a significant role only at pressures that are lower than atmospheric pressure by a factor of several hundreds, when there is no appreciable self-heating of the reaction mixture. For combustion accompanied by any significant self-heating, the temperature rise in the reacting gas has been considered to be the only factor determining the process (see, e.g., [1–8]). In monographs, encyclopedias, treatises of chemical kinetics, and journal papers, the pressure range of chain combustion is bounded by the first and second critical autoignition pressures [1–5, 9–13], which are lower than atmospheric pressure by a factor of several tens or even several hundreds. The third autoignition limit, which passes through atmospheric pressure, is also believed to be thermal in nature [1–5, 9–16]. The kinetic networks used in the numerical modeling of combustion, which consist of a large number of diverse reactions, often include reactions that can be viewed as steps of a chain reaction. However, if the gas pressure exceeds a few tenths of atmospheric pressure, ignition and combustion are considered to be thermal rather than chain processes [14–16].

In some works, it is accepted that, in principle, the chain mechanism plays an important role in gas-phase combustion. However, in the same works or in other works of the same authors, the chemical process underlying combustion is represented as a single-step reaction; that is, self-heating is believed to be the only cause of the self-acceleration of the process [17, 18]. The temperature dependence of the specific reaction rate is conventionally expressed in terms of the Arrhenius law:

$$w/[\mathrm{A}][\mathrm{B}] = k^0\exp(-E/RT), \qquad (1)$$

where [A] and [B] are the concentrations of the original reactants, k^0 is the preexponential factor, E is the activation energy, T is temperature, and R is the universal gas constant.

In this formalism, E usually depends on process conditions. Furthermore, k^0 often exceeds the number of binary collisions by one order of magnitude, being in conflict with its own physical meaning.

The widespread statement that calculations neglecting the competition between chain branching and termination provide close fits to experimental data is a way of denying the significance of the chain avalanche. Indeed, this statement is equivalent to the statement that the neglected chain factor plays no role. In fact, good fits between calculated and observed data have been observed only in some particular cases and in a narrow range of process conditions, especially at a large number of input parameters.

Another argument against the significance of the chain avalanche in combustion at any fairly high pressure (when self-heating takes place) is that the temperature dependence of the reaction rate is exponential, obeying the Arrhenius equation, while the concentration dependence of the reaction rate is described by a power-law function [2, 4, 5]. This argument is also encountered in a later publication [19]. However, it has been demonstrated that the power-law concentration dependence of the reaction rate does not mean that the branched-chain reaction is accelerated to a lesser extent by a rising temperature than the ordinary reactions [20–22]. Indeed, while the rate equation of an ordinary reaction (Eq. (1)) includes only the concentrations of the original reactants, which decrease monotonically in the course of the reaction, the rate equation of a branched-chain reaction takes into account the concentration of the reactive intermediate serving as the chain propagator:

$$w = \omega_0 + k_{\mathrm{br}} n[\mathrm{B}], \tag{2}$$

where w is the overall rate of the chain reaction, k_{br} is the rate of the chain branching step, [B] is the concentration of the original molecular reactant, n is the concentration of the chain propagator, and ω_0 is the chain initiation rate (i.e., the rate at which reactive intermediates appear in the reactions involving only the original molecules).

The rate of the change of n is given by the familiar equation [1]

$$\mathrm{d}n/\mathrm{d}t = \omega_0 + (f - g)n, \tag{3}$$

where f and g are the multiplication and loss rates of the chain propagator when its concentration is unity. The rate f is given by

$$f = 2k_{\mathrm{br}}[\mathrm{B}]. \tag{4}$$

If chain branching dominates over chain termination, so that

$$f > g, \tag{5}$$

n and, correspondingly, the overall reaction rate increases progressively because of the positive feedback between n and dn/dt, as is clear from Eqs. (2) and (3). This implies chain ignition.

Since k_{br} is an exponential function of temperature, raising the temperature strengthens the positive feedback between dn/dt and n in an exponential way. This causes an increase in the rate of the avalanche multiplication of the chain propagator. In view of Eq. (3) and the presence of the Boltzmann factor in the expression for k_{br}, the temperature dependence of the concentration of these reactive species obeys a double exponential law [20–22] and, therefore, the rate of the branched-chain process depends on temperature as strongly as the rate of ordinary reactions:

$$w/[\mathrm{B}]n_0 = k_0 \exp\int_{t_0}^{t} [f_0 \exp(-E_{\mathrm{br}}/RT) - g]\mathrm{d}t. \tag{6}$$

Here, [B] is the concentration of the original reactant; t is time; n_0 is the concentration of the chain propagator at the time point t_0, after which the ω_0 value can be neglected; and f_0 is the preexponential factor of the branching factor f, which is equal to

$$f_0 = 2k_2^0[\mathrm{B}]. \tag{7}$$

Expression (6), which is in quantitative agreement with experimental data [23], implies that the rate of branched-chain reactions depends on temperature in an essentially non-Arrhenius way.

The sharp temperature-induced increase in the self-acceleration rate of the multiplication of the chain propagator and the equal increase in the self-acceleration rate of the overall reaction mean indicate that, as self-heating takes place, the role of the chain mechanism in gas-phase combustion increases rather than decreases. Therefore, in the case of self-heating, which is correlated with the chain avalanche by a positive feedback, the avalanche is the determining factor not only at extraordinarily low but also at atmospheric and higher pressures.

Thermal ignition occurs when the following conditions are simultaneously satisfied:

$$q_+ > q_-, \tag{8}$$

$$\mathrm{d}q_+/\mathrm{d}T > \mathrm{d}q_-/\mathrm{d}T, \tag{9}$$

where q_+ and q_- are the heat release and heat removal rates [1–3].

If both of conditions (8) and (9) are satisfied, the rate of heat accumulation in the system increases progressively with rising temperature. This is the thermal explosion regime [1–3]. If combustion proceeds by the branched-chain mechanism and conditions (5), (8), and (9) are satisfied, the thermal explosion takes place along with a chain avalanche [20]. This regime is called chain–thermal explosion [20, 22, 24]. It provides the most favorable conditions for a deflagration–detonation transition.

It follows from Eq. (6) that, in the presence of an inhibitor, which will favor chain termination and, accordingly, increase the value of g, the overall reaction rate w will be lower and less strongly dependent on temperature [22] and inequality (9) will be difficult to satisfy. If the inhibitor concentration is so high that $g > f$, the inhibitor will prevent ignition and combustion will be impossible. These theoretical deductions have been confirmed by experimental data indicating that inhibitors can prevent ignition, diminish the combustion rate of H_2 in a closed reactor [21, 22, 24, 25], prevent the deflagration–detonation transition [21, 26, 27], Combustion properties of propylene and isopropanol

Compound	Q, kJ/mol	LCL	UCL	V, cm/s	β_1	β_2
C_3H_6	2058 ± 15	2.2 ± 0.2	10.5 ± 0.5	50 ± 1	4.5	3.0
iso-C_3H_7OH	2053 ± 15	2.1 ± 0.2	12.8 ± 0.8	50 ± 1	4.5	3.0

and break a stationary detonation wave [28]. In all of these experiments, combustion was locally initiated with a spark or a hot wire at room temperature.

In this study, combustion in the reaction mixture was initiated with a shock wave at various high temperatures. Obviously, the initial temperature determines, to a large extent, the combustion kinetics both in the absence and in the presence of an inhibitor. A shock wave generates a much larger ignition site than a spark or a wire. Our procedure allows one to vary the initial conditions and watch the motion of the combustion zone, which is confined between the pusher gas and the wave front.

Combustion was initiated and developed inside a “plug” of a shock-compressed hot reaction mixture confined between the pusher gas and the front of the initiating shock wave. The object of our study was combustion in the hydrogen–oxygen system. In the free valence multiplication step of this process,

$$H + O_2 = OH^{\bullet} + O, \quad \text{(I)}$$

part of the chemical energy of the system is converted into free-valence energy, which is the most reactive form of chemical energy.

This step is followed by the regeneration and multiplication of reactive species through the reactions

$$OH^{\bullet} + H_2 = H_2O + H, \quad \text{(II)}$$

$$O + H_2 = OH^{\bullet} + H, \quad \text{(III)}$$

which result in chain branching [1, 4, 5]. In the pressure range examined, the reaction

$$H + O_2 + M = HO_2^{\bullet} + M, \quad \text{(IV)}$$

which replaces the H atom with $HO_2^{\bullet}$, a low-reactivity radical, is the main chain-termination channel in the absence of an inhibitor.

Selection of inhibitors. Combustion under the conditions examined is accompanied by a considerable temperature rise, which acts together with the chain avalanche to accelerate the reaction. For this reason, in order to gain deeper insight into the role of chain branching, the competition between chain branching and chain termination in different experiments was controlled using either of two inhibitors with nearly identical combustion properties and different inhibiting activities, namely, propylene and isopropanol. These compounds were chosen for the reason that, as is clear from the table, they are characterized by very similar heats of combustion (Q) [5, 29], flame velocities in air (V), and lower and upper concentration limits (LCL and UCL) of flame propagation (limiting percentages of fuel in the mixture). Furthermore, these compounds require the same O_2 : fuel molar ratios for oxidation to CO_2 and H_2O and to CO and H_2O (the stoichiometric coefficients β_1 and β_2, respectively).

The UCLs of these compounds differ only slightly. However, since the inhibitor concentrations examined are close to the LCLs, this slight difference between the UCLs is of no consequence. The fact that the propylene and isopropanol flame velocities are equal indicates that the combustion rates of these compounds are very similar [2, 9].

Although C_3H_6 and *iso*-C_3H_7OH vapor possess nearly identical combustion properties, their reactions with hydrogen atoms consist of different elementary steps and proceed at different rates. Since the propylene molecule has a π-bond, it can attach a hydrogen atom without having to overcome any significant energy barrier:

$$H + C_3H_6(+M) = C_3H_7^{\bullet}\ (+M). \quad \text{(V)}$$

Here, M is a species capable of taking excess energy from the $C_3H_7^{\bullet}$ radical resulting from this recombination. Reaction (V), which replaces free H atoms with $C_3H_7^{\bullet}$ radicals, is a chain-termination step, because, as compared to free H and O atoms and $OH^{\bullet}$ radicals, $C_3H_7^{\bullet}$ radicals are less capable of regenerating reactive intermediates in H_2 combustion.

At atmospheric pressure, reaction (V) is second-order owing to the high frequency of ternary collisions. The rate constant data reported for this reaction are scattered between $1.13 \times 10^{13}\exp(-820/T)$ [30] and $4.6 \times 10^{14}\exp(-2568/T)$ cm^3 mol^{-1} s^{-1} [31]. Even a comparison of the smallest of these values with the rate constant of reaction (I), which is $1.8 \times 10^{14}\exp(-8350/T)$ cm^3 mol^{-1} s^{-1} [32, 33], suggests that, even at propylene concentrations as low as a few tenths of a percent in the H_2–O_2 mixture, the chain-termination reaction (V) competes effectively with the branching reaction (I).

Unlike reaction (V), the reaction between H atoms and isopropanol, whose molecule has no π-bonds, proceeds through H detachment:

$$H + C_3H_8O = H_2 + C_3H_7O^{\bullet}. \quad \text{(VI)}$$

Again, the replacement of hydrogen atoms with low-reactivity radicals leads to chain termination. How-

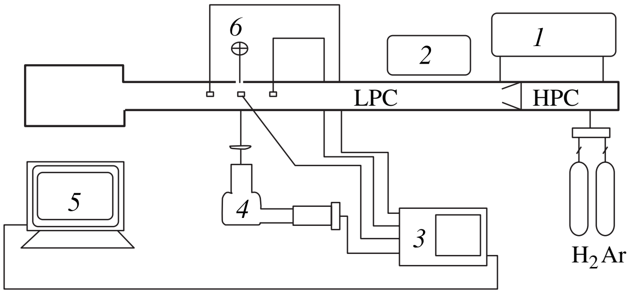

Fig. 1. Experimental setup: (*1*) fore pump, (*2*) gas mixer, (*3*) four-beam oscilloscope, (*4*) grating spectrograph with a photomultiplier, (*5*) computer, and (*6*) xenon lamp.

ever, since the detachment of an H atom from the isopropanol molecule requires the breaking of a σ-bond, the energy barrier in this reaction (≅33 kJ/mol [3, 34, 35]) is much higher than the energy barrier in reaction (V). As a consequence, at equal propylene and isopropanol vapor concentrations, reaction (VI) is much slower than reaction (V).

Aside from differently reacting with hydrogen atoms, propylene and isopropanol are oxidized via different mechanisms and, therefore, show different inhibiting efficiencies. Reaction (II) is followed by the fast reaction

$$C_3H_7^{\bullet} + O_2 = C_3H_7O_2^{\bullet}. \qquad \text{(VII)}$$

Most of the $C_3H_7O_2^{\bullet}$ radicals undergo isomerization followed by the decomposition reaction

$$C_3H_7O_2^{\bullet} = C_3H_6 + HO_2^{\bullet}, \qquad \text{(VIII)}$$

which regenerates propylene [36–39].

The formation of the $HO_2^{\bullet}$ radical by the reaction between the alkyl radical and O_2 was observed directly in a hydrocarbon-inhibited hydrogen flame by laser magnetic resonance (LMR) [38, 39]. In this experiment, introducing a small amount of an inhibitor into the hydrogen flame caused a decrease in the combustion rate and in the concentrations of H and O atoms and $OH^{\bullet}$ radicals (which were measured by EPR spectroscopy) and an increase in the $HO_2^{\bullet}$ concentration.

Unlike the propyl radical, the $C_3H_7O^{\bullet}$ radical, which forms by reaction (VI), has an O atom and, therefore, reacts by a mechanism that does not yield a regenerable compound with a π-bond. As a consequence, the intermediates resulting from the oxidation of $C_3H_7O^{\bullet}$ are less effective inhibitors than propylene.

Thus, because reaction (V) is faster than reaction (VI) and a considerable proportion of propylene is regenerated, this compound markedly slows down the combustion process. This was demonstrated by experimental studies of the initiation of combustion in a constant-volume reactor at room temperature [40]. It was expected that the difference between propylene and isopropanol would also manifest itself as different effects on the initiation and development of detonation and on the initiation of combustion in mixtures preheated to a high temperature.

EXPERIMENTAL

Combustion was studied in a shock tube with an inner diameter of 5.7 cm. The experimental setup included a vacuum system, a gas mixing system, a gas admission system, equipment for measuring the shock wave velocity and pressure profiles, and emission and absorption spectroscopic units (Fig. 1). The shock tube consists of a 1-m-long high-pressure chamber (HPC) and a 3.9-m-long low-pressure chamber (LPC) separated by a membrane. The LPC served as the reactor, and the HPC was filled with a pusher gas (30–55 atm). Once the membrane was broken, a shock wave propagated in the LPC, compressing and heating the gas to be examined. The shock wave was pumped with a fore pump to a residual pressure of ≈1 Pa. The rate of air inleakage because of the faulty sealing of the system did not exceed 10^{-2} Pa/min. The error in the amount of gas admitted into the tube was 0.5%. Combustion was studied in the stoichiometric hydrogen–oxygen mixture (18%) diluted with helium either in the absence or in the presence of propylene or isopropanol vapor (0.7–3.8%). The mixture was prepared by introducing appropriate partial pressures of the components into a sealable stainless-steel mixer of volume 40 l. In this procedure, we used an IPDTs-1 digital pressure gage, which allowed the mixture to be prepared with an accuracy of 0.1 vol % or higher.

Helium was used as the diluent because, for easier observation of the initial stage of ignition and of the onset of detonation, it was necessary that the Mach number be relatively small and the gas temperature be not very high at a sufficiently high velocity of the initiating shock wave. In most runs, the initial gas pressure in the LPC was 6×10^3 Pa. The pusher gas in the HPC was hydrogen at a pressure of 30–55 atm. The velocity of the initiating shock wave was varied between 2.3 and 3.5 km/s, and the corresponding Mach numbers were 2.8–4.6. The shock front temperature and pressure were 900–1900 K and 0.6–1.2 atm, respectively. For fine adjustment of the parameters of the initiating shock wave, we either added argon (1–2 atm) to the HPC gas or varied the initial vacuum in the HPC. Gas parameters in the shock front were calculated from the observed shock velocity and initial mixture parameters for each particular run using the Gaseq program. Furthermore, this program allowed detonation parameters to be calculated using the Chapman–Jouguet model.

Shock velocity and pressure were measured with piezoceramic resonator units with a resonance frequency of 300 kHz and a sensing element diameter of 0.1 cm. These units were built in the tube wall at 5 cm each way from the observation cross section. Their sensitivity was ~0.3 V/atm. At the observation cross section, there were quartz windows for admitting and letting out optical radiation and an extra piezoelectric sensor for monitoring gas pressure in this cross section. The signals from the piezoelectric sensors were received by a TEKTRONIX TDS-3014 four-beam digital oscilloscope (passband frequency 100 MHz) connected to a PC. The shock velocity measurement error was <1% and arose mainly from the measurement error in the distance between the piezoelectric sensitive elements.

Radiation from the gas in the observation cross section after the passage of the shock front was focused on the entrance slit of an MS-300 grating spectrograph with a focal length of 30 cm and was detected with an FEU-100 photomultiplier mounted in the back focal plane of the spectrograph. Chemiluminescence was measured at a wavelength of 306.4 nm in a spectral range of 10 nm, which covered the frontal part of the emission band of the electronically excited radical $OH^{\bullet}$ ($A^2\Sigma^+$). To determine the actual length of the "plug" of the shock-heated gas, we recorded the time-base sweep of the Schumann–Runge absorption band at $\lambda = 227$ nm.

RESULTS

Ignition and Detonation of the 18% ($2H_2 + O_2$) + 82% He Mixture

Figure 2 displays the time-base sweep traces of the radiation from $OH^{\bullet}$ radicals (curve *1*) and of the signal from the pressure sensor located at the same cross section (curve *2*). Each panel pertains to one run (one "shot" in the shock tube). Different combustion regimes (including combustion–detonation transition), which were identified at the observation cross section, were established by slightly varying the velocity of the initiating shock wave (V_{sh}). The maximum change of wave velocity in these runs was ≈0.08 km/s at a mean wave velocity of 2.43 km/s. The gas velocity (V_g) behind the shock front was 1.6–1.7 km/s, and the temperature and pressure were calculated to be ≈940 K and 0.6 atm (in the figures, the signal amplitudes are expressed in volts).

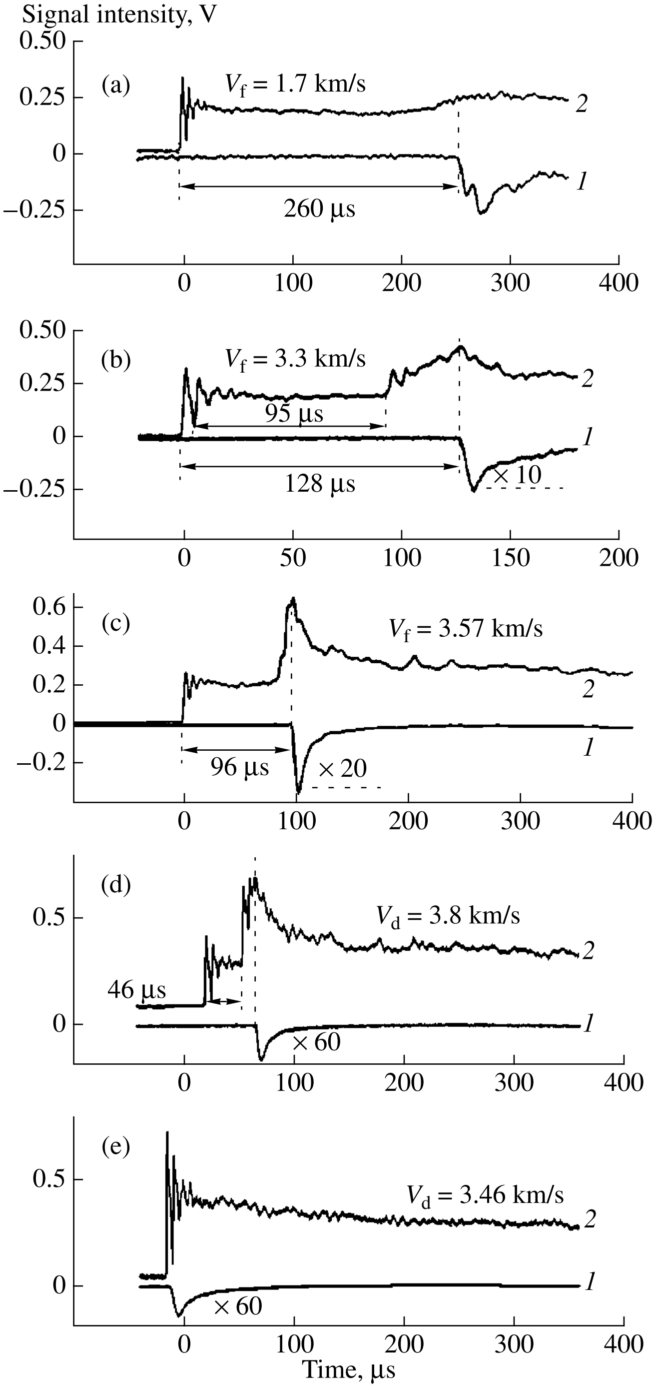

Fig. 2. Time dependence of the properties of the flame in the 18% ($2H_2 + O_2$) + 82% He mixture under various initial conditions: (*1*) radiation from $OH^{\bullet}$ radicals and (*2*) pressure. V_f is the flame velocity in the hot gas, and V_d is the detonation velocity in the hot gas.

In all of the panels of Fig. 2, one can see radiation signals from the electronically excited radical $OH^{\bullet}$, which are evidence of the ignition of the mixture. The oscillograms from the piezoelectric sensor in the observation cross section show two pressure rise points. The abrupt pressure rise at the beginning of the sweep trace indicates the arrival of the shock wave at the observation cross section (the high-frequency oscillations arise from the transient process in the piezoelectric sensor). The second pressure rise occurs simultaneously with the onset of radiation from $OH^{\bullet}$ radicals and indicates a densification in the combustion zone propagating towards the front of the initiating shock wave. Clearly, the pressure peak profile in the reaction zone is progressively sharpened as the pressure peak approaches the shock front. Initially, the combustion zone is drastically accelerated relative to the gas flow. At a delay time of

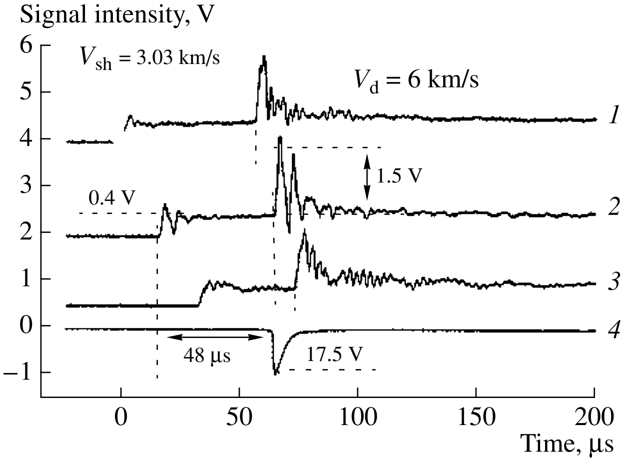

Fig. 3. (*1–3*) Pressure and (*4*) 306.4 nm radiation oscillograms for the flame in the 18% ($2H_2 + O_2$) + 1.9% C_3H_6 + 80.1% He mixture obtained from three sensors.

260 μs between the radiation front and the initiating shock wave (Fig. 2a), the velocity of the pressure peak relative to the gas flow is ~0.05–0.08 km/s. At a delay time of 130 μs (Fig. 2b), this relative velocity is 1.64 km/s. At a delay time of 46 μs, it is as high as 2.1 km/s (Fig. 2d). Under these conditions and a flow temperature of 940 K, the speed of sound in the mixture is 1.5 km/s. At this temperature, a supersonic combustion wave is formed before it reaches the initiating shock front (Fig. 2d) and merges with it (Fig. 2e). Calculations have demonstrated that, at higher temperatures, supersonic combustion in the mixture containing 1.9% propylene changes to detonation. The formation of a detonation wave before the merging of the combustion and initiating shock fronts is clearly illustrated by Fig. 3.

The mean velocities of the initiating shock and combustion waves over the 10-cm-long section including the observation cross section were derived from the oscillograms from the three piezoelectric sensors (Fig. 1). This allowed us to control the shock and combustion velocities in this section.

The data presented in Fig. 4 (points *1*) illustrate the correlation between the flame velocity (V_f) and ignition delay time. Furthermore, Fig. 4 plots V_{sh} (points *2*), the corresponding temperature (T), and the calculated gas velocity behind the shock front (V_g). The constancy of calculated V_{sh} in all runs represented in Fig. 4 (points *2*) is evidence that the measurements are very accurate and quantitatively reproducible. It follows from Fig. 4 that, at short ignition delay times, the combustion wave initially moves with acceleration. After exceeding the speed of sound, it moves with a nearly constant velocity up to the nearest proximity of the initiating shock front. The velocity of the initiating shock wave was nearly the same in all runs. At a distance of 1–5 μs from the shock front, the velocity of the joint wave shows chaotic fluctuations not correlated with the ignition delay time.

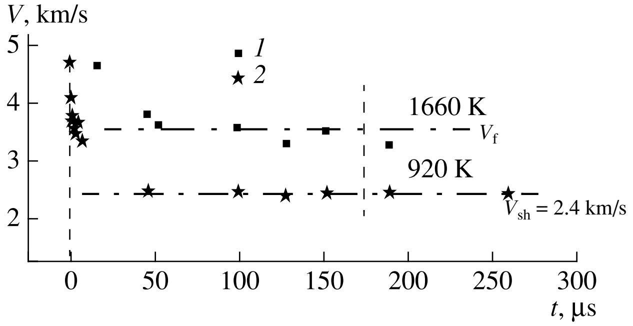

Fig. 4. (*1*) Flame velocity V_f and (*2*) initiating shock velocity V_{sh} for various ignition delay times.

Comprehension of the ignition, combustion, and detonation of the H_2–O_2 mixture containing no inhibitor allowed us to elucidate the effects of propylene and isopropanol vapor on these processes.

Effects of Propylene and Isopropanol on the Combustion of the Hydrogen–Oxygen Mixture

In the mixtures containing propylene or isopropanol vapor, the amount of helium was reduced so that the molar concentration of the stoichiometric mixture $2H_2 + O_2$ remained unchanged. Experiments have demonstrated that small amounts of propylene are effective inhibitors of the combustion of the hydrogen–oxygen mixture. For example, no ignition is observed at an initiating shock velocity of 2.4 km/s and a propylene concentration of 0.7%. At the same shock velocity and shock front temperature (940 K) and pressure (0.6 atm), the mixture containing no propylene ignites with a well reproducible intensity. To ignite the mixture containing 0.7% propylene, the velocity of the initiating shock wave has to be increased to 2.74 km/s. The corresponding shock front temperature and pressure are 1140 K and 0.84 atm. As the propylene concentration is further raised, progressively higher temperature and pressure are required to ignite the hydrogen–oxygen mixture. For example, at C_3H_6 concentrations of 1.5 and 2.5%, the initiating shock velocity should be increased to 3.02 and 3.07 km/s, respectively (Fig. 5). The corresponding minimum ignition temperatures are 1320 and 1415 K, and the corresponding pressures are 1.00 and 1.15 atm.

Provided that the initiation temperature is appropriately increased, the deflagration–detonation transition in the hydrogen–oxygen mixture is also observed in the presence of small amounts of an inhibitor (Figs. 3, 6). As would be deduced from the retarding effects of inhibitors, an inhibitor diminishes the detonation velocity if the other conditions are equal. Furthermore, an inhibitor lengthens the deflagration–detonation transition delay. This is evident from a comparison of the oscillograms presented in Figs. 2e and 3. In the propy-

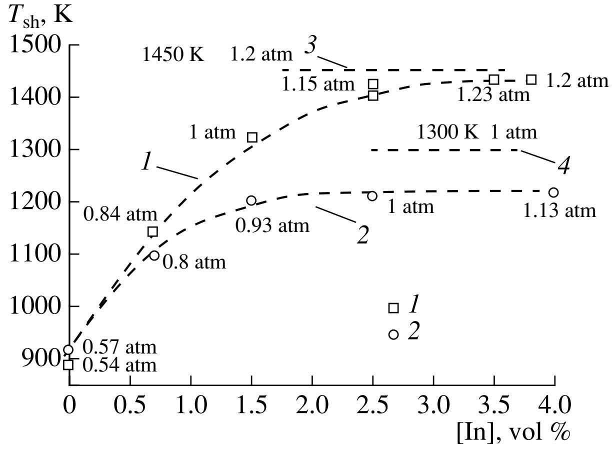

Fig. 5. Minimum ignition temperature of the 18% ($2H_2$ + O_2) + 82% He mixture in the shock wave as a function of inhibitor concentration: (*1*) C_3H_6 and (*2*) *iso*-C_3H_7OH. The ordinates of horizontal lines *3* and *4* are the minimum ignition temperatures of propylene and isopropanol, respectively, in the absence of hydrogen.

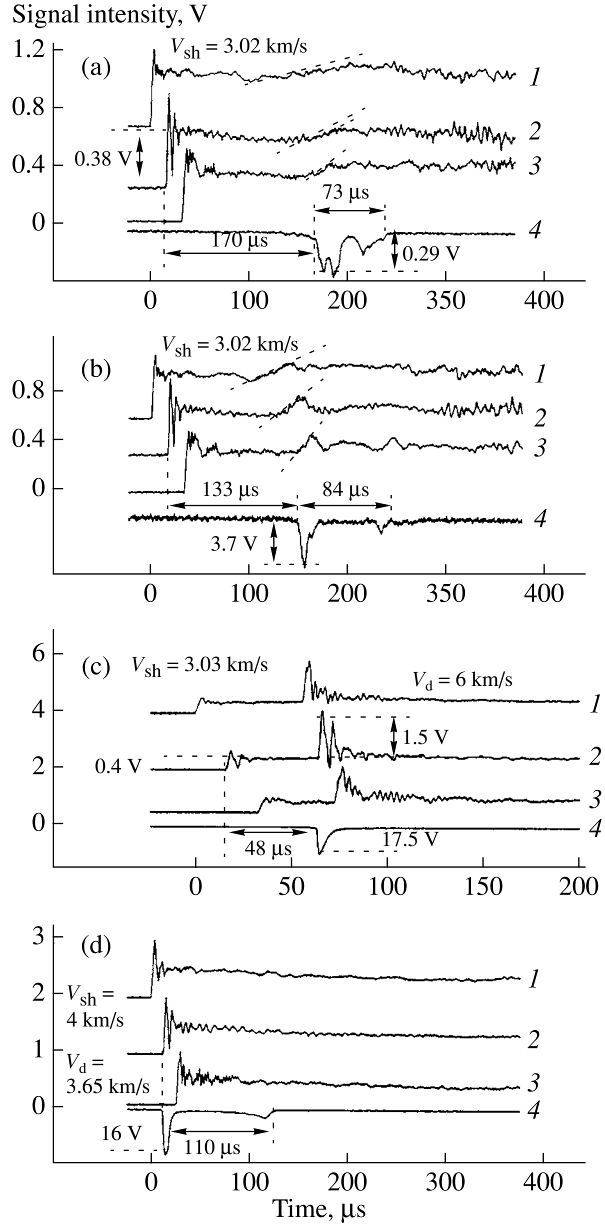

Fig. 6. Development of detonation in the 18% ($2H_2$ + O_2) + 1.9% C_3H_6 + 80.1% He mixture monitored using three sensors: (*1–3*) pressure and (*4*) 306.4 nm radiation. The initiating shock velocity V_{sh} increases in passing from (a) to (d). V_d is the detonation velocity in the hot gas.

lene-free mixture (Fig. 2e), the detonation wave is sufficiently fast to catch up and merge with the shock wave. In the mixture containing 1.9% propylene (Fig. 3), the detonation wave lags behind the shock wave, although the initial temperature of this mixture is somewhat higher than that of the inhibitor-free mixture.

In the mixtures with an inhibitor concentration of 1.9% or above, there is no detonation at initiating shock velocities below 3.0 km/s. For a deflagration–detonation transition, it is necessary to raise the temperature and pressure by increasing the velocity of the initiating shock wave. The detonation occurring at these increased temperatures and pressures is more intensive than the detonation occurring in the inhibitor-free mixture at a lower initial temperature and pressure (Fig. 6). Each panel of Fig. 6 corresponds to a particular value of V_{sh}. Here, the intensifying effect of temperature is stronger than the retarding effect of the given amount of inhibitor. Further increasing the inhibitor concentration prevents detonation at this temperature. For example, at a propylene concentration of 3.5%, there is no deflagration–detonation transition up to an initial temperature of 1800 K; that is, at these propylene concentrations and initiating shock velocities, the mixture does ignite, but no detonation takes place and combustion proceeds slowly and does not reach a supersonic velocity. The radiation signal and pressure peak corresponding to the reaction zone are flattened and diffuse, and their amplitude is reduced by a factor of 10–50 (Fig. 7). For the combustion wave to overcome the sonic barrier and catch up with the initiating shock wave at the observation cross section, the shock velocity should be increased from 3.07 to 3.50 km/s, at which the shock front temperature will be above 1800 K (Fig. 6d).

It has been demonstrated by special experiments that, in mixtures in which 3.5% propylene is replaced with 3.5% argon, a gas with nearly the same molecular weight, combustion and combustion–detonation transition occur at the same low shock velocities and temperatures as in the original, propylene-free mixture. Therefore, the retarding effect of propylene on the combustion and detonation of hydrogen–air mixtures is due to the enhancement of chain termination. The nonchemical factors are of little, if any, importance.

Our results indicate that, in the laboratory coordinate system, the detonation velocity in the "plug" (≈6 km/s) is well above the velocity of the merged

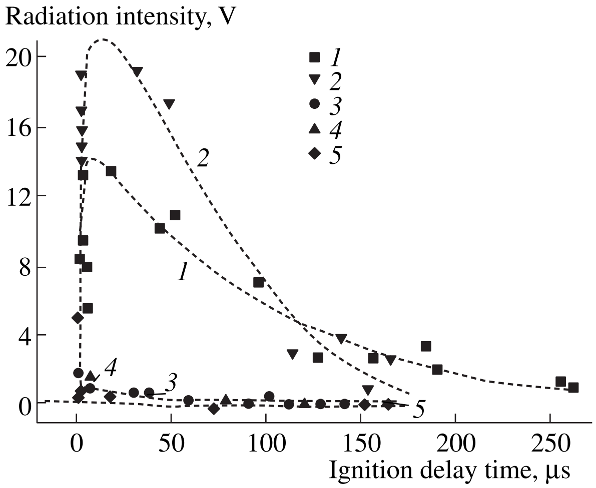

Fig. 7. Intensity of radiation from the radical $OH^{\bullet}$ ($A^2\Sigma^+$) as a function of ignition delay time for the 18% ($2H_2 + O_2$) + He mixture in the presence of (*1–4*) C_3H_6 and (*5*) *iso*-C_3H_7OH. The inhibitor concentrations are (*1*) 0, (*2*) 1.9, (*3*) 3.8, and (*4*, *5*) vol %.

wave (≈4 km/s). In this wave, detonation catches up with the shock wave, because the gas temperature and pressure are higher in the plug than before the plug.

Isopropanol admixtures act in qualitatively the same way as propylene admixtures. However, the retarding effects of isopropanol vapor on ignition and deflagration–detonation transition are considerably weaker, as would be expected from the different inhibiting powers of propylene and isopropanol. As is clear from Fig. 5, at equal concentrations of these inhibitors, hydrogen ignition in the presence of isopropanol vapor requires much lower temperatures. Another difference between the inhibitors is in the way in which their inhibiting power depends on temperature (see below). Furthermore, as the inhibitor concentration is increased, the ignition temperature grows at a progressively decreasing rate and tends to some limit, which is ~1450 K for propylene and ~1300 K for isopropanol.

DISCUSSION

According to the above data, small amounts of propylene and isopropanol vapor retard all regimes of hydrogen–air combustion initiated by a shock wave at elevated temperatures. They can prevent combustion, raise the minimum ignition temperature, lengthen the ignition delay, reduce the intensity of combustion, lengthen the induction period preceding the deflagration–detonation transition, and prevent detonation under the experimental conditions examined. None of these effects can be explained without assuming the chain avalanche to be the determining factor in ignition.

The retarding effect of the admixtures on H_2 combustion cannot be explained on the assumption that oxygen is consumed in the oxidation of these admixtures and no reactive intermediates resulting from hydrogen combustion are involved in this reaction [41]. This assumption stems from the denial of the branched-chain mechanism of hydrogen combustion and is in conflict with numerous earlier findings and with the results of this study. Indeed, when the ignition of the hydrogen–air mixture is prevented by propylene, the components are not consumed and, therefore, the oxidizer cannot be deficient. Neither can this hypothesis explain the effect of the admixtures on the H_2 combustion intensity. It has been demonstrated by a special series of experiments that a mixture containing helium instead of hydrogen (6% O_2 + 3.5% C_3H_6 + 90.5% He) does not ignite below 1450 K. At the same time, even lower concentrations of propylene retard combustion throughout a temperature range of 940–1400 K; that is, the small propylene concentrations examined in this study retard combustion and detonation even well below the ignition temperature of propylene at these concentrations. Furthermore, isopropanol vapor retards hydrogen combustion less strongly than propylene, although these compounds have the same combustion properties.[1]

The retardation of the ignition, combustion, and detonation of the hydrogen–oxygen mixture cannot be explained by the fact that propylene increases the heat capacity of the mixture. Indeed, 0.7% propylene cannot increase the heat capacity so that the ignition temperature is increased by 240 K. As is demonstrated in this study, a much large isopropanol concentration is required to prevent the ignition of the same hydrogen–oxygen mixture under the same conditions, although isopropanol vapor somewhat exceeds propylene in heat capacity.

The observed effects of the small propylene and isopropanol admixtures on hydrogen combustion can readily be explained if the branched-chain mechanism of the process is taken into account. In an H_2 flame, propylene and isopropanol are consumed only by reacting with hydrogen combustion intermediates, primarily through reactions (V) and (VI), which cause chain termination. If, as a consequence, g increases so as to invert inequality (5), which represents the chain combustion condition, then ignition will be impossible. If g increases not so greatly as to invert inequality (5), it will nevertheless diminish the integrand in expression (6) for the process rate. Since this integrand appears in the exponent, the reaction heat release rates decrease exponentially and the combustion slows down. Furthermore, a decrease in the integrand of expression (6) will cause a decrease in dw/dT, which is the measure of the temperature dependence of the reaction rate. This will make it difficult to satisfy the chain–thermal explosion

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[1] A more detailed analysis of the mistakes made in [41] is presented in [42].

condition (Eq. (8)) and will, therefore, be unfavorable for a deflagration–detonation transition.

Figures 7 and 8 plot the maximum luminescence intensity and the increase in pressure in the pressure oscillogram, respectively, versus the propylene or isopropanol vapor content of the mixture. The amplitudes of these quantities decrease sharply as the propylene or isopropanol concentration is increased to 3.5–4.0%. This is further evidence that the deflagration–detonation transition is retarded. At the same time, these results demonstrate that the effects of propylene and isopropanol are by no means due to the oxygen-consuming reactions of these admixtures that are independent of hydrogen combustion. If O_2 had been consumed at an appreciable rate not only in its reaction with H_2 but also in inhibitor oxidation involving no hydrogen oxidation intermediates, then the inhibitor would have intensified combustion by giving rise to a parallel oxygen-consuming reaction. In fact, the inhibitors retard combustion from its very onset. In agreement with relationships (5), (6), and (9), a smaller amount of inhibitor is required for preventing a transition from thermal combustion to chain–thermal explosion or from deflagration to detonation than for preventing a chain ignition.

Let us turn to the effect of temperature. Since the activation energy of chain branching is higher than the activation energy of chain termination, f grows more rapidly than g as the temperature is raised, so if the chain ignition condition (5) has been violated by the presence of an inhibitor, it will be satisfied again. Therefore, a mixture that cannot ignite at a given temperature because of the presence of an inhibitor will ignite on increasing the initiating shock velocity and, accordingly, the mixture temperature. Furthermore, as follows from Eq. (6), raising the initial temperature causes an increase in f and thereby increases dw/dT. This favors the satisfaction of condition (8). These circumstances are believed to be favorable for a transition from combustion to chain–thermal explosion and for the onset of detonation, and this notion has been verified experimentally. Transition from combustion chain–thermal explosion causes a further increase in temperature through the adiabatic (or quasi-adiabatic) compression of the mixture by adjacent gas layers, which expand when burning.

As the temperature rises, the difference between the rate constants of chain branching and chain termination (which involves the inhibitor) decreases. This weakens the dependence of the ignition temperature on the inhibitor concentration (Fig. 5). The effect of inhibitor combustion comes into play at very high temperatures. The fact that the minimum ignition temperature of the H_2–O_2 mixture is higher in the presence of C_3H_6 than in the presence of *iso*-C_3H_7OH vapor is explained by the higher inhibiting power of propylene.

Further investigation is necessary to understand why the ignition temperature of isopropanol is lower than that of propylene in the absence of hydrogen (Fig. 5). Here, we only note that the concentration limit and flame velocity data listed in the table refer to the initiation of combustion at room temperature. By contrast, the results presented in Fig. 5 refer to initial temperatures of 1300 K and above, at which the ratio of flame velocities may be different because of another reaction mechanism.

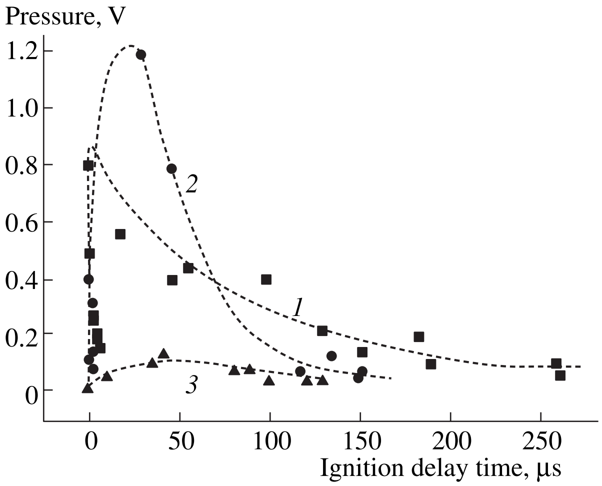

Fig. 8. Height of the pressure peak in the oscillogram as a function of ignition delay time for the 18% $(2H_2 + O_2)$ + He mixture containing (*1*) 0, (*2*) 1.9, and (*3*) 3.8 vol % C_3H_6.

As to the denial of the role of branched chains in combustion and explosion at atmospheric pressure and above, we would like to note the following. The conventional notion of the effect of antiknock agents on the combustion of hydrocarbon fuels is based on the hypothesis that these agents prevent the accumulation of molecular intermediates involved in the degenerated branched-chain process, primarily peroxides and aldehydes, whose reactions cause an explosion once their critical concentration is reached [3–5, 43, 44]. Reaction chains do not branch in degenerated branched-chain processes (see, e.g., [1, 38, 45, 46]). In these processes, which occur at temperatures not exceeding the range of so-called cold flames (below 600 K), there is only a very slow buildup of unbranched chains owing to the initiation of these chains in reactions involving molecular intermediates. Therefore, degenerated branched-chain reactions simulate branched-chain processes, but they proceed at extremely slow rates. Their characteristic time may be many tens of seconds or even minutes counted from the end of the induction period. The rate and self-acceleration of these chain reactions are so low that they alone cannot cause an ignition or explosion. In view of this, it is believed that antiknock agents prevent the explosion of hydrogen fuels that could be caused by the self-heating resulting from fast exothermic reactions of above-critical amounts of molecular intermediates (primarily peroxide decomposition). Thus, the explanation of the effect of antiknock agents was based on the hypothesis that the thermal explosion is prevented through the termination of unbranched chains, a decrease in the chain initiation rate, and, accordingly, prevention of the establishment of the critical peroxide concentration. The role of chain branching in combustion was denied, except for extremely low pressures, at which the reaction is accompanied only by a slight, if any, self-heating of the system.

The above data demonstrate that the competition between chain branching and chain termination is the determining factor in all of the regimes of hydrogen–air combustion (a model process), including the strong initiation by a shock wave, no matter what the initial gas temperature. Therefore, varying the rates of the competing reactions by introducing small amounts of reactive components enables one to effectively control the initiation and development of combustion, including the combustion-to-detonation transition in a propagating shock wave in the absence of peroxides or aldehydes. Furthermore, the above data suggest that, because of the crucial role of the chain avalanche in gas-phase combustion and detonation, the correlation between chemical structure and reactivity manifests itself in the fact that changing a single functional group in the admixture molecule exerts a strong effect on the kinetics, macrokinetics, and gas dynamics of the overall combustion process.

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