Effect of the Molecular Structure of Olefin Admixtures on the Combustion and Explosion of Hydrogen–Air Mixtures

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Abstract—Small admixtures of propylene, hexene, and isobutylene efficiently inhibit the combustion and explosion of hydrogen–air mixtures at an initial pressure of 1 bar. The inhibition effect depends on the chemical properties of the admixture. The difference between the effects produced by inhibitors manifests itself in all combustion parameters. Since the chain avalanche plays the determining role in combustion, the inhibition efficiency depends on both the length and the structure of the hydrocarbon chain in the inhibitor molecule. Taking into account the competition between the branching and termination of reaction chains and the correlation between the molecular structure and reactivity of the admixture makes it possible to explain and describe all of the observed regularities of combustion.

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Sensitivity to small amounts of reactive admixtures is among the most important features of chain combustion. Theoretical science shows increasing interest in this phenomenon, because reactive admixtures enable the researcher to distinguish and study the role of the chain avalanche in combustion under gas self-heating conditions [1, 2]. Such admixtures make it possible to knowingly vary combustion parameters without changing any gas kinetic or thermal parameter of the reacting gas mixture. This highlights the chemical factors determining the kinetics of the process. Furthermore, reactive admixtures are of applied interest as means of combustion and explosion control.

The purpose of this study is to elucidate the dependence of the combustion and explosion of hydrogenair mixtures on the molecular structure of the inhibitor (In).

Until recently, very little attention was given to the inhibition of combustion accompanied by self-heating. The main reason for this neglect was the imperfection of combustion theory, which generally disregarded the crucial role of the avalanche multiplication of reactive intermediates in a reaction mixture undergoing selfheating, as is the case in practical applications.

The progressive self-acceleration of the chemical reaction responsible for combustion can arise from two radically different factors. One is a positive feedback between the self-heating rate of the reaction mixture and the temperature. Ignition due to self-heating will take place if the following two conditions are satisfied

$$q_+ > q_-, \tag{1}$$

and, as the temperature increases, heat generation accelerates more rapidly than the heat dissipation rate,

$$\mathrm{d}q_{+}/\mathrm{d}T > \mathrm{d}q_{-}/\mathrm{d}T,\tag{2}$$

where T is temperature [3, 4]. Ignition and combustion caused by self-heating are conventionally called thermal ignition and combustion.

The other factor that can cause ignition and combustion is the avalanche multiplication of reactive intermediates (free atoms and radicals) in their multiply recurring reactions with initial reactants and sometimes with one another [3–7]. The multiply alternating regeneration and multiplication of reactive intermediates form a branched reaction chain. Ignition and combustion caused by a chain avalanche are called chain ignition and combustion. The rate of a developed chain combustion reaction is given by

$$W = k_{\rm p}[\mathbf{B}]n,\tag{3}$$

where [B] is the concentration of the initial reactant B, n is the concentration of the reactive intermediate, and k_p is the rate constant of the rate-limiting step of the consumption of B.

The rate of change of n is given by the following equation, which was validated against isothermal chain combustion data:

$$dn/dt = \omega_0 + (f - g)n, \tag{4}$$

simultaneously: the heat generation rate (q_+) exceeds the heat dissipation rate (q_-) ,

[†] Deceased.

where *t* is time and ω_0 is the rate of generation of reactive species in the reactions involving only initial reactants [3, 7].

The chain ignition condition is that the chain branching rate exceeds the chain termination rate:

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

where f and g are, respectively, the chain branching and termination rates at a reactive species concentration equal to unity [3].

Until recently, chain combustion kinetics were studied only at pressures hundreds of times lower than atmospheric, at which reaction mixture could undergo only a slight, if any, self-heating. The theory of branched-chain processes was limited to isothermic processes (see, e.g., [3, 7]). At higher pressures such that self-heating is significant, the role of the chain avalanche in the initiation and development of combustion was usually ignored and the self-heating was regarded as the only factor responsible for ignition and combustion (see, e.g., [3–13]). Even at present, the chemical process is conventionally treated as a single-step reaction when deriving analytical expressions relevant to combustion. The temperature dependence of the reaction rate is expressed in terms of an Arrhenius-like function. Although kinetic networks used in the numerical simulation of combustion sometimes abound with insignificant reactions, they often include reactions that can indeed constitute a reaction chain. However, in any case, the roles of the chain and thermal factors are not considered or, if the gas pressure is above several kilopascals, implying significant self-heating, ignition and combustion are regarded as resulting from a thermal avalanche rather than a chain avalanche (see, e.g., [14– 16]). The authors of some publications recognize the importance of the chain mechanism in combustion accompanied by self-heating. However, in the same or subsequent publications by the same authors, the reaction is written as a single step and, accordingly, ignition and explosion are considered to result only from progressive temperature growth. In encyclopedias, monographs, treatises, and nearly all articles dealing with chemical kinetics, the pressure range corresponding to the branched-chain mechanism of ignition and combustion is limited to pressures tens or hundreds of times lower than atmospheric (see, e.g., [3–10, 13–18]). Furthermore, the chain mechanism of the process is not taken into account in some works devoted to gas combustion under filtration conditions [19, 20].

The role of the chain avalanche is frequently denied by stating that the data calculated with neglect of the chain branching and termination reactions are in agreement with experimental data (see, e.g., [12, 13, 19– 21]). Obviously, this statement is equivalent to the statement that the neglected chain factor is insignificant. However, reaction networks ignoring the chain mechanism and calculations based on these false networks are incapable of explaining some basic features of combustion, including the autocatalysis phenome-

non. Such calculations can agree with an experiment only with respect to some particular features of combustion and only if they use empirical input data obtained in the same experiment under similar conditions. As was demonstrated in an earlier paper [2], the rate constants thus calculated are usually physically implausible. In this connection, it is noteworthy that some authors [19, 20] represent the oxidation of H_2 and CO as stoichiometric, single-step, trimolecular reactions involving only the initial compounds and the ultimate products, ignoring the chain mechanism of these processes. This representation implies that the selfacceleration of a reaction can be due only to self-heating. Furthermore, empirical second-order "rate constants" were assigned to both of the above overall reactions [19, Tables 1, 2], and it was stated that this model is in good agreement with experimental data. Kostenko et al. [21] suggest that the ignition condition for a gas mixture should be defined as the temperature at which the heat generation rate is equal to the heat dissipation rate. Thus, contrary to the principles of combustion theory, Kostenko et al. [21] equate the self-heating condition with the ignition condition. Furthermore, it is suggested the heat generation rate be described in terms of a first-order rate equation [21, Eq. (4)] and the Arrhenius law, although this formalism is inapplicable to the chain process, including its heat generation kinetics, because it is functionally inadequate for describing the chain combustion of H_2 and CO.

Some authors [22, 23] came to the point of stating that self-heating is not unnecessary for ignition, thus denying the basic principle of the theory of branchedchain processes.

The denial of the significance of the chain avalanche in combustion accompanied by self-heating is sometimes substantiated by noting that the reaction rate is an exponential function of the gas temperature and only a power-law function of the concentrations (see, e.g., [4-6]).

However, it was demonstrated that, as the temperature rises, the significance of the chain avalanche increases rather than decreases [24, 25]. It was emphasized that the specific chain branching rate (f) increases exponentially as the temperature increases. As this takes place, the specific chain termination rate (g) increases much more slowly. In the case of trimolecular chain termination, g even decreases slightly. As a consequence, the difference f - g, which determines the feedback between dn/dt and n according to Eq. (4), grows sharply as the temperature increases. This causes a further speedup of the accelerating multiplication of active species and results in a more rapid increase in the rate of the overall chain process (W).

Furthermore, it was demonstrated that, even if there is no quadratic-law chain branching, chain ignition and combustion can still occur in a reaction mixture undergoing no self-heating and even in a mixture being monotonically cooled [2]. If the reaction proceeds by a branched-chain mechanism, ignition can be caused only by a chain avalanche. A fundamental feature of branched-chain processes is that, outside the ignition region, even near the third limit, the reaction rate is negligible and the characteristic reaction time is one order of magnitude longer than the characteristic time of heat dissipation from the reactor. Accordingly, the self-heating of the reaction mixture does not exceed a few kelvins and can by no means cause thermal ignition. At the same time, even at such a low extent of self-heating, the chain branching rate can exceed the chain termination rate under these conditions, because f depends more strongly on temperature than g. The change of the sign of the difference f - g from negative to positive causes chain ignition, which always happens earlier than thermal ignition. The thermal avalanche condition (2) is met only in highly developed chain combustion [2, 24].

It was noted in earlier publications [2, 25] that gasphase combustion has numerous features inexplicable in terms of the conventional thermal theory of combustion. These include the above-noted strong effect of small admixtures on ignition, the absence of correlation between the heat of combustion and the combustibility of a given substance, and the hysteresis of the concentration limits of flame propagation.

These and other phenomena that were not explained by thermal theory have recently been adequately explained by accepting the key role of the competition between chain branching and termination [1, 2, 25].

By varying the rates of the competing branching and termination reactions using small admixtures of certain types, it is possible to control combustion, explosion, and detonation of gases, for example, hydrogen and carbon monoxide [1, 2, 25-29]. Inhibitors with similar heats of combustion and combustion properties may exert different effects, depending on their chain termination capacity. This was demonstrated by examining propylene versus isopropanol [28]. These compounds were found to act via different mechanisms and at different rates. These differences arise from the fact that, as distinct from isopropanol, propylene has a π -bond and is regenerated during H₂ oxidation. Allyl alcohol and isopropanol vapors also show different inhibition efficiencies because of the presence of a π -bond in the former and the absence of such a bond in the latter [29].

In this study, we chose to examine different olefins since chain processes primarily involve the π -bond because of its high reactivity. Therefore, any difference in the inhibiting capacity can arise only from the π bond being in different positions in the molecule. This difference should be used as a measure of the sensitivity of combustion to this structural property of small admixtures.

EXPERIMENTAL

Reactions were carried out in an airtight, cylindrical, stainless-steel reactor 12.6 cm in diameter and 25.2 cm in height. The components were mixed in the reactor using a partial pressure–based method with an accuracy of 0.5% for the H_2 and air concentrations and 4% for the inhibitor concentration. The components were admitted into the reactor in the following order: small admixture, hydrogen, and air. The initial mixture pressure and temperature were 1.0 bar and 293 K, respectively. The mixture was spark-ignited at the lower end of the reactor after the time necessary for the perfect mixing of the components (20 min). The spark energy could be varied. In most runs, it was 3.6 J.

The gas pressure and luminescence were recorded simultaneously starting at the ignition point up to the completion of combustion. The signal from the piezoelectric pressure gauge was amplified and was then recorded with an S9-8 double-beam memory oscilloscope. The discretization time was 2 μ s. The chemiluminescence of the flame in the wavelength range 300– 600 nm was recorded on the same oscilloscope with the use of an FEU-39 photomultiplier. After each run, the reactor was pumped down to ~2 Pa. This experimental procedure is detailed in an earlier publication [28].

Since the number of moles of the gas mixture decreases steadily during H₂ oxidation, the increase in pressure (ΔP) observed in the reactor during developing combustion is due only to the increasing temperature. Obviously, the gas temperature in the moving flame, which is the place where heat is generated, is higher than the temperature of the unburnt gas. Therefore, ΔP characterizes the temperature rise averaged over the reactor volume (and the average temperature as well). The temperature rise is determined by the ratio between the rate of heat generation due to combustion and the rate of heat dissipation. The volume-average temperature is closer to the combustion zone temperature the shorter the characteristic time of the reaction in comparison with the characteristic time of heat dissipation. Therefore, ΔP is a measure of the heat generation rate and, accordingly, the combustion rate. This is the reason why the chemiluminescence intensity and pressure (Fig. 1), which grow at an increasing rate (the initial portions of their curves are convex downwards), peak almost simultaneously.

We studied the dependence of the energy necessary for ignition, the upper concentration limit of flame propagation, and the combustion rate on the amount and structure of lower olefin admixtures. The upper limit was determined as the average between the highest H_2 percentage at which the mixture could be ignited and a higher H_2 percentage starting at which the mixture could not be ignited any longer. The concentration of an olefin did not exceed the lower concentration limit of flame propagation for this olefin in air.



Fig. 1. (1) Luminescence intensity (1) and (2) pressure rise (ΔP) curves for the combustion of 7% H₂ in air.

RESULTS AND DISCUSSION

Effects of Admixtures: An Increase in the Power Necessary for Initiation and Slowdown of the Development of Combustion

Our data indicate that even olefin concentrations as low as a fraction of a percent prevent the ignition of hydrogen-air mixtures and raise the energy necessary for ignition (Figs. 2, 3). Furthermore, the higher the admixture concentration, the higher the minimum ignition energy. Olefins decrease the upper concentration limit of flame propagation (Fig. 3); that is, they hamper ignition. They reduce the combustion development rate: throughout the process, the pressure and chemiluminescence curves are flatter in the presence than in the absence of an admixture (Fig. 4). Olefins reduce the ultimate consumption of O_2 and H_2 ; that is, combustion terminates sooner in the presence than in the absence of an olefin.

Like the pressure variation curves (which are, in essence, temperature variation curves), the luminescence curves are also flatter in the presence of an inhibitor, and both indicate that the higher the olefin concentration, the lower the combustion development rate. Thus, olefins hamper combustion in all respects.

Because the amount of olefin in the mixture was no larger than 2 vol %, the effect of the olefin cannot be explained in terms of the increased in heat capacity or dilution. Furthermore, since the heat dissipation from the reactor does not increase as an admixture is progressively added, the observed slowdown of self-heating and the decrease in the maximum temperature rise are due only to the slowdown of the chemical reaction. This is also evident from the fact that equal amount of chemically different inhibitors exert different effects on the mixture ignition and the combustion rate.



Fig. 2. Effect of the propylene concentration on the concentration limit of flame propagation in the hydrogen–air mixture as a function at combustion initiation energies of (1) 0.07 and (2) 3.6 J.

Obviously, since the olefin concentration was always below the lower ignition limit for the olefin–air mixture, the ignition of the olefin was ruled out irrespective of whether hydrogen was burning. Furthermore, since H_2 does not ignite at all above a certain admixture concentration, implying that there is no O_2 consumption, the hypothesis that combustion is retarded because of a lack of O_2 [30] is groundless. The necessity of raising the spark energy in the presence of an admixture is direct evidence that the spark initiates the chain ignition, which is hampered by chain termination by the admixture.

It was demonstrated, using lean hydrogen combustion in a tube as an example, that the characteristic time



Fig. 3. Effect of isobutylene on the concentration limit of flame propagation in the hydrogen–air mixture as a function at combustion initiation energies of (1) 1.0 and (2) 3.6 J.



Fig. 4. (a) Combustion rate of 30% H₂ in air (1) in the absence of an admixture, (2) in the presence of 0.5% propylene, and (3) in the presence of 0.5% isobutylene. (b) Combustion rate of the same mixture (1) in the absence of an admixture, (2) in the presence of 0.9% propylene, and (3) in the presence of 0.9% isobutylene.

of heat generation in a nonchain reaction is thousands of times longer that the characteristic time of heat dissipation [2]. Therefore, in the absence of reaction chains, the extent of self-heating does not exceed a few kelvins and can cause neither ignition nor flame propagation. Thus, layer-by-layer ignition, which gives rise to laminar flame propagation, is a chain, not thermal, process, contrary to earlier beliefs. Accordingly, the flame velocity and the critical conditions for flame propagation are primarily determined by the competition between chain branching and chain termination [1, 2, 28] rather than by thermal ignition conditions. Therefore, flame propagation is a chain, not thermal, process. It is due to this fact that most of the observed regularities of combustion differ radically from those predicted by thermal theory.

Under the conditions examined, the key role in H_2 combustion is played by the following reactions

involved in the competition between chain branching and termination [3, 4, 31]:

$$H_2 + O_2 = H + HO_2^{,}$$
 (0)

$$H + O_2 = OH' + O, \qquad (I)$$

$$O + OH' = O_2 + H, \qquad (-I)$$

$$OH' + H_2 = H_2O + H, \tag{II}$$

$$O + H_2 = OH' + H, \tag{III}$$

$$H + O_2 + M = HO_2 + M, \qquad (IV)$$

$$HO_2^{\bullet} \longrightarrow (HO_2)_s,$$
 (V)

$$HO_2^{\cdot} + H_2 = H_2O_2 + H,$$
 (VI)

$$H + HO_2 = OH' + OH', \qquad (VII)$$

$$H + RH = R_1.$$
 (VIII)

Here, RH is an olefin molecule, R_1^{\cdot} is an alkyl (propyl, isobutyl, or hexyl) radical, and $(HO_2)_s$ is an adsorbed OH_2^{\cdot} radical.

The alkyl radical is involved in the fast reaction

$$\mathbf{R}_1^{\cdot} + \mathbf{O}_2 = \mathbf{R}_1 \mathbf{O}_2^{\cdot}, \qquad (IX)$$

which is most likely followed by the olefin regeneration reaction yielding HO_2 [32, 33]:

$$\mathbf{R}_1 \mathbf{O}_2^{\cdot} = \mathbf{R} \mathbf{H} + \mathbf{H} \mathbf{O}_2^{\cdot}. \tag{X}$$

The σ - π^* conjugation in the propylene molecule increases the reactivity of the H atoms in the α -position. This facilitates the abstraction of an H atom with the formation of an allyl radical [34]:

$$H + CH_3CHCH_2 = H_2 + CH_2CHCH_2$$
. (XI)

Nevertheless, the activation energy of the addition of a hydrogen atom to the π -bond, which is no higher than 6.5 kJ/mol [35, 36], is much lower than the activation energy of H abstraction, so inhibition is mainly due to reaction (VIII). The increased chain termination capacity of compounds having a π -bond as compared to compounds without a π -bond manifests itself, for example, as the fact that propylene and allyl alcohol are stronger inhibitors of hydrogen combustion than isopropanol [28, 29], which has similar gas kinetic and thermal properties.

It is clear from the above mechanism that free valences are multiplied only by reaction (I). Reactions (II) and (III) multiply reactive intermediates, specifically, atoms and radicals. In stoichiometric and rich hydrogen–air mixtures, nearly all of the O atoms and OH' radicals react with H_2 because of the large rate

constants of reactions (II) and (III) and the rather high H_2 content. Therefore, the branching rate in such mixtures is limited by reaction (I) rather than reaction (II) or (III). The bimolecular, nonlinear, chain-termination reaction (–I) plays a significant role in the kinetics of developed combustion [31]. At the same time, since this reaction is the reverse of the branching step and its rate is proportional to the product of the concentrations of active species, which are scarce at the onset of combustion, the ignition limit is independent of its rate.

Reaction (V) is adsorption eliminating free valences. This reaction competes with reaction (VI), which regenerate hydrogen atoms. The trimolecular recombination reaction (IV) causes chain termination only if the HO_2 radical is adsorbed to react with O_2 or decompose instead of participating in reaction (VI) or (VII).

The reaction between a hydrogen atom and the HO_2

radical primarily yields the OH radical [36]. In view of reactions (V)–(VII), we arrive at the following expression for the fraction of reaction (IV) events resulting in chain termination:

$$\xi = \frac{k_5}{k_5 + k_6[\text{H}_2] + k_7[\text{H}]},\tag{6}$$

where rate constants are numbered in the same way as reactions in the above mechanism.

It follows from the above mechanism that the chain ignition condition (f > g) can be expressed as

$$2k_1[O_2] \ge k_4[O_2][M]\xi + k_8[In]. \tag{7}$$

Here, the equality sign corresponds to the ignition limit.

In this study, the initial concentration of the mixture was the same in all runs and only the initial mole fractions of components were varied. For this reason, the component concentrations in Eq. (7) are conveniently expressed in terms of mole fractions:

$$2k_1 f_{O_2} \ge k_4 f_{O_2}[\mathbf{M}] \xi + k_8 f_{\text{In}}.$$
 (7a)

Let us now consider the role of a temperature rise in the spark initiation of combustion. It can readily be seen that, even if the last two terms in the dominator of Eq. (6) are neglected, ξ at a temperature of, e.g., 900 K will be smaller than unity by a factor of several hundreds. This temperature is established in the immediate proximity of the spark and causes chain ignition. This ignition, which is a fast exothermic reaction, causes self-heating capable of initiating layer-by-layer ignition (i.e., flame propagation) under certain conditions.

The activation energy of reaction (I) is close to 70 kJ/mol, while that of reaction (VIII) is no higher than a few kilojoules per mole [35, 36]. The value of k_4 decreases slightly with increasing temperature since reaction (IV) is trimolecular. As a consequence, the chain branching reactions would be accelerated by

spark-induced self-heating to a greater extent than the chain termination reactions even if ξ did not decrease. In fact, as the initiation rate increases, ξ does decrease primarily because of the increase in the H concentration, which appears in the denominator of Eq. (6). Furthermore, as the temperature increases, ξ decreases because of the increase in the rate constant of reaction (VI), which appears in the denominator of the right-hand member of Eq. (6).

Taking into account the competition between chain branching and chain termination makes it possible to explain the dependence of the initiation energy on the inhibitor concentration. Indeed, in the presence of an inhibitor, the right-hand side of the critical condition of chain ignition contains the term $k_8 f_{\text{In}}$. Therefore, as compared to the inhibitor-free mixture, the same mixture containing an inhibitor requires a larger increase in k_1 and a greater reduction in ξ for ignition. This is achieved by raising the initiation power, which results in a temperature rise and higher H and O concentrations. Note that, in the presence of an inhibitor, combustion proceeds less rapidly and is less capable of heating the adjacent layers of the fresh mixture. This is one way in which inhibitors hamper the initiation of combustion.

The effect of an inhibitor on the necessary initiation power is determined by the k_8 value for this inhibitor. Since a π -bond at a tertiary carbon atom is more reactive than the same bond at a secondary atom, k_8 is larger for isobutylene than for propylene. Therefore, at a given olefin concentration, the isobutylene-containing mixture will require a higher initiation power for inequality (7a) to be true (i.e., for ignition).

Thus, accepting the determining role of the branched-chain mechanism and the competition between chain branching and termination makes it possible to explain the above effects of the inhibitors on the minimum energy required for the initiation of combustion and the difference between the inhibition efficiencies of olefins.

Let us compare the effects of isobutylene and propylene on the development of combustion. The combustion kinetic curves are flatter for *i*-C₄H₈ than for propylene (Fig. 4); that is, combustion in the presence of isobutylene develops at a lower rate. Furthermore, isobutylene produces a much stronger effect on the slope of the combustion curve of the pure mixture than do equal amounts of propylene. Curve slopes as a function of the admixture concentration differ more widely for isobutylene than for propylene. The data obtained for a mixture containing 40% H₂ also indicate that isobutylene exerts a stronger effect on combustion. Furthermore, the stronger effect of isobutylene on H₂ combustion manifests itself as a stronger dependence of the ΔP_{max} and I_{max} values and of the ultimate oxygen consumption on the admixture concentration.

The decelerating effect of the inhibitors on combustion and the difference between their efficiencies are



Fig. 5. Effects of (1) isobutylene, (2) propylene, and (3) hexene on the upper concentration limit of flame propagation in the hydrogen–air mixture.

explicable in terms of the following formula for the rate of a nonisothermal branched-chain process:

$$W/[O_2] = k_1 n_0 \exp \int_{t_0}^{t} \{2k_1^0 f_{O_2} \exp(-E_1/RT) - k_4 f_{O_2}[\mathbf{M}] \xi - k_8 f_{I_0}\}[\mathbf{M}] dt.$$
(8)

In this expression, the indices given to rate constants are consistent with the above reaction numbering, k_1^0 is the preexponential factor of reaction (I), E_1 is the activation energy of reaction (I), f_{O_2} and f_{In} are the mole fractions of O_2 and the inhibitor, [M] is the mixture concentration, t_0 is the time after which the contribution from ω_0 to the multiplication rate of reactive species is insignificant, and n_0 is the concentration of reactive species at the time t_0 .

It is clear from Eq. (8) that an inhibitor, implying the presence of a third term in the braces, reduces the integrand and, accordingly, causes an exponential decrease in the combustion reaction rate. This causes a decrease in the self-heating of the mixture. It is equally important that a decrease in the braced quantity causes an exponential weakening of the temperature dependence of the reaction rate (dW/dT). As a consequence, self-heating exerts a much weaker speedup effect on combustion.

It follows from Eq. (8) that the slowdown due to inhibition must increase with increasing k_8 . Since the rate constant is larger for the reaction between H and i-C₄H₈ than for the reaction between H and C₃H₆, isobutylene exerts a stronger effect on combustion, in accordance with expectations (Figs. 3, 4).

Note that, in the oxidation of propyl and isobutyl radicals, olefin regeneration is primarily due to the reaction between the alkyl radical and O_2 followed by the decomposition of the resulting alkyl peroxy radical. Therefore, to the extent to which the levels of regeneration of propylene and isobutylene are similar, the observed difference between the effects of these olefins is due to kinetic differences in the primary stage of the process, specifically, the capture of a hydrogen atom. At the same time, the difference between propylene and isobutylene in terms of thermal and gas kinetic parameters is too small to be significant when small amounts of an olefin are used.

Thus, although the combustible mixture undergoes strong self-heating, which additionally speeds up the combustion process, there is a marked difference between the effects of propylene and isobutylene. This difference arises only from the fact that the π -bonds at the secondary and tertiary carbon atoms differ in reactivity and is further evidence that the chain avalanche plays the determining role in combustion even in the case of strong self-heating.

The Effects of the Admixtures on the Concentration Limits of Flame Propagation

The data presented in Fig. 5 indicate that C_3H_6 and $i-C_4H_8$ decrease the upper limit by different values even at very low concentrations. For example, 1% propylene changes the upper concentration limit from 75 to 50%. An equal amount of isobutylene decreases this limit to 40%. It is also clear that, as the inhibitor concentration is raised, the difference between the effects of C_3H_6 and $i-C_4H_8$ increases. This finding is in good agreement with Eqs. (7a) and (8). The effect of isobutylene exceeds not only the effect of propylene but also the effect of *n*-hexene (Fig. 5). This result is quite consistent with the well-known fact that the π -bond at a tertiary carbon atom is more reactive than the same bond at a secondary carbon atom. This regularity manifests itself as differences in both critical ignition conditions and combustion intensity.

Taking into account the crucially significant competition between chain branching and chain termination makes it possible to explain the dependence of the upper limit of flame propagation on the mole fraction of the inhibitor (the shape of the curves plotted in Figs. 1-3). Since the concentration limit is determined both by the ignition condition and by the capacity of the burning layer to ignite the adjacent layer of the fresh mixture, we will consider the dependence of the combustion reaction rate on the inhibitor concentration. A measure of this dependence is the derivative of the reaction rate with respect to f_{In} . It is clear from Eq. (8) that this derivative, as well as the reaction rate, is proportional to an exponential function in which the inhibitor concentration is in the exponent. Furthermore, it follows from Eq. (8) that, as f_{In} increases, the integrand decreases, implying an exponential decrease in $\frac{\partial W}{\partial f_{\text{In}}}$ (a weakening

of the dependence of the combustion rate on the inhibitor concentration). The way in which the combustion rate decreases with increasing f_{In} means that, as the inhibitor concentration is raised, the progressively greater increase in f_{In} is required to produce the desired inhibiting effect. This inference is in good agreement with the fact that the upper concentration limit was an exponentially descending function of f_{In} in all runs, including the runs presented in Fig. 3.

Suppression of the Chain Thermal Explosion

As is noted above, the pressure curve shows an upward excursion in the absence of an inhibitor (Fig. 4). As judged from the sound effect (plop) accompanying ignition in these runs, as well as from the maximum pressure value, the gas pressure is not uniformly distributed throughout the reactor. This nonuniformity is due to the local gas compression caused by the rapidly propagating combustion wave at the opposite end of the chamber. This compression causes extra gas heating before the combustion front and facilitates the fulfillment of the thermal explosion condition (3) at already fulfilled conditions (1) and (2). This leads to a chain thermal explosion. Thus, the pressure at the moment of the excursion of the first postinitiation point in Fig. 2 is, in essence, the instantaneous explosion pressure. The effect of the inhibitors on the chain thermal explosion will be analyzed in terms of Eqs. (2) and (3). A quantitative characteristic of the temperature dependence of the reaction rate is $\frac{\partial W}{\partial T}$. Obviously, the exponential function appearing on the right-hand side of Eq. (8) will also appear in the expression for the derivative $\frac{\partial W}{\partial T}$. Above a certain inhibitor concentration, the exponent and, accordingly, $\frac{\partial W}{\partial T}$ will be so small as to make the thermal explosion condition (3) unsatisfiable. This pre-

vents the mixture from chain thermal explosion (Fig. 3). Thus, inhibitors prevent this particularly intensive regime of chain combustion. This inference is in good agreement with previous results [2, 25].

As in the case of combustion rate reduction, the hampering effect of an inhibitor on the chain thermal explosion is proportional to the chain termination capacity of this inhibitor. Isobutylene, which has a higher capacity to add H atoms than propylene or hexene, is a more effective inhibitor of the chain thermal explosion.

Thus, as distinct from the thermal theory of gasphase combustion, which cannot explain the existence of two regimes of developed chain combustion and the strong effect of admixtures on these regimes, the theory

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of nonisothermal chain reactions not only provides an explanation for these facts but also enables the researcher to predict and reveal the effects of admixtures by considering their molecular structures. The correlation between the molecular structure and reactivity in gas-phase chain combustion is so strong that changing a single functional group in the molecule of the admixture causes marked changes in the kinetic, macrokinetic, and gas dynamic parameters of the process as a whole.

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