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PHYSICS

On a Possibility to Reduce the Ignition Threshold for Combustible Mixtures by Selective Excitation of Molecular Vibrations in Initial Reagents

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In recent years, a possibility to control combustion processes, while exciting vibrational degrees of freedom in molecules was subjected to sufficiently wide discussions in literature [1–4]. It was shown that the excitation of vibrations in H_2, O_2, and even N_2 results in both intensifying formation of active O, H, and OH centers and accelerating the combustion of the H_2 + air mixture. In this study, we investigate another aspect of the problem, which is associated with the effect of exciting molecular vibrations of initial reagents on the self-ignition threshold.

First, we show for the general case that the selective excitation of molecular vibrational degrees of freedom in the case of the chain mechanism of the process must result in reducing the self-ignition threshold. We will assume that the thermodynamic equilibrium exists between the rotational and translational molecular degrees of freedom, while a local Boltzmann distribution with its proper vibrational temperature T_ξ ($\xi = 1, \ldots, n$) is established very rapidly in each ξth mode.

The simplest scheme of reactions describing the initiation (the appearance of an active radical), propagation, and the break of a chain has the form:

(I) $A \xrightarrow{k_1} r + D,$

(II) $r + A \xrightarrow{k_2} C + lr,$

(III) $r + r \xrightarrow{k_3} r_2.$

Here, A is an initial reagent, whose decomposition leads to the formation of an active radical; r; C, D, and r_2 are reaction products; $l = 1$ and $l = 2, 3$ correspond to a nonramified and ramified chain reactions, respectively; k_1, k_2, and k_3 are the reaction-rate constants for the corresponding process. The equations specifying the formation of active radicals r in the processes I–III can be represented in the form:

$$\frac{d[A]}{dt} = -k_1[A] - k_2[r][A], \tag{1}$$

$$\frac{d[r]}{dt} = k_1[A] + (l-1)k_2[r][A] - 2k_3[r]^2. \tag{2}$$

We seek the solution for $[r]$ in the form [5]:

$$[r] = \frac{y'(t)}{2k_3 y(t)}. \tag{3}$$

Here, $[A]$ and $[r]$ are the concentrations of molecules for the mixture components A and r, and $y(t)$ is a certain continuous function of time.

Substituting (3) into (2), we obtain

$$y''(t) - (l-1)k_2[A]y'(t) - 2k_3k_1[A]y(t) = 0.$$

In the general case, k_1, k_2, and k_3 depend on the gas temperature T, while k_1 and k_2 depend also on the vibrational temperature T_V for the molecule excited mode of the component A. The values of T, T_V, and $[A]$ vary in the process of combusting the mixture. However, within the range $[0, \tau_{\text{in}}]$, where τ_{in} is the induction period, we may assume that $T = T_0$, $T_V = T_{V0}$, and $[A] = [A]_0$ (the subscript zero corresponds to $t = 0$). In this case, we have for $[r(t)]$ that

$$[r(t)] = \frac{C_1 Z_1 e^{Z_1 t} + C_2 Z_2 e^{Z_2 t}}{2k_3(C_1 e^{Z_1 t} + C_2 e^{Z_2 t})}, \tag{4}$$

$$Z_{1,2} = \frac{b}{2} \pm \sqrt{\left(\frac{b}{2}\right)^2 + a^2}, \quad a^2 = 2k_1k_3[A]_0,$$

$$b = (l-1)k_2[A]_0,$$

where C_1 and C_2 are the integration constants. If $[r]_0 = 0$

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for $t = 0$, then

$$[r(t)] = \frac{Z_1 Z_2 (e^{Z_1 t} - e^{Z_2 t})}{2k_3 (Z_2 e^{Z_1 t} - Z_1 e^{Z_2 t})}. \tag{5}$$

As $t \longrightarrow \infty$, it follows from (5) that $[r(t)] = Z_1/2k_3$.

For $l = 1$ (a nonramified chain reaction),

$$[r(t)] = \frac{1 - e^{-2at}}{1 + e^{-2at}} \sqrt{\frac{[A]_0 k_1}{2k_3}}.$$

For $t > t_*$, $t_* = (2a)^{-1}$, the value $[r]$ tends to its ultimate value $[r_*] = \sqrt{[A]_0 k_1/2k_3}$. In the case of a ramified chain reaction ($l > 1$), $k_2^2 [A]_0/k_1 k_3 \gg 1$, and the maximum concentration of active radicals (furthermore, we denote it by the subscript l) is defined by the expression $[r_*]_l = (l - 1)k_2[A]_0/2k_3$. Since $k_2 > k_1$, then $[r_*]_l > [r_*]$.

The self-ignition regime is realized if $[r_*] > [r_{\text{ign}}]$, where $[r_{\text{ign}}]$ is the critical concentration of active radicals for which the chain mechanism develops steadily [6]. The value of $[r_{\text{ign}}]$ depends on $[A]_0$, on the rates of formation and disintegration of active radicals, and on the rate of their diffusion or convective outflow from the reaction zone. The quantity $[A]_0$ determines the concentration threshold for the self-ignition, while the relationship between k_1, k_2, and k_3 determines the temperature threshold. The chemical-reaction rate constant for $T_\xi \neq T$ can be presented in the form

$$k_q(T, T_\xi) = \varphi_q(T, T_\xi) k_q^0(T), \tag{6}$$

where $k_q^0(T)$ is the reaction-rate constant for the qth reaction at $T_\xi = T$, and $\varphi_q(T, T_\xi)$ is the nonequilibrium-state factor. For determining a particular form of $\varphi_q(T, T_\xi)$, we use the theoretical results of [7]:

$$\varphi_q(T, T_\xi) = \frac{\prod_{j=1}^{b_q} [1 - \exp(-\theta_j/T_j)]^{-g_j}}{\prod_{j=1}^{b_q} [1 - \exp(-\theta_j/T)]^{-g_j}} \times \exp\left[\frac{E_q^*}{k}\left(\frac{1}{T} - \frac{\sum_{j=1}^{b_q} \beta_{qj}^2}{\sum_{j=1}^{b_q} \beta_{qj}^2 T_j}\right)\right]. \tag{7}$$

Here, θ_j is the characteristic vibrational temperature for the jth vibration, and g_j is the multiplicity of its degeneration; β_{qj} are the expansion coefficients for the qth reaction in coordinates of normal vibrations; b_q is the number of modes participating in the qth reaction; E_q^* is the energy corresponding to a certain vibrational level, being as though a “narrow neck” in the case of passing vibrationally excited molecules to the quasi-continuous (with respect to the energy) continuum in the qth reaction.

Let only one type of vibrations ($T_\xi = T_V$) be excited in molecules A. With allowance for (6) and (7), it is convenient to present the expressions for $[r_*]$ and $[r_*]_l$ in the form

$$[r_*] = [r_{*0}]\sqrt{\varphi_1(T, T_V)}, \quad [r_*]_l = [r_{*0}]_l \varphi_2(T, T_V).$$

Here, $[r_{*0}]$ is the maximum concentration of active radicals at $T_V = T$ and $l = 1$, while for $l \geq 1$, ($[r_{*0}] = \sqrt{k_1^0 [A]_0/2k_3^0}$; $[r_{*0}]_l = (l - 1)k_2^0 [A]_0/2k_3^0$).

In the case of excitation of the component A ($T_V > T_0$) $\varphi_1(T, T_V) > 1$ and $\varphi_2(T, T_V) > 1$. Therefore, $[r_*] > [r_{*0}]$ and $[r_*]_l > [r_{*0}]_l$. We assume that $[r_{*0}]_l < [r_{\text{ign}}]$ for the given $[A]_0$ and T_0; i.e., no regime of self-ignition is realized for both nonramified and ramified chain reactions. Exciting vibrations of molecules A to a certain value T_V, it is possible to make the condition $[r_*]_l > [r_*] > [r_{\text{ign}}]$ fulfilled, i.e., to reduce both the temperature threshold and concentration threshold of the self-ignition. A relative increase in the concentration of active radicals $r_* = [r_*]/[r_{*0}]$ for $l = 1$ depends on $T'_V = T_V/T$ and $E'_{V1} = E_1^*/T$, while for $l > 1$, $r_{*l} = [r_*]_l/[r_{*0}]_l$ depends on T'_V and $E'_{V2} = E_2^*/T$ (E_1^*, and E_2^* are the values of E_q^* for the reactions of initiation and chain ramification).

In Figs. 1a and 1b, we show r_* as a function of T'_V and E'_{V1} and r_{*l} as a function of T'_V and E'_{V2} for $l = 2$, respectively. In the same figures, we show in the ordinate axis certain values $r_{\text{ign}} = [r_{\text{ign}}]/[r_{*0}]_l > 1$ for $l = 1$ and $l = 2$; i.e., for the values $[A]_0$ and T_0 corresponding to $[r_{*0}]_l$, no self-ignition occurs. As is seen, the higher is E'_{V1} for $l = 1$ or E'_{V2} for $l = 2$, the lower is the degree of excitation for which the regime of the self-ignition ($r_* \geq r_{\text{ign}}$) is realized. It is natural that the degree of excitation must be lower in a ramified chain reaction for equal E'_{V1} and E'_{V2}.

We illustrate the results obtained by the example for the $H_2 + O_2$ mixture. We consider the ignition of the mixed mixture in a certain region with the radius R_a. In this case, the time for active radicals to escape from the

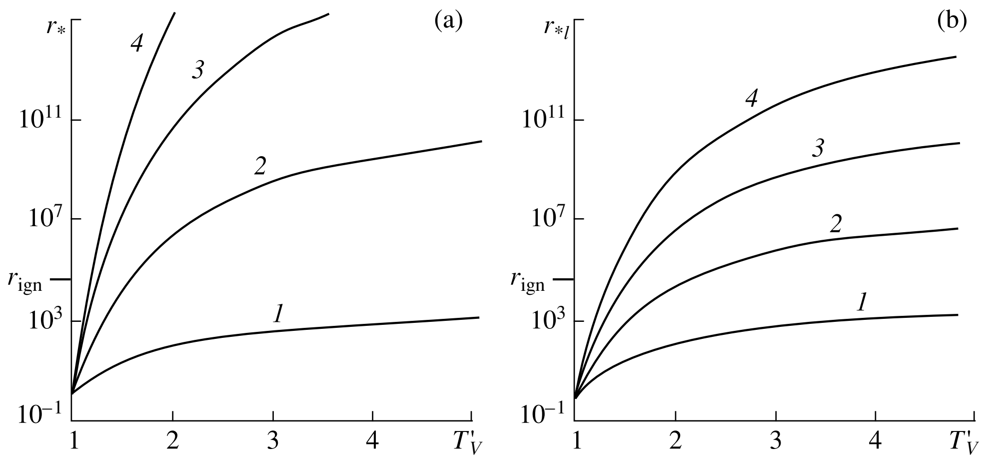

Fig. 1. Relative increase in the number of active radicals as a function of T'_V for (a) nonramified reaction with E'_{V1} equal to: (*1*) 20; (*2*) 60; (*3*) 100; and (*4*) 140 and (b) ramified reaction ($l = 2$) with E'_{V2} equal to: (*1*) 10; (*2*) 20; (*3*) 30; and (*4*) 40.

reaction zone corresponds to the time of diffusion $\tau_i^D = \min\{\tau_{ik}^D\}$, and $\tau_{ik}^D = R_a/D_{ik}$, where D_{ik} is the coefficient of the multicomponent diffusion occurring between the *i*th and *k*th components. The formation of active radicals is specified by the time τ_i^{ch} of the chemical reaction. If $\tau_i^{\mathrm{ch}} > \tau_i^{\mathrm{D}}$, no self-ignition occurs. For the $H_2 + O_2$ mixture, τ_i^{D} corresponds to the diffusion time ($\tau_{\mathrm{H}}^{\mathrm{D}}$) for hydrogen atoms.

To describe the process of self-ignition in a vibrationally nonequilibrium reacting gas for $t < \tau_{\mathrm{H}}^{\mathrm{D}}$, the set of equations is valid, which involves the equation for energy, the kinetic equations for concentrations of components and for the mean content of vibrational quanta in each mode participating in the reactions of molecules [2]. The analysis performed has shown that, for describing the low-temperature initiation of combustion in $H_2 + O_2$ mixtures, it is necessary to use the kinetic scheme including chemical reactions with participation of not only H_2, O_2, H_2O, OH, O, and H, but also HO_2, H_2O_2, and O_3:

(1C) $H_2O + M = OH + H + M$,

(2C) $H_2 + M = 2H + M$,

(3C) $O_2 + M = 2O + M$,

(4C) $H + O + M = OH + M$,

(5C) $H_2 + O = OH + H$,

(6C) $O_2 + H = OH + O$,

(7C) $H_2O + O = 2OH$,

(8C) $H_2O + H = OH + H_2$,

(9C) $H_2 + O_2 = 2OH$,

(10C) $HO_2 + M = H + O_2 + M$,

(11C) $H_2 + O_2 = H + HO_2$,

(12C) $H_2O + O = H + HO_2$,

(13C) $H_2O + O_2 = OH + HO_2$,

(14C) $H_2O + OH = H_2 + HO_2$,

(15C) $2OH = H + HO_2$,

(16C) $OH + O_2 = O + HO_2$,

(17C) $H_2O_2 + M = OH + OH + M$,

(18C) $H + H_2O_2 = HO_2 + H_2$,

(19C) $H + H_2O_2 = H_2O + OH$,

(20C) $2HO_2 = H_2O_2 + O_2$,

(21C) $HO_2 + H_2O = H_2O_2 + OH$,

(22C) $OH + HO_2 = H_2O_2 + O$,

(23C) $H_2O + O_2 = H_2O_2 + O$,

(24C) $O_3 + M = O_2 + O + M$,

(25C) $O_3 + H = OH + O_2$,

(26C) $O_3 + O = O_2 + O_2$,

(27C) $O_3 + OH = HO_2 + O_2$,

(28C) $O_3 + H_2 = HO_2 + OH$,

(29C) $O_3 + HO_2 = OH + O_2 + O_2$.

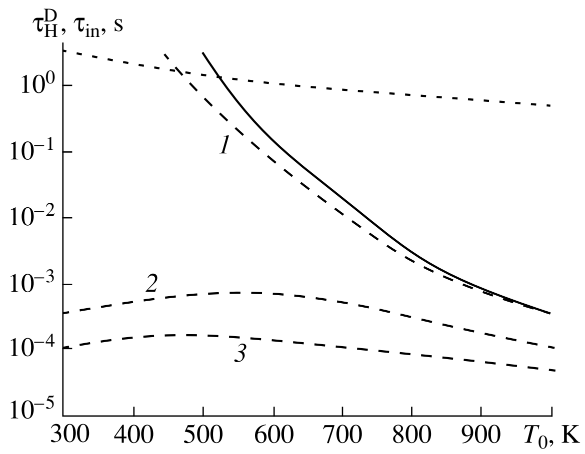

Fig. 2. Dependences (for the $2H_2 + O_2$ mixture at a pressure $P_0 = 10$ kPa) $\tau_{in}(T_0)$ in the absence of the preliminary excitation of initial reagents (solid line) and $\tau_H^D(T_0)$ with the preliminary excitation of vibrations in H_2 (dashed lines). T_{40} = (*1*) 1000; (*2*) 2000; and (*3*) 3000 K.

In addition to the reactions indicated, we included into the kinetic model the processes of the vibrational-vibrational (*V–V*') exchange between the symmetric, deformational, and asymmetric modes of H_2O and O_3 molecules and modes of H_2, O_2, and OH molecules. We also included processes of the vibrational-translational (*V–T*) relaxation of the deformational modes for H_2O and O_3 and modes of the H_2, O_2, and OH molecules. It was assumed that the vibrational energy released into modes of the HO_2 and H_2O_2 molecules when proceeding chemical reactions relaxes very rapidly into the translational degrees of freedom. (As estimates have shown, the rates of the *V–V*' and *V–T* processes for these molecules are higher than the rates of processes of the vibrational energy exchange in H_2O.) The temperature dependences $k_q^0(T)$, $W_{\xi,p}(T)$, and $W_{\xi,0}(T)$ for the chemical-reaction rate constants and for the *V–V*' and *V–T* exchange processes, respectively, are taken from [4]. For the processes $O_3(100, 001) + M = O_3(020) + M$ and $O_3(010) + M = O_3(000) + M$, the values of the reaction-rate constants are known only at $T = 300$ K (they are 5×10^{-14} cm^3/s and 2×10^{-14} cm^3/s, respectively) [8]. The temperature dependences for these processes were determined in accordance with the SSH theory [9]. The values of E_q^* and the energy E_r released into vibrational degrees of freedom, while

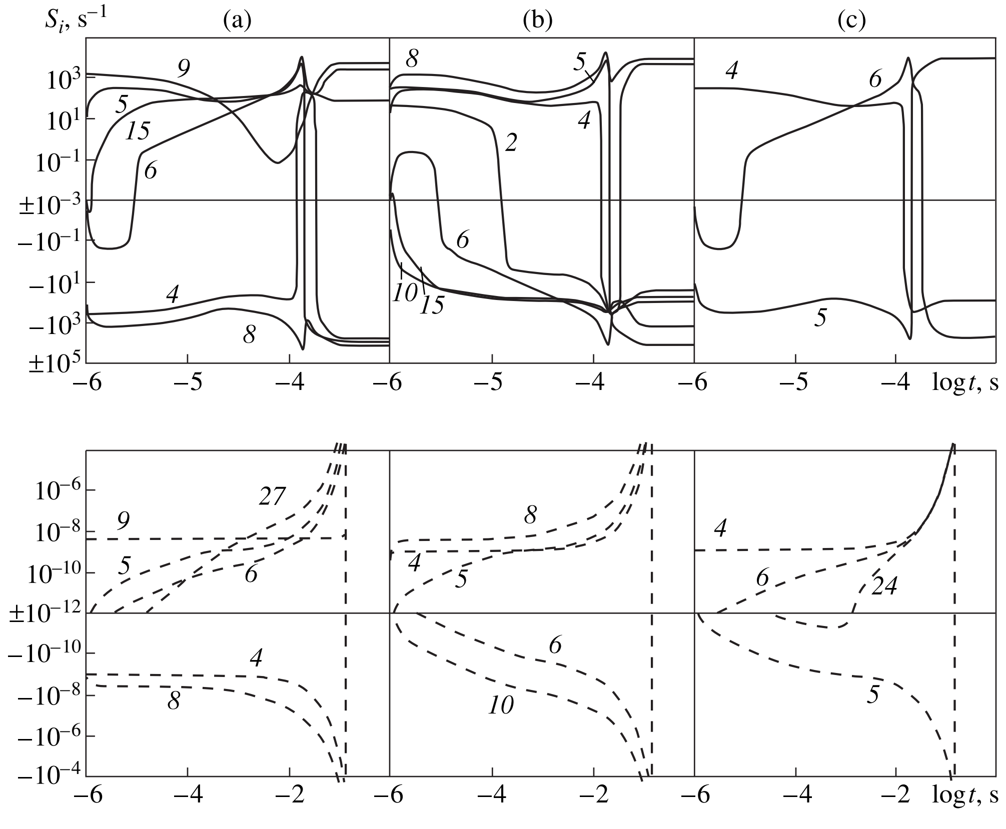

Fig. 3. Changing in the rates S_i of the formation and disintegration of (a) OH; (b) H; and (c) O with time, while burning the $2H_2 + O_2$ mixture at $T_0 = 600$ K and $P_0 = 10$ kPa with ($T_{40} = 3000$ K) and without exciting vibrations in H_2 (solid and dashed lines, respectively). Ciphers near the curves $S_i(t)$ correspond to the numbers of chemical reactions.

forming a molecule in the *r*th chemical reaction, were calculated in the same manner as in [4].

At low temperatures ($T_0 \leq 600$ K), there are marked differences in the mechanism of the combustion initiation of the $H_2 + O_2$ mixture as compared to higher values of T_0 even in the case of the absence of the preliminary excitation of the H_2 or O_2 molecules. At the initial stage, as for high values of T_0, the principal reaction initiating the formation of active OH radicals is the (9C) reaction. Furthermore, OH radicals dissociate [the (4C) reverse reaction] and also react with H_2, which is accompanied by the formation of H_2O molecules and H atoms [the (8C) reverse reaction]. These products participate in two different processes. The former of them results in formation of O atoms [the (6C) reaction] and initiates the chain-combustion mechanism. The latter process results in the disappearance of H atoms and formation of HO_2 radicals [the (10C) reverse reaction]. At $T \geq 800$ K, the rate of the former process becomes higher than that of the latter one, but the situation alters to the opposite one at $T \leq 600$ K. At $T \leq 600$ K, an important source of O atoms is the dissociation of O_3 [the reaction (24C)], which is preliminary formed as a result of the interaction between HO_2 and O_2 [the (27C) reverse reaction]. The rate of the (24C) reaction is comparable to that of formation of O atoms in the reaction of the chain initiation. The (5C) reaction closes the chain mechanism for the combustion of $H_2 + O_2$ mixtures.

The preliminary excitation of H_2 or O_2 molecules significantly change the mechanism of the combustion initiation and results in decreasing τ_{in} at the same T_0. In Fig. 2, we show the dependences $\tau_{in}(T_0)$ in the case of the absence ($T_{\xi 0} = T_0$) and of the presence of the excitation of H_2 for various vibrational temperatures T_{40} in H_2 and the dependence $\tau_H^D(T_0)$ for $R_a = 0.1$ m. As is seen, the condition $\tau_{in} > \tau_H^D$ is realized at lower T_0 in the case of the excitation of the H_2 molecules. Thus, at $T_{40} = 1000$ K, the self-ignition is possible at $T_0 = 500$ K, while at $T_{40} = T_0$—only at $T_0 = 550$ K. For a significant excitation of H_2 ($T_{40} \geq 2000$ K), the character of the dependence $\tau_{in}(T_0)$ changes in the range $T_0 = 600$–300 K; namely, the value of τ_{in} decreases with the reduction of T_0. In the case of a strong excitation of H_2 molecules, variation in the form of the dependence $\tau_{in}(T_0)$ is caused by a change in the mechanisms of production of O and H atoms, as well as OH radicals compared to unexcited gas. This is illustrated in Fig. 3 in which we show the variation of the OH, H, and O formation rates in the process of combustion of the hydrogen–oxygen mixture with and without the excitation of H_2 at $T_0 = 600$ K. It is seen that the excitation of H_2 leads primarily to a significant increase in the formation rate for OH radicals in the (9C) reaction and H atoms in the (8C) reverse reaction. In this case, an efficient source of H atoms becomes the reaction of dissociation of OH and H_2 [the (4C) and (2C) reactions, respectively]. An increase in the concentration of H atoms results in accelerating the formation of HO_2 radicals in the (10C) reaction. This process initiates increasing the rate of the (15C) reverse reaction, the growth in the concentration of OH radicals and, as a consequence, of H and O atoms as well.

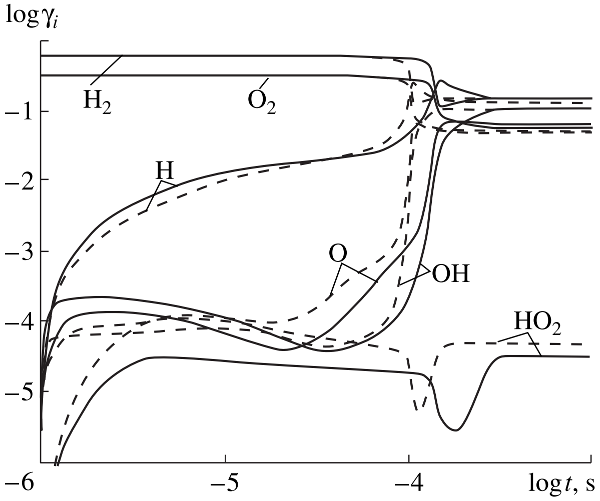

Fig. 4. Variation in concentrations for the OH, O, H, HO_2, H_2, and O_2 components with time in the case of combustion of the $2H_2 + O_2$ mixture at $P_0 = 10$ kPa, $T_0 = 600$ and 300 K (solid and dashed lines) in the case of exciting molecular vibrations in H_2 ($T_{40} = 3000$ K).

With decreasing T_0 from 600 to 300 K, the formation rate for HO_2 radicals in the (10C) recombination reaction increases. This fact, as was already noted above, results in increasing the concentration of OH radicals and H and O atoms, and thus, in intensifying the chain mechanism of the process and in reducing the period of induction. This can be clearly seen from Fig. 4, in which the dependences $\gamma_i(t)$, i = OH, H, O, HO_2, H_2 and O_2 are shown for $T_0 = 600$ and 300 K.

The results obtained indicate a possibility of a significant (by the factor of two or higher) reducing the ignition threshold for combustible mixtures when exciting the molecular vibrations in initial reagents. In the case of the low-temperature initiation of combustion by means of a selective excitation of vibrational degrees of freedom in the reacting molecules, new mechanisms of formation of active atoms and radicals appear. These mechanisms can lead to a qualitative change in the dependence for the induction period on the initial temperature of a mixture.

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