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Abstract

Full Text

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ON THE MECHANISM AND LIMITS OF CHAIN SELF-IGNITION OF HYDROGEN WITH OXYGEN IN SHOCK WAVES

The influence of the kinetics of an exothermic reaction on the dynamics of gas flow is clearly manifested in various detonation processes. For example, the principal cause of deviations from stationarity of the reaction zone in detonation waves is the strong dependence of the induction delays in a gas adiabatically compressed by a shock wave on pressure and temperature. Chemical factors also play an important role in the nonstationary processes of detonation formation in front of the flame in compression waves that arise during the expansion of combustion products.

In work (^{1}) it was shown that, as the temperature is lowered in certain gas systems when they are compressed by shock waves, a noticeable change is observed in the character of ignition and of the onset of detonation upon passage through a certain temperature region. Figure 1 (see insert, p. 1415) shows typical Schlieren photographs and oscillograms of pressure and luminosity characterizing different ignition mechanisms. At high temperatures, for detonation to arise it is sufficient for a single ignition center to form. Additional compression and heating of the layers of unburned gas adjacent to the expanding combustion products leads to a sharp acceleration of the reaction and to the rapid formation of a detonation wave (mechanism *a*). At lower temperatures the reaction is initiated at many points, the ignition centers multiply freely, the combustion surfaces merge and may form a single flame front without sharply expressed explosive self-ignition (mechanism *b*). On the basis of these data, it could be assumed that we were dealing with some new qualitative effect.

Upon a more detailed examination of the data obtained at various gas temperatures and pressures behind the reflected shock wave, it was found that the temperature of transition from one detonation regime to another in the $H_2 + O_2$ mixture decreases as the pressure decreases. In addition, it proved that the boundary separating these two regions in the (p, T) plane coincides rather closely with the theoretical curve obtained by extrapolating to the experimental

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Fig. 2. Limiting curves of chain ignition of the $H_2 + O_2$ mixture

Figure 1: Fig. 2. Limiting curves of chain ignition of the $H_2 + O_2$ mixture

conditions the so-called upper ignition limit of hydrogen with oxygen p_2, reliably determined (^{2}) in the region of lower temperatures and pressures. Since this limit is due to the competition between the chain-branching reaction
$H + O_2 \rightarrow OH + O$ (k_2)
and the homogeneous termolecular chain-breaking reaction
$H + O_2 + M \rightarrow HO_2 + M$ (k_6),
then crossing the curve (Fig. 2) $p = p_2 = 2k_2/k_6$ at high pressures and temperatures means that we pass from a region of entirely branched chains into a region of long straight chains with rare branchings, and that precisely this transition determines the change in the character of the initiation and development of ignition. To verify and refine the proposed hypothesis concerning the possibility of describing the onset of detonation in an adiabatically heated combustible mixture by means of concepts developed in the analysis of combustion kinetics at low pressures and temperatures, it was necessary to find such a characteristic of the ignition process as could be calculated quantitatively from kinetic data. As such a characteristic it was natural to choose the delay time, i.e., the time τ (see Fig. 1) from the moment the shock wave passes until the appearance of the first ignition center.

It follows from the kinetic scheme of hydrogen combustion that, as $T \rightarrow T(p_2)$ (see Fig. 2), the reaction proceeds through the following sequence of elementary steps:

$$\begin{array}{ll}
(k_0)\ H_2 + O_2 \rightarrow 2OH^*; & (k_6)\ H + O_2 + M \rightarrow HO_2 + M; \\
(k_1)\ OH + H_2 \rightarrow H_2O + H; & (k_7)\ OH \rightarrow \text{death on the wall}; \\
(k_2)\ H + O_2 \rightarrow OH + O; & (k_8)\ HO_2 + H_2 \rightarrow H_2O_2 + H^{**}. \\
(k_3)\ O + H_2 \rightarrow OH + H. &
\end{array}$$

The rate constants of these processes and their temperature dependences have been measured with sufficient reliability, and therefore, by writing the corresponding kinetic equations, we obtain an expression for the induction period in the form$^{(2)}$: $\tau = \frac{1}{\varphi} \ln \alpha$, where φ is the coefficient of the exponent in the exponential time dependence of the rate of the leading reaction, and α is the ratio of the current reaction rate attained by the moment of explosion to the rate of the initiation reaction.

Fig. 2. Limiting curves of chain ignition of the $H_2 + O_2$ mixture

In the temperature range 1100-1800°K, φ will differ little from the quantity $2k_2(O_2) - k_6(O_2) \cdot (M)$, while in the remaining temperature region of ignition

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(down to $T \sim 800°\mathrm{K}$) φ should be understood as the larger characteristic root of the following system of equations:

$$d(\mathrm{H})/dt = [2k_2 - k_6(\mathrm{M})](\mathrm{H}) + k_8(\mathrm{HO_2})(\mathrm{H_2}) + W_0;$$

$$d(\mathrm{HO_2})/dt = k_6(\mathrm{M})(\mathrm{O_2})(\mathrm{H}) - [k_7 + k_8(\mathrm{H_2})](\mathrm{HO_2}).$$

The value of α can be estimated by using the known rate constant of homogeneous initiation of the reaction $k_0 = 10^{-10}\exp(-45\,000/RT)$ cm^3/sec. For example, at $p = 1$ atm and $T = 1000°\mathrm{K}$, assuming that by the moment of explosion a nonequilibrium concentration of atomic hydrogen $(\mathrm{H})_{\mathrm{max}}/e$ has been reached, where $(\mathrm{H})_{\mathrm{max}}$ is determined from the rates of reaction (k_2) and recombination: $(\mathrm{H})_{\mathrm{max}} \simeq 6 \cdot 10^{20}\exp(-18\,000/RT)$ cm^{-3} $^{(2)}$, we obtain $\alpha = W'/W_0 \simeq 10^5$. In the region of low temperatures the value of α will be several orders of magnitude smaller, since although W_0 decreases as $\exp(-45\,000/RT)$, W' decreases still faster as a consequence of the transition through the limit p_2. Carrying out the corresponding calculations at various p and T, we obtain the curve of the dependence of $\lg\tau$ on $1/T$ for various pressures. In Fig. 3 the results of these calculations are compared with experimental data on the determination of τ at pressures of 1, 2, and 3 atm in the temperature interval 850-1650°K. First of all it should be noted that in all cases there is a more or less sharp drop in the experimental values of $-\lg\tau$ at $T = 960$, 1025, and 1070°K, respectively, i.e. precisely at temperatures at which a change in the character of the detonation is observed (see above). The same deviations, and at precisely these temperatures, are also observed in the calculated curves. From this agreement, and also from the fact that in the high-temperature region $(\tau)_{\mathrm{calc}}$ agrees quite satisfactorily quantitatively with (τ_{expt}), it should be assumed that the chemical mechanism under these ignition conditions and under the conditions of ordinary kinetic experiments ($T = 750$-$880°$ K, $p = 10$-760 mm Hg) is very similar. This is also indicated by the fact that, when the temperature is lowered outside the region bounded by the limiting curve p_3 (Fig. 2), found experimentally (^{4}) and determined quantitatively on the basis of the same mechanism (^{5}) given above, ignition after passage of the shock wave is not observed at all. The limit corresponds to the so-called chain, third limit (^{2}). The thermal-explosion limit, calculated by D. A. Frank-Kamenetskii, lies in the region of lower temperatures and does not appear under these conditions.

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* The process of chain initiation may occur somewhat differently, for example $\mathrm{H_2 + O_2 \rightarrow H + HO_2}$; for us only the possibility of using the rate constant given by N. N. Semenov is essential.

** The reaction $\mathrm{HO_2 + H_2 \rightarrow H_2O + OH}$ is also quite probable. What is essential is only the possibility of chain propagation through the radical $\mathrm{HO_2}$. The value k_8 was determined by V. N. Kondrat' ev$^{(3)}$.

The effect of "breakdown" on passing through p_2 is observed the less sharply, the lower the pressure region, which also corresponds to the chemical picture, since under these conditions the limiting curve p_3 comes very close to the curve p_2 (see Fig. 2).

The only quantitative discrepancy between the results presented in this paper and kinetic calculations based on known values of the reaction-rate constants is the magnitude of the ignition delays in the temperature interval between the curves p_2 and p_3. The measured values τ are approximately 100 times smaller than the calculated ones (see Fig. 3, in which $(-\lg\tau)_{\text{calc}}$ is shown as a solid line). If, in order to explain these data, one assumes that the constant k_8 has been determined inaccurately, then

Fig. 3. Calculation and experimental data on measurement of the self-ignition delay of the mixture $H_2 + \frac{1}{2}O_2$ at various pressures and temperatures.
a $-p = 1 = 1 \pm 0.35$ atm; b $-p = 2 \pm 0.3$ atm; 1 −pure mixture, 2 −admixture of 1% CO_2, 3 −treatment of the vessel walls with KCl; v $-p = 2.9 \pm 0.4$ atm.

the introduction of the corresponding corrections would sharply change the picture of the limits, and the discrepancy between experiment and theory would become still greater.

It seems more probable that, in the temperature range under consideration, where ignition and the subsequent detonation have a milder, more diffuse character, the delay τ may depend substantially on the specific conditions of the process in the gas heated by the shock wave, as a result of which the ignition mechanism may prove to be more complex. As one of the possible hypotheses, one may suppose that the difference from ordinary thermal reactions consists in the fact that, in our case, vibrationally excited molecules $(O_2)^*$, whose relaxation times are of the order of 10^{-4}–10^{-3} sec. ([1]), may play a certain role in the course of the process. These molecules can enter into the reaction

$$H + O_2^* \rightarrow OH + O \tag{1}$$

practically without activation energy. If it is assumed that at very high temperatures (above the temperatures corresponding to intersection with the curve p_2 at the given pressure) k_2 is sufficiently large, then, in view of the large values of $[(O_2)/(O_2)^*]$, the contribution of reaction (1) to the equation for τ will be insignificant and the position of p_2 will remain practically unchanged, while the quantities $(t)_{\text{expt}}$ and $(\tau)_{\text{calc}}$ at $T \gg T_2$ will coincide. With a sharp change in rates after passing through p_2, the rate of reaction (1) may become substantial, which will lead to a decrease in τ in comparison with the calculation made without taking it into account. With a comparatively small change in τ in the interval from 10^{-4} to 10^{-3} sec. ($T < T_2$), the number of $(O_2)^*$ molecules drops sharply; therefore the limit is observed at approximately the same temperatures as in thermal experiments.

The proposed hypothesis was qualitatively checked by us by introducing into the mixture a 1% impurity of CO_2, the addition of which should have sharply accelerated the deactivation of $(O_2)^*$ molecules. Figure 3 gives data on the measured ignition delays in a mixture with a CO_2 impurity, indicating an increase in τ in the region of low temperatures by approximately a factor of two in comparison with the data for the pure mixture. In the region of high temperatures no such discrepancy is observed. These results may be regarded as qualitative confirmation of the suggestion made above concerning the role of $(O_2)^*$.

To clarify the influence of the walls and wall effects on the development of ignition, the walls of the explosion chamber were treated with a solution of potassium chloride. This treatment did not introduce substantial changes in the values of the delays and only stabilized the position of the limit p_3 (Fig. 3), which once again indicates that thermal ignition is not manifested under our conditions. Finally, in order to exclude the possible influence of temperature deviations associated with the interaction of the reflected wave with the boundary layer (^{1}), the design of the shock tube was changed: the central part of the gas flow behind the incident wave was led off into a special thin-walled tube, where ignition after reflection of the wave was observed. Despite the fact that in these experiments the trace of the reflected wave on the records proved to be much thinner, which indicates a weakening of the wall effects, the magnitude of the delays practically did not change. Thus, there is no basis for assuming that the regularities described above may be associated with wall effects.

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