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

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The specific peculiarities of hydrogen-oxygen ignition in shock-wave conditions [T = 800−1700 K, p = 0.5−4 atm] are quantitatively explained on the basis of the kinetic scheme of low-temperature and low-pressure hydrogen-oxygen combustion.

Introduction

The dependence of gas-flow dynamics on exothermic reaction kinetics is essential in various detonation processes. The high temperature and pressure dependence of induction lags in combustible gas mixtures adiabatically compressed by shock waves is the main source of detonation-front instability. Chemical factors also play a great part in nonstationary flame-detonation transitions.

It was shown [1] that, in some shock-compressed gaseous systems at constant pressure, one could observe a distinct change in the ignition and detonation processes at a given temperature. Fig. 1 shows typical schlieren streak photographs and oscillograms characterizing various ignition mechanisms in reflected shock waves. A single ignition locus is sufficient to form a detonation front at high temperatures. Additional layers ahead of the expanding combustion products give rise to a sharp acceleration of the reaction followed by the establishment of the detonation wave (Mechanism a).

At lower temperatures the reaction is initiated in many loci; their number increases sharply, their surfaces merge together, and they may form a uniform flame front leading to a "mild" ignition (Mechanism b). According to these data, we concluded that this observation is due to a new effect.

From a detailed analysis of the data obtained at various pressures and temperatures behind reflected shock waves it followed that the "transition" temperature in the $H_2 + O_2$ mixture falls as the pressure decreases. Moreover, the curve separating these two areas in the (*p, T*) plane was rather close to the theoretical curve extrapolated from the so-called "upper" .hydrogen-oxygen explosion limit p_2 reliably measured$_2$ at lower temperatures and pressures.

As this limit results from competition of the reaction of chain branching $H + O_2 \rightarrow OH + O$ (K_2) and the reaction of homogeneous termolecular rupture $H + O_2 + M \rightarrow HO_2 + M$ (K_6), the crossing of the curve $p = p_2 = 2K_2/K_6$ (Fig. 2) from right to left at high pressures means that a fully-branched mechanism is supplanted by a straight-chain mechanism with rare branchings. This very transition evidently determines the change in the character of ignition development.

Chemical Kinetic Model

In order to describe the ignition mechanism in terms of kinetic schemes it was necessary to define such a parameter of the ignition processes which could be quantitatively calculated from kinetic data. We chose the induction lag, i.e., the time (see Fig. 1) from the moment of the shock-wave propagation until the appearance of the first ignition locus.
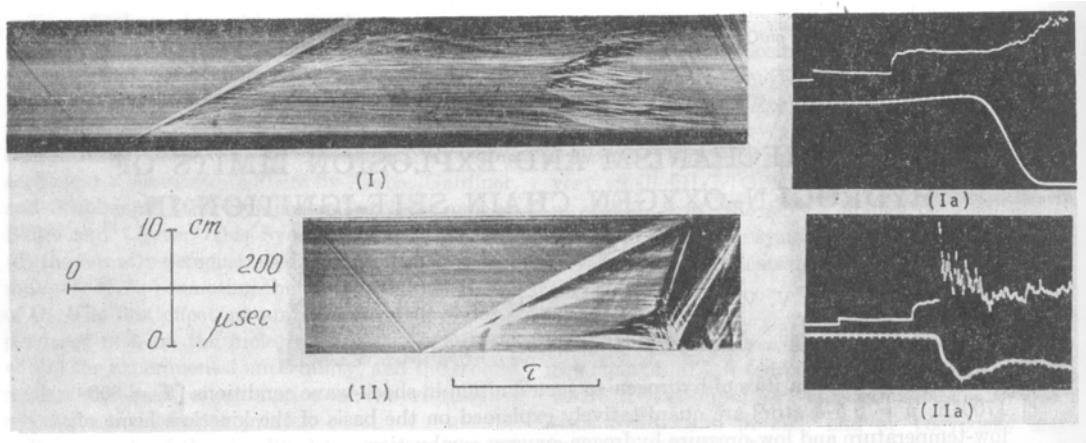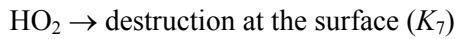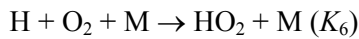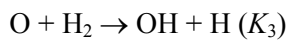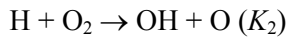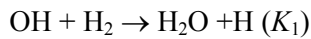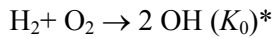
Fig. 1. Schlieren streak-photographs (I, II) and tracings of pressure (upper) and luminosity (lower) records [I(a), II(a)] for shock ignition in ($H_2 + O_2$), $p \sim 2$ atm; I, $T = 1010$ K; II, $T = 1060$ K

The kinetic scheme of hydrogen ignition at $T \to T(p_2)$ (see Fig. 2) consists of the following elementary processes:

$H_2 + O_2 \to 2$ OH (K_0)*

OH + $H_2 \to H_2O$ + H (K_1)

H + $O_2 \to$ OH + O (K_2)

O + $H_2 \to$ OH + H (K_3)

H + O_2 + M $\to HO_2$ + M (K_6)

$HO_2 \to$ destruction at the surface (K_7)

$HO_2 + H_2 \to H_2O_2$ + H (K_8)**

The rate coefficients of these reactions and their temperature dependences have been reliably measured with acceptable accuracy [2, 3]. The induction period can be calculated by means of the formula [2] $\tau = 1/\phi \ln\alpha$, where $\phi \approx 2K_2(O_2) - K_6(O_2)(M)$ in the temperature range 1100–1800 K. At temperatures between 800 and 1100 K, ϕ is determined by the largest characteristic value of the equation system

$$\frac{d(H)}{dt} = [2K_2 - K_6(M)](O_2)(H) + K_8(H_2)(HO_2) + W_0;$$
$$\frac{d(HO_2)}{dt} = K_6(M)(O_2)(H) - [K_7 + K_8(H_2)](HO_2).$$

α is equal to $W'/W_0 \approx 10^5$, where W' is the rate determined within the limitations of our experimental methods and W_0 is the rate of the homogeneous chain-initiation reaction. Some lack of precision in α-value definition leads to small change of τ.
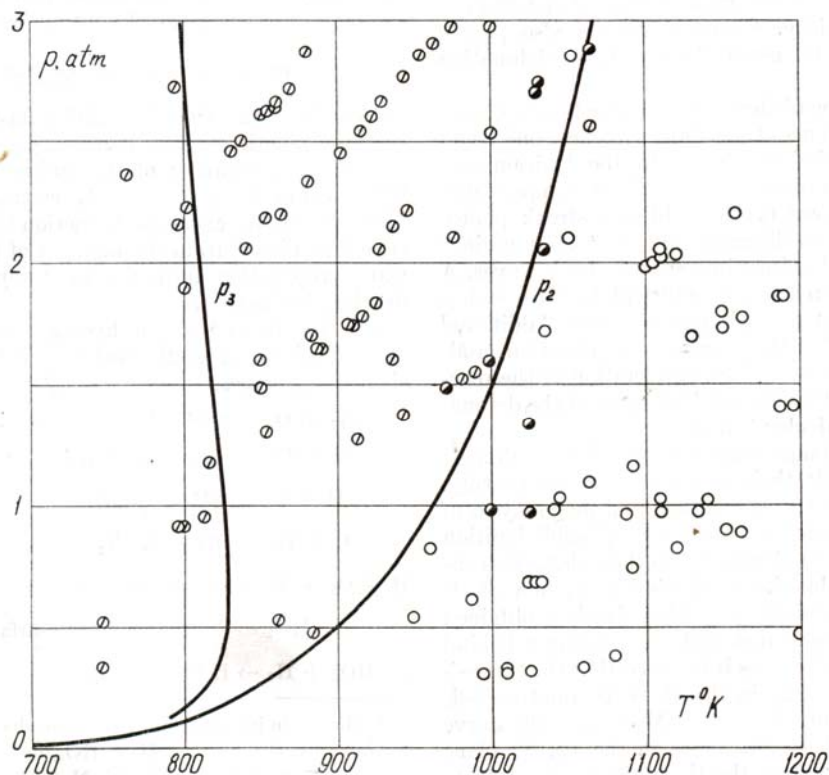
Fig. 2. Data on explosion limits in $H_2 + O_2$. O, sharp ignition; ∅, "mild" ignition; ◐, intermediate cases. 1, limit $p = p_2 = 2K_2/K_6$; 2, limit $p = p_3$, [3], Solid lines: calculated values of $\tau = 1/\phi \ln \alpha$

Results and Discussion

Using the formulas given above, we can compare calculated data with experimental results (Fig.3). Primarily, it must be noted that both in experimental and calculated data there is a sharp fall of $\log \tau$ values at $T = 970, 1020, 1070$ K ($p = 1, 2, 3$ atm, respectively) i.e., at the same temperatures at which changes in the characteristics are observed (see above). Close correspondence between experiment and theory shows that the low-temperature kinetic scheme holds under our conditions. This also follows from the close agreement between $\log \tau$ (calc) and $\log \tau$ (exptl) in the high-temperature range.

Another confirmation of the scheme validity is the absence of deflagration outside the explosion limit p_3 (Fig. 2). This limit is sometimes called the third "chain" explosion limit [2]. The thermal explosion limit calculated by D. A. Frank-Kamenetsky equations [2, 3] corresponds to somewhat lower temperatures and is not realized under our conditions. The lower the pressure, the less distinct is the "break-down" effect. This also corresponds to the chemical model as the explosion limit p_3 curve is very close to the curve p_2 (Fig. 2).

The only quantitative discrepancy between the experimental data presented in this paper and the kinetic calculations based on the kinetic scheme and well-known values of rate coefficients is observed in the temperature range corresponding to the area between p_2 and p_3 (see Fig. 2). The calculated values of т are greater than measured ones by a factor of 10^2 (Fig. 3).
One possible way of explaining these data would be to suppose that the rate coefficient K_8 is not precise. However an alteration of this coefficient leads to an observable displacement of the limits and the difference between calculations and experiments would be even more evident.
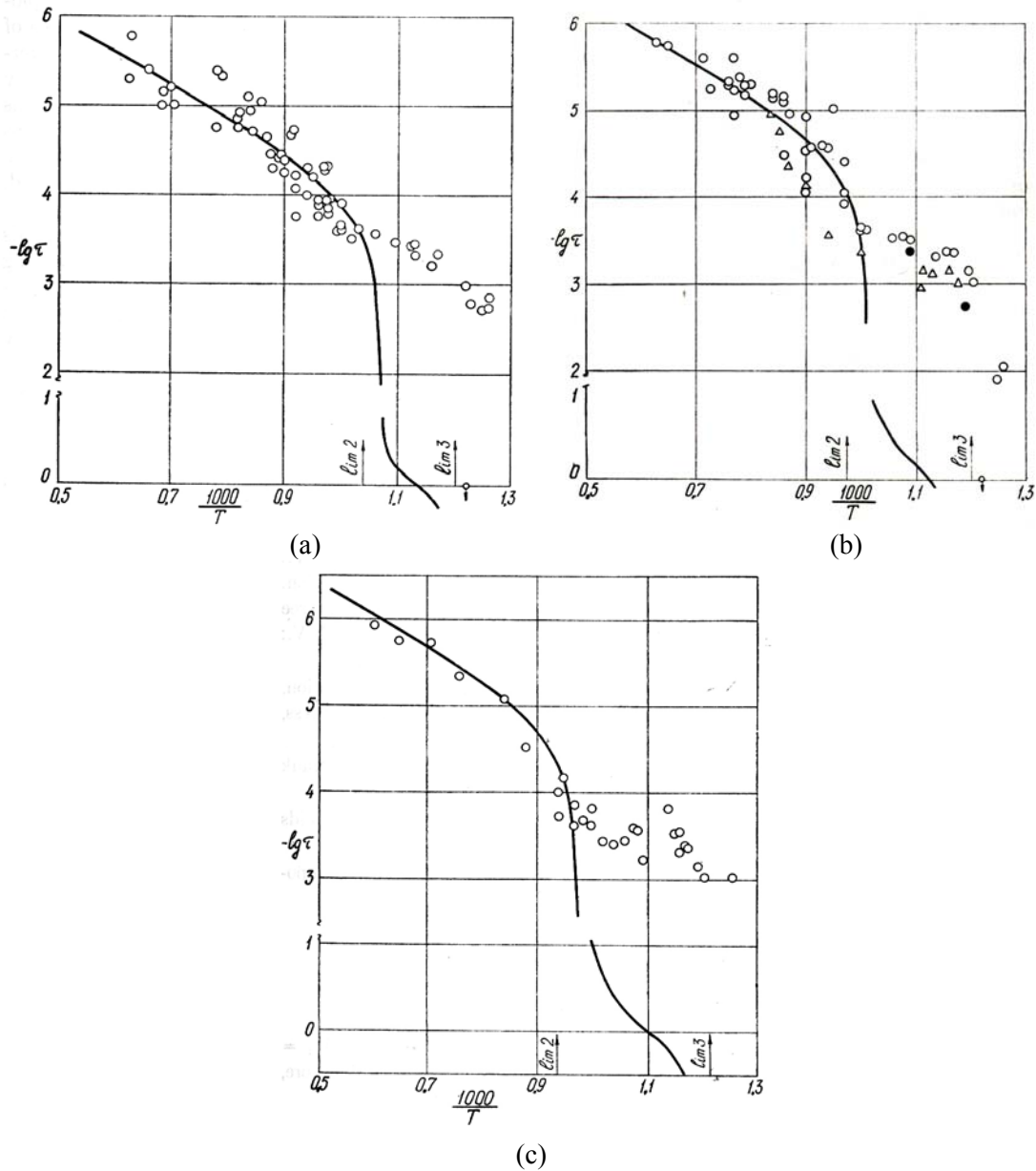
(a)

(b)

(c)

Fie. 3. Comparison of observed and calculated lags at various final pressures:
(a) $p = 1 \pm 0.35$ atm. (b) $p = 2 \pm 0.3$ atm: O, pure mixture;

△, 1% CO2 impurity; ●, KCl-coated tube. (c) $p = 3 \pm 0.4$ atm

It seems more probable that in the range of temperatures under consideration in which ignition and detonation development are "mild" enough, the lags may depend greatly on specific conditions in the ignition volume. As a possible hypothesis, we may suppose that the difference from the usual thermal reactions lies in the fact that in shock-wave ignition a certain role must be ascribed to vibrationally excited molecules O_2. The relaxation times of pure oxygen molecules may be of the order [1] 10^{-4}–10^{-3} sec and are thus comparable with the induction lags in the temperature range where the discrepancy to be explained exists. According to White and Moore [6] however, the relaxation times O_2 in O_2-H_2 mixture are considerably smaller than in pure oxygen. Thus, the influence of relaxation times on ignition lags should be excluded here.

In order to ascertain the influence of the walls and boundary effects on the ignition, the walls of the explosion chamber were coated with potassium chloride. This treatment did not lead to any considerable change in the time lag values [Fig. 3(b)]. This showed again that, in our case, we dealt with a "chain" and not a thermal explosion. At last, to exclude the possible influence of temperature

deviations connected with the interaction of the reflected wave with the boundary layer [1, 5] the construction of the shock tube was changed: the central part of the gas flow was separated by a special thin-walled pipe, where ignition after reflection of the wave was observed. In spite of the fact that in these experiments the trace of the reflected wave in the streak records became much thinner, due to the weakening boundary effects, the measured lags were practically the same. Thus, there is no reason to believe that the regularities described above may be connected with boundary effects.

References

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COMMENTS

Prof. Z. A. Szabo (University of Szeged): Soloukhin assumed a set of elementary reactions and, on this basis, derived the most important kinetical parameters of ignition. I wonder if he has a special reason for taking the second elementary reaction $H + O_2 = HO + O$ into account as controlling ϕ, the branching, rather than the third one: $O + H_2 = HO + H$ which is less endothermic and therefore, can contribute more to the branching.

Prof. R. I. Soloukhin: Reactions (1) and (3) are not very significant in chain branching because of their low activation energy. If $p = 2$ atm ($H_2 + O_2$) and $T \sim 1400$ K,

$$K_1 \sim 1.5 \times 10^9 \exp\left(-10,000 / RT\right)$$

$$K_2 \sim 10^9 \exp\left(-18,000 / RT\right)$$

$$K_3 \sim 4 \times 10^7 \exp\left(-6000 / RT\right)$$

in sec^{-1}, respectively (Refs. [2] and [3] in our paper).
These values of the rate constants were used in "break-down" effect evaluation, and they are very close to our experimental data at the temperature considered. The steady-state simplification is in good accordance with a well known experimental fact for very high hydrogen-atom concentrations. At high temperatures and for precise calculations, of course, all the above-mentioned reactions must be considered together.