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Features of initiation of spherical flames in mixtures of natural gas and isobutylene with oxygen in the presence of inert additives

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The regularities of formation of spherical laminar flames in stoichiometric mixtures of natural gas and isobutylene with oxygen and Kr or CO_2 additives in a constant volume reactor have been established by means of color speed cinematography at 100 Torr and 298 K.

In the majority of combustion processes, chemical reactions in flames have a complicated branched chain nature involving active intermediates (atoms, radicals), therewith the rate of branching strongly depends on temperature.[1–4]

The normal velocity U_n of propagation of flame front (FF) accounts for both (chain and thermal) accelerating factors of combustion. In the mechanisms of hydrocarbons oxidation, the reaction of nonlinear branching, which can provide non-thermal flame propagation, is missing.[4–6] Therefore, the only feedback factor responsible for the occurrence of a stationary propagating flame is warming-up. Thus, the thermal theory[1] with regard to combustion kinetics[5,6] is applicable to the flame propagation processes.

A zone of laminar FF in the flame of hydrocarbon combustion is comparatively broad. As is known,[2] an intense chain self-acceleration occurs in the low temperature parts of flames; in this case, the nature of branching step is under discussion. The peculiarities of the flames at the stage of their origin under spark initiation are scantily known in combustion physics.[1,2,4,7,8]

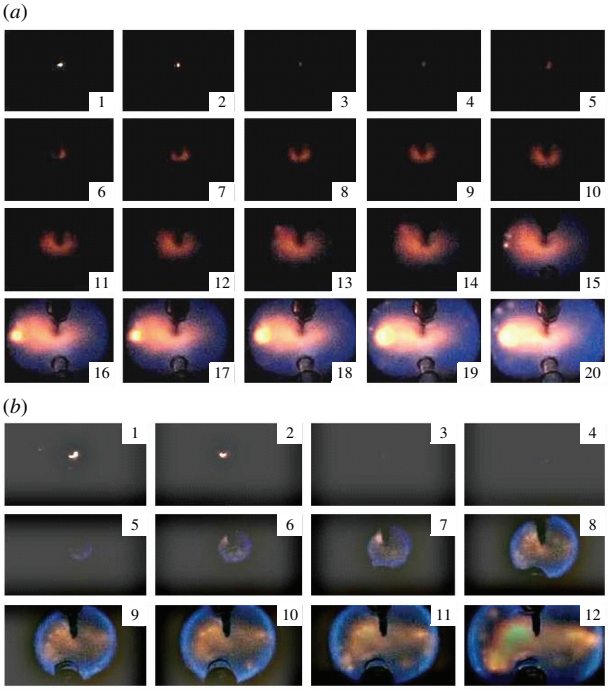

Figure 1 Filming of the propagation of spherical FF (1200 frames per second), P = 100 Torr, T_0 = 298 K, E_0 = 0.91 J: (*a*) $(NG + O_2)_{stoich}$ + 50% CO_2. (*b*) $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 70% Kr.

The work is aimed at the experimental determination of conditions of formation of steady spherical laminar FF by means of color speed cinematography of FF chemiluminescence. Note that the zone of intense chemiluminescence of FF and the zone of maximal change in gas density being recorded by shadow or schlieren methods do not coincide with each other.

The experiments were carried out under static conditions at 298 K and a total pressure of 100 Torr. A cylindrical quartz reactor (8 cm in diameter; 12 cm in height) was equipped with inlets for gas evacuation, spark initiation and optical windows, as well as a pressure transducer. A signal from the pressure transducer was recorded by means of a digital C9-8 oscilloscope and stored in computer memory. Chemiluminescence from FF was recorded by means of a color high-speed digital camera Casio Exilim F1 Pro (1200 frames per second); each set of frames was stored in computer memory. Ignition was provided with a spark (0.91 J) at the centre of the reactor; the distance between electrodes was 0.05 cm. The reactor was evacuated to 10^{-2} Torr before each experiment. The stoichiometric mixtures of natural gas (NG) and isobutylene (iso-C_4H_8) with CO_2 or Kr additives were prepared before experiments. The additives of CO_2 and Kr to the mixture of NG + O_2 were 20–45 and 30–75%; and to the mixture of iso-C_4H_8 + O_2 were 35–60 and 60–80%, respectively. NG contained 2% propane and butane.

At the initial stage, the laminar flames investigated in the present work appear to be smooth and nearly spherical. Figure 1 shows the evolution of captured spherical flames [1200 frames per second, $(NG + O_2)_{stoich}$ + 50% CO_2, $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 70% Kr, P = 100 Torr, T_0 = 298 K]. A blue spherical FF due to the emission of electronically excited intermediates CH* (431 nm), CH_2O* (470 nm)[2,11] followed by a high-temperature orange area of FF can be easily observed in the frame sets.

Note that the process of formation of the steady FF in H_2–O_2–N_2 and H_2–hydrocarbon–O_2–N_2 flames at 1 atm was investigated.[9] The results obtained were considered from the standpoint that the curvature of FF at the initial stage determines the velocity of the rise of origin of initiation. However, as seen in Figure 2(*a*),(*b*), in which temporal dynamics of the dependence of the increase in visible radius r_1 of emission of spherical FF on the composition of the mixture is shown, the time of FF formation increases with decreasing combustibility, *i.e.*, with increasing dilution of a combustible mixture. Moreover, though local occurrence of secondary hot spots is observed in the mixtures containing NG [Figure 1(*a*), frames 13–20], it is seen in Figure 2(*a*) that the instabilities do not cause any

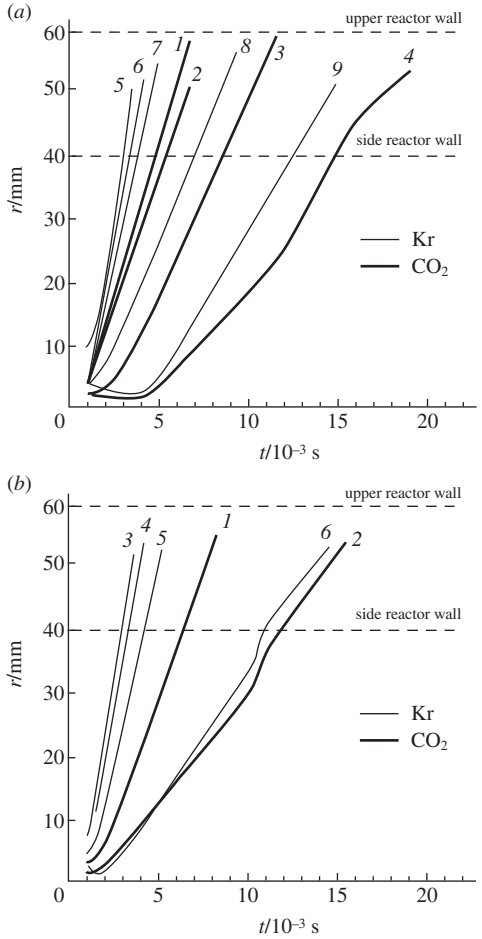

Figure 2 Temporal dynamics of the dependence of the increase in visible radius r_1 of emission of spherical FF on the composition of the mixture (P = 100 Torr, 298 K). (*a*): (*1*) 70% $(NG + O_2)_{stoich}$ + 30% CO_2, (*2*) 65% $(NG + O_2)_{stoich}$ + 35% CO_2, (*3*) 60% $(NG + O_2)_{stoich}$ + 40% CO_2, (*4*) 55% $(NG + O_2)_{stoich}$ + 45% CO_2, (*5*) 55% $(NG + O_2)_{stoich}$ + 45% Kr, (*6*) 50% $(NG + O_2)_{stoich}$ + 50% Kr, (*7*) 40% $(NG + O_2)_{stoich}$ + 60% Kr, (*8*) 30% $(NG + O_2)_{stoich}$ + 70% Kr, (*9*) 25% $(NG + O_2)_{stoich}$ + 75% Kr; (*b*): (*1*) 50% $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 50% CO_2, (*2*) 40% $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 60% CO_2, (*3*) 40% $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 60% Kr, (*4*) 35% $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 65% Kr, (*5*) 30% $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 70% Kr, (*6*) 20% $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + 80% Kr.

acceleration of the flame. However, in the case of methane–air mixtures, no instability effects were observed.[10] This indicates that combustibility of the mixture but not only the curvature of FF determines the time of FF formation.

Notice that there is no published data on the secondary hot spots in NG combustion detected in this work. The phenomenon needs further investigation.

The data obtained indicate the occurrence of an initial hot spot of finite dimension from which the combustion wave can develop. From the data in Figures 2 and 3, the times of formation of steady FF (τ) were determined. The certain complexity in the determination dealt with the error in measurement of FF initial radius (~30% of its mean value), which was ≈ 0.4 cm for all compositions of gaseous mixtures. The value of τ was determined from the abscissa of point of interaction of the line r = 0.4 cm and a tangent to experimental dependence $r(t)$. The results of determination of the values of τ are shown in Figure 3. The data are evidence for the occurrence of both the hot spot of finite dimension, from which a steady combustion wave can develop,[12] and a minimal energy of ignition Q_{min} corresponding to this hot spot.

Let us estimate the value of Q_{min} from the data of Figure 2(*a*),(*b*) and correlate it with literature values of Q_{min}.[9,12] We set up heat

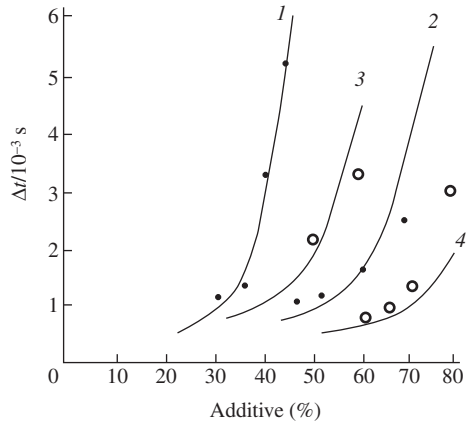

Figure 3 Dependence of the time of formation of steady spherical FF on the composition of a combustible mixture (P = 100 Torr, 298 K): (*1*) $(NG + O_2)_{stoich}$ + CO_2, (*2*) $(NG + O_2)_{stoich}$ + Kr, (*3*) $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + CO_2, (*4*) $(iso\text{-}C_4H_8 + O_2)_{stoich}$ + Kr. Dotted line – estimation from equation (8).

balance for the element of the flame with a dimension about the width of steady FF:

$$Q_{min} = V_{min}\rho Cp(T_b - T_0), \quad (1)$$

where Cp is the heat capacity (cal mol^{-1} K^{-1}), ρ is the density of products in the hot spot (mol cm^{-3}), T_b is the temperature of combustion, T_0 is the initial temperature, $V_{min} \sim 4/3\pi r_{min}^3$ is the minimal volume of the spherical hot spot heated to T_b; the hot spot will pass into propagating flame if its size is of the order of the width of the steady FF.[12] In view of equation (1) and with allowance made for $\rho = (1/N)(P/P_0)(T_0/T_b)$, putting experimental value $T_b \sim 1600$ K, $N = 22.4\times10^3$ cm^3, P_0 = 750 Torr, T_0 = 298 K, P = 100 Torr, Cp ~ 10 cal mol^{-1} K^{-1}, $r_{min} \sim 4$ mm, we get $Q_{min}(P) \sim 4.4\times10^{-3}$ cal = 1.9×10^{-2} J at 100 Torr for combustible mixture of $(NG + O_2)_{stoich}$ with addition of Kr or CO_2. As is known,[12] $Q_{min}(P_0) \approx 0.33\times10^{-3}$ J for a methane–air mixture under spark initiation under normal conditions. To compare the values of $Q_{min}(P)$ and $Q_{min}(P_0)$, let us estimate the pressure dependence of $Q_{min}(P)$. According to ref. 12 minimal dimension of the hot spot makes up $r_{min} = b\delta$, where b is a nondimensional number ~ 3, δ is the FF width, $\delta = \alpha/U_n$, $\alpha = \lambda/\rho$Cp is the temperature conductivity and λ is the thermal conductivity. Substituting values of r_{min} and δ into equation (1), one can obtain:[12]

$$Q_{min} = 4/3\pi(b\lambda/U_n)^3(P_0/P)^2(NT_b/CpT_0)^2(T_b - T_0) = \\ = \text{const}(1/U_n^3)(P_0/P)^2 \quad (2)$$

With regard to a weak dependence of U_n on total pressure (U_n slightly changes under change of pressure from 0.1 to 1 atm for methane–air mixtures[5,8]) the value of Q_{min} from ref. 12 for total pressure makes up 3.3×10^{-2} J. A good agreement between the values obtained by distinct ways is evidence in favour of the chosen value of FF initial radius.

Let us estimate the relationship between the values of τ from Figure 3. We consider a heat balance at the limit of initiation. The occurrence of the steady hot spot leading to FF propagation is probable under the following condition:

$$q_{min} \geq q_t, \quad (3)$$

where q_{min} is the rate of heat release in the hot spot, and q_t is the rate of heat emission:

$$q_{min} = V_{min}Q_0\omega, \quad (4)$$
$$q_t = \chi S_{min}(T_b - T_0), \quad (5)$$

where V_{min} is the volume of the hot spot with radius r_{min}, Q_0 is the heat of combustion per mole of combustion products, ω is the rate of chemical transformation, χ is a heat-transfer coefficient, S_{min} is an area of surface of the hot spot. With regard

to both $r_{min} \approx$ const and $Q_0 =$ const, the value of q_{min} can be represented in the form

$$q_{min} = Q^0_{min}/\Delta t, \quad (6)$$

where $Q^0_{min} \approx Q_{min}$, and $\Delta t \sim 1/\omega$ is the characteristic time of chemical transformation. According to equations (4)–(6) we have:

$$Q^0_{min}/\Delta t \geq \chi S_{min}(T_b - T_0). \quad (7)$$

On dilution of initial stoichiometric mixture with an inert additive, the following relation between the times Δt_1 and Δt_2 for different amounts of the same inert additive must assert:

$$\Delta t_2/\Delta t_1 = (T_{b1} - T_0)(T_{b2} - T_0) = (\varepsilon_{T1} - 1)/(\varepsilon_{T2} - 1), \quad (8)$$

where $\varepsilon_T = \nu T_b/T_0$ is a degree of expansion of combustion products at the given composition of combustible mixture, ν is the change in number of moles in combustion. The value of ν for hydrocarbons under investigation can be put ~1,[5] that is, $\varepsilon_T \approx T_b/T_0$. The value of ε_T was determined from the value of the end pressure for adiabatic conditions of combustion of combustible mixture P_{bv}:[1,8] $P_{bv}/P_0 = 1 + \gamma(\varepsilon_T - 1)$, where γ is adiabatic exponent taken equal to 1.2. The value of U_n was determined from the relation $U_n = V/\varepsilon_T$ (V is the visible flame velocity).[5,8]

The values of Δt_1 with respect to one of experimental values taken as $\Delta t_2 = 0.7\times10^{-3}$ s were estimated on the basis of equation (8) with consideration for known values of ε_T. Results of comparison of experimental values of $\Delta t \sim 1/\omega$ and those obtained on the basis of equation (8) are shown in Figure 3 and demonstrate reasonable agreement.

As is seen in Figure 2, CO_2 additives have a more effective influence on the limit of ignition than Kr additives. It can be explained by the fact that CO_2 has greater capacity than Kr; therefore, CO_2 additives reduce the combustion temperature to a greater extent than Kr and according to equation (8) increase the values of Δt. This causes the breakdown of ignition at a lower concentration of the additive. In addition, an increase in Δt may be a result of greater effectiveness of termolecular chain termination of active centers of combustion in the case of CO_2 as a third body.[5]

It was also shown that repeated spark initiation is required in the immediate vicinity of the limit of ignition of diluted with CO_2 or Kr combustible mixtures to provide flame propagation. This is evidence for the important role of low temperature reactions close to the limit of ignition. It means that a portion of energy of a spark discharge is consumed to run endothermic reactions of formation of long-lived intermediates (peroxides, aldehydes, *etc*.); their accumulation provides the ignition of the combustible mixture.

Note that both a solution of a problem on a hot spot thermal explosion and the analysis of nonsteady ignition of a hot spot for chemical zero-order reaction were carried out.[13,14] The consideration was restricted to a qualitative treatment due to the complicated nature of chemical mechanisms of combustion of hydrocarbons.

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