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Investigation into self-ignition in chain oxidation of hydrogen, natural gas and isobutene by means of high-speed colour cinematography

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Features of spatial development of self-ignition in chain oxidation of hydrogen, natural gas and isobutene with oxygen at 10–100 Torr and 750–1000 K have been revealed by means of high-speed colour cinematography; the features could be controlled by addition of chemically active gaseous additives (promoters and inhibitors).

Data on spatial evolution of self-ignition (SI) of combustible gases contacting with heated surfaces are of immediate interest in relation to the use of hydrocarbons and hydrogen as fuels in engines and other power devices.

SI of $H_2 + O_2$ at low pressures (~1 Torr) is considered to be uniform over reactor volume.[1] However, the required time of warming-up to attain uniform distribution of gas temperature over reactor volume increases as total pressure increases. The inhomogeneity of warming-up makes SI originate in the vicinity of reactor surface. It means that one-dimensional problem on SI[1] can pass on to the problem on ignition with heated surface.[2–4] The state of reactor surface also influences the uniformity of ignition because the occurrence of heterogeneous reactions provides origination of SI at reactor surface. It has been just high-speed filming that allows distinguishing whether SI in gases occurs over volume or at reactor wall.

The work is aimed at the experimental investigation of spatial development of SI of chain oxidation of H_2, natural gas and isobutene by means of high-speed colour cinematography. The work is also aimed at qualitative numerical treatment of the influence of the time of warming-up, the nature of heterogeneous chain termination and surface reactions on spatial evolution of SI.

Experiments were carried out at 750–1000 K and the total pressure P_0 = 10–100 Torr. A heated quartz cylindrical reactor (3.6 cm in diameter, 25 cm in length) had an inlet for gas evacuation, photomultiplier and an optical window at the butt-end. The signal from photomultiplier equipped with interference filter (λ = 306 nm) was recorded with a digital oscilloscope. Stoichiometric mixtures of H_2, natural gas (NG) and isobutene (iso-C_4H_8) with O_2 were prepared prior to experiments. The mixture under investigation was quickly injected into the heated evacuated reactor from a storage volume to necessary P_0. SI of $2H_2 + O_2$ was performed over quartz surface and over magnesium oxide (MgO) as well. SI of NG + $2O_2$ and iso-$C_4H_8 + 6O_2$ was performed over quartz surface. Visible emission was recorded by means of a Casio Exilim F1 Pro colour high-speed digital camera (1200 frames per second), sensitive over the spectral range of 420–740 nm.

The sets of frames of spatial development of SI in $2H_2 + O_2$ over quartz surface (in kinetic area of chain termination[1]) are shown in Figure 1(*a*)–(*c*). As is seen in Figure 1(*a*),(*b*), homogeneity of SI depends on the state of surface. If the surface is treated with HF immediately before ignition, SI of $2H_2 + O_2$ in the first experiment occurs in the vicinity of the surface [Figure 1(*a*)], but in further experiments the origination of SI changes over surface to reactor volume [Figure 1(*b*)]. The colours of the ignition over freshly treated surface and in reactor treated with several ignitions are different; *i.e.*, the emissions in both cases vary in spectral composition.

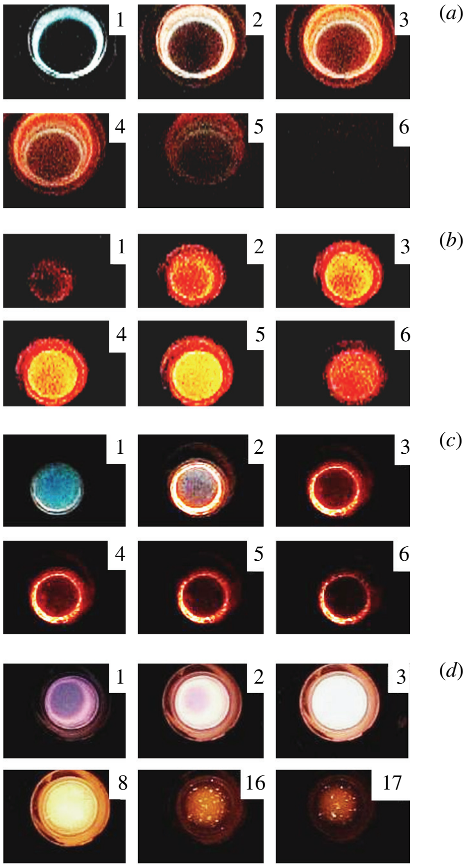

Figure 1 Spatial development of self-ignition in mixtures of (*a*)–(*c*) $2H_2 + O_2$ and (*d*) NG + $2O_2$ over quartz surface, 1200 frames s^{-1}. The ordinal number of the frame from the moment of chemiluminescence origination is given. (*a*) P_0 = 55 Torr, T_0 = 823 K, surface freshly treated with HF, the first experiment; (*b*) P_0 = 55 Torr, T_0 = 823 K, the fifth experiment; (*c*) P_0 = = 11 Torr, 2% iso-C_4H_8, T_0 = 983 K; (*d*) P_0 = 78 Torr, T_0 = 993 K.

The induction period τ_i of SI was estimated as the time interval between the moment of injection and the moment when the intensity of chemiluminescence of SI made up $1/e$ (e = 2.1828...)

of its total intensity.[1] Under conditions of Figure 1(*a*),(*b*), τ_i makes up < 0.3 s, *i.e.*, SI of combustible mixture near reactor surface can be caused by inhomogeneous warming-up during τ_i and probably catalytical reactions on reactor walls. We showed earlier that, in the presence of iso-C_4H_8, the value of τ_i markedly increases.[5] Therefore, 2 vol% iso-C_4H_8 was added to a $2H_2 + O_2$ mixture to provide homogeneous heating of combustible mixture. Under conditions of Figure 1(*c*), $\tau_i = 6$ s. Simple estimation shows that this time is enough to heat the mixture uniformly in diameter. As is seen from Figure 1(*c*), SI in this mixture is almost uniform in diameter, *i.e.*, the relation between the time of warming-up and the characteristic time of chemical reaction specifies the uniformity of SI.

On the other hand, short values of τ_i are indicative of high rate of chain initiation.[1] Therefore, the possibility of SI at the surface increases as the rate of chain initiation increases. The rate of this step is the next governing factor determining the uniformity of SI.

It was shown that, over MgO coating (in diffusive area of chain termination[1]), SI of $2H_2 + O_2$ at $P_0 = 20$–40 Torr and $T_0 = 900$ K develops uniformly in reactor volume almost similar to the frame set shown in Figure 1(*c*). It should be noted, however, that the emission due to surface reaction could be observed in Figure 1(*c*) (frames 1, 4–6); therefore, the origination of SI could be probably recorded near reactor walls at higher speed of filming; this possibility needs further investigation.

The set of frames of spatial development of SI in NG + $2O_2$ mixture over quartz surface is shown in Figure 1(*d*). The values of P_0 in the experiments are close to lower SI limit of $CH_4 + 2O_2$ mixture;[6] in this case, the value of τ_i is ~30 s. Therefore, the combustible mixture is warmed up homogeneously to the temperature of walls for this value of τ_i. However, as is seen in Figure 1(*d*), SI originates on the reactor surface and then propagates into reactor volume. We have also shown that SI of iso-$C_4H_8 + 6O_2$ propagates in similar way. It means due to aforesaid that reactions of oxidation of NG and iso-C_4H_8 on the quartz surface have catalytic heterogeneous steps.

The results obtained were qualitatively considered using numerical simulation by the example of H_2 chain oxidation because its kinetic mechanism (as distinct from hydrocarbon oxidation) is well-understood.[1,7] The influence of the time of warming-up, heterogeneous chain termination and surface reactions on spatial evolution of SI in a confined channel was investigated. The reduced kinetic mechanism of H_2 oxidation can be represented as follows:[8,9]

$$H_2 + O_2 \rightarrow 2OH\ (HO_2 + H) \tag{0}$$
$k_0 = 1.92\times10^{14}\exp(-21890/T)$ cm^3 mol^{-1} s^{-1} (ref. 10)

$$OH + H_2 \rightarrow H_2O + H \tag{1}$$
$k_1 = 4.63\times10^{12}\exp(-2100/T)$ cm^3 mol^{-1} s^{-1} (ref. 11)

$$H + O_2 \rightarrow OH + O \tag{2}$$
$k_2 = 1.99\times10^{14}\exp(-8460/T)$ cm^3 mol^{-1} s^{-1} (ref. 12)

$$O + H_2 \rightarrow OH + H \tag{3}$$
$k_3 = 1.88\times10^{14}\exp(-6897/T)$ cm^3 mol^{-1} s^{-1} (ref. 13)

$$H + O_2 + M \rightarrow HO_2 + M \tag{4}$$
$k_4 = 6.47\times10^{15}(T/298)^{-0.8}$ cm^6 mol^{-2} s^{-1} (ref. 14)

$$H + HO_2 \rightarrow 2OH \tag{5}$$
$k_5 = 1.69\times10^{14}\exp(-440/T)$ cm^3 mol^{-1} s^{-1} (ref. 12)

$$H_2 + HO_2 \rightarrow H_2O_2 + H \tag{6}$$
$k_6 = 3\times10^{13}\exp(-14400/T)$ cm^3 mol^{-1} s^{-1} (ref. 12)

$$OH + O \rightarrow H + O_2 \tag{7}$$
$k_7 = 9.29\times10^{12}$ cm^3 mol^{-1} s^{-1} (ref. 15)

$$O + HO_2 \rightarrow OH + O_2 \tag{8}$$
$k_8 = 3.25\times10^{13}$ cm^3 mol^{-1} s^{-1} (ref. 12)

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{9}$$
$k_9 = 2.89\times10^{13}\exp(250/T)$ cm^3 mol^{-1} s^{-1} (ref. 14)

$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{10}$$
$k_{10} = 2\times10^{12}$ cm^3 mol^{-1} s^{-1} (ref. 16)

$$H_2O_2 + M \rightarrow 2OH + M \tag{11}$$
$k_{11} = 1.3\times10^{17}\exp(-22750/T)$ cm^3 mol^{-1} s^{-1} (ref. 12)

$$H + H + M \rightarrow H_2 + M \tag{12}$$
$k_{12} = 2.2\times10^{15}$ cm^6 mol^{-2} s^{-1} (ref. 14)

A two-dimensional planar problem was examined. Characteristic scales of the process were chosen as follows: $t_0 = 1/(k_1^0[H_2]_0)$, $x_0 = y_0 = (D_3/k_1^0[H_2]_0)^{1/2}$ [the scales of time and length, respectively, D_3 is diffusivity of H_2 and k_1^0 is the preexponential factor of the step (1)]. We determine the dimensionless variables and parameters $\tau = t/t_0$, $\xi = x/x_0$, $\eta = y/y_0$, Y_i = [concentration of *i*th component]/$[H_2]_0$, $\delta_i = D_i/D_3$ (D_i is diffusivity of *i*th component), K_p is dimensionless rate constant of the reaction. For bimolecular reaction, $K_p = k_p/k_1^0$, the value of *p* corresponds to the ordinal number of the step ($p \neq 4$, 12) in set (I). For termolecular reaction, $K_p = k_p[H_2]_0/k_1^0$, $p = 4$, 12. The indexes *m*, *n* of the dimensionless concentrations of the reagents, which change from 0 to 6, correspond to dimensionless concentrations of OH, O, H, H_2, O_2, HO_2 and H_2O_2. Dimensionless diffusivities (D_i/D_3, $i = 0$–6) δ_0, δ_1, δ_2, $\delta_3 = 1$, δ_4, δ_5, δ_6 in $2H_2 + O_2$ mixture refer to OH, O, H, H_2,O_2, HO_2 and H_2O_2, respectively.

The set of reaction-diffusion equations for the above reaction mechanism takes the form:

$$\begin{aligned} \partial Y_i/\partial\tau &= \delta_i(\partial^2 Y_i/\partial\xi^2 + \partial^2 Y_i/\partial\eta^2) + \sum_p \sum_{m \neq i,\, n} K_p Y_m Y_n - \sum_p \sum_{m = i,\, n} K_p Y_m Y_n \\ \partial T/\partial\tau &= \delta_7(\partial^2 T/\partial\xi^2 + \partial^2 T/\partial\eta^2) + 1/(C\rho)\sum_p \sum_{m,\, n} Q_p K_p Y_m Y_n \end{aligned} \tag{I}$$

The rate of heat release in reaction chain is given by the latter equation of set (I). Here, *C* is the mass-weighted mean specific heat capacity at constant pressure (cal g^{-1} K^{-1});[17] $\delta_7 \approx \delta_3$ is thermal diffusivity of the mixture, *T* is temperature (K) and ρ is density (g cm^{-3}).[17] Specific heats Q_p and D_i were taken from refs. 18, 19; symbol *f* is the mole fraction of an initial component (H_2, O_2).

The reaction-diffusion equation for O atoms as an example is illustrated below:

$$\partial Y_1/\partial\tau = \delta_1(\partial^2 Y_1/\partial\xi^2 + \partial^2 Y_1/\partial\eta^2) + K_2Y_2Y_4 - K_3Y_1Y_3 - K_7Y_0Y_1 - K_8Y_1Y_5.$$

The solutions of set (I) fulfill the following initial conditions (L_0 is the reactor length, *L* is the distance between the reactor axis and its wall; symmetry conditions are specified along the axis):

$$0 < \xi < L_0,\ 0 < \eta < L;\ \tau = 0;\ Y_i(0, \xi, \eta) = 0\ (i \neq 3, 4),$$
$$Y_3(0, \xi, \eta) = f_{H_2},\ Y_4(0, \xi, \eta) = f_{O_2},\ T(0, \xi, \eta) = 300\ \text{K}.$$

Boundary conditions are: $T(\tau, \xi, \eta = L) = 1000$ K,

$$0 < \eta < L\text{: } T(\tau, 0, \eta) = 300\ \text{K},\ T(\tau, L_0, \eta) = 300\ \text{K}. \tag{II}$$

Boundary conditions of types II and I were used for modeling of the termination of active centres in diffusive or kinetic area of chain break, respectively:

$$\begin{aligned} &0 < \xi < L_0,\ 0 < \eta < L;\ \mathrm{Y}_i(\tau, \xi, L) = 0\ \text{(boundary conditions of type I)}, \\ &(i \neq 3, 4),\ 0 < \xi < L_0\ [\partial Y_i(\tau, \xi, \eta)/\partial\eta]_L = 0\ (i = 3, 4) \\ &\text{or } [\partial Y_i(\tau, \xi, \eta)/\partial\eta]_L = 0\ \text{(boundary conditions of type II)} \end{aligned} \tag{III}$$

1600 points of partition on ξ coordinate and 600 points of partition on η one, corresponding to a canal diameter of 3.2 cm and its length of 4.2 cm for characteristic scales chosen were used in calculations. In calculations, $P_0 = 10$ Torr because under our conditions at this P_0 the value of τ_i is comparable with the time of warming-up. It is the P_0 value that one can turn from

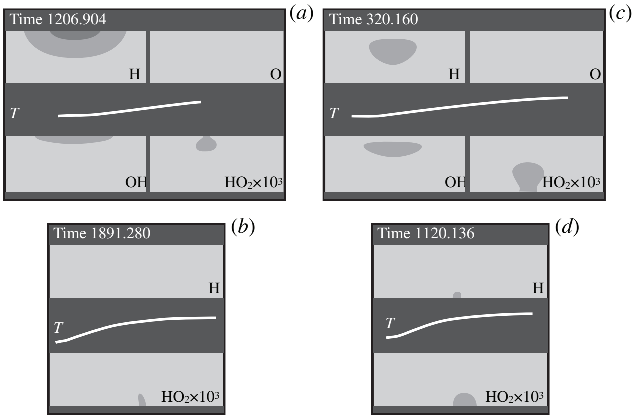

Figure 2 Numerical modeling of self-ignition of $2H_2 + O_2$ in (*a*), (*b*) kinetic and (*c*), (*d*) diffusive areas of chain termination. $T_0 = 1000$ K, $P_0 = 10$ Torr. (*a*) $E_0/R = 16500$ K; (*b*) $E_0/R = 20000$ K; (*c*) $E_0/R = 12000$ K; (*d*) $E_0/R = 18000$ K.

the surface origination of SI to the volume one over a small-scale interval of governing parameters.

Calculated profiles of intermediates in the initial stage of SI of $2H_2 + O_2$ mixture at the moment τ_F are shown in Figures 2, 3. τ_F was considered as the moment when the concentration of one of intermediates exceeded some threshold (10^{-3} dimensionless units for HO_2). Evidently, the value of τ_F is substantially close to experimental value of τ_i. As in ref. 20, in Figures 2 and 3 the bloom of grey colour indicates spatial distributions of Y_i, the colour borders correspond to fixed concentrations, and a darker colour corresponds to greater values of Y_i. The top of each frame is the wall of the channel; the bottom is its axis. The homogeneity of the warming-up can be qualitatively characterized by the difference in axial and wall temperatures. Both the temperature of hot wall and time dependence of axial temperature are also shown in Figures 2, 3 in the interval $0 < \tau < \tau_F$. The curves coalesce when the temperature distribution in canal width becomes uniform.

The influence of the rate of initiation step (0) on spatial development of SI was investigated. One can act upon the rate of the step by addition of gaseous inhibitor[21] (iso-C_4H_8 in this work) or by a promoter,[22] which decays to yield two free valences (*e.g.*, organic peroxide). Spatial distributions of H, O, OH and HO_2 at the initial stage of SI in kinetic area of chain termination $\{[\partial Y_i(\tau, \xi, \eta)/\partial\eta]_L = 0, i \neq 3, 4$, type II of boundary conditions$\}$ at different values of the rate of step (0) are shown in Figure 3. Formal changing of activation energy (E_0) of the step (0) varied its rate in calculations. As is seen in Figure 3(*a*), the value of τ_F decreases from 1900 to 1200 as E_0/R decreases from 20000 to 16500 K. At $E_0/R = 16500$ K, the ignition occurs in the vicinity of the surface because axial temperature is less than the one of hot wall. As E_0/R increases the warming-up becomes more homogeneous, and SI is accordingly more uniform in channel width. It means that one can influence the uniformity of SI with a chemically active gaseous additive using a promoter to make SI inhomogeneous or an inhibitor to make SI uniform over reactor volume.

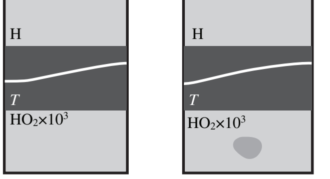

Figure 3 Numerical modeling of spatial development of self-ignition of $2H_2 + O_2$ in diffusive area of chain termination for OH, O, HO_2 with the flux of H atoms originated at the surface into the volume. $T_0 = 1000$ K, $P_0 = 10$ Torr, $E_0/R = 18000$ K.

Spatial distributions of H, O, OH and HO_2 at the initial stage of SI in diffusive area of chain termination [$Y_i(\tau, \xi, L) = 0$, $i \neq 3, 4$, type I of boundary conditions] at different rates of step (0) are shown in Figure 2(*c*),(*d*). The value of τ_F decreases from 1100 to 320 as E_0/R decreases from 18000 to 12000 K. SI becomes more uniform in reactor diameter as E_0/R increases; in this case, the value $E_0/R = 18000$ K provides SI in the centre of the channel [Figure 2(*d*)] at the cost of change in the relation between the time of warming-up and the characteristic time of chemical reaction. Therefore, uniform SI is expected in diffusive area if the time of warming-up is considerably more than the value of τ_i.

The case of chain initiation only on the surface was also considered. For this purpose, the flux of H atoms from the channel surface was included into the boundary conditions of type II. Results of numerical simulations of spatial development of SI of $2H_2 + O_2$ mixture in diffusive area of termination for OH, O and HO_2 with the flux of H atoms originating at the surface into the volume are shown in Figure 3(*a*),(*b*). The flux makes up 10^{-7} dimensionless units ($k_0[H_2]_0[O_2]_0/k_1[H_2]_0$, where $k_0 = 10^{-19}$ cm^3 molec^{-1} s^{-1}). Two consequent calculated ‘frames’ in the very beginning of SI at $E_0/R = 18000$ K are shown in Figure 3. As is seen, the flux of H atoms into volume provides inhomogeneous development of SI. Note that, at the same governing parameters but in the absence of the flux of H atoms [Figure 2(*d*)], uniform SI occurs.

Experiments and calculations performed show that homogeneity of SI over reactor volume strongly depends on the relation between the time of warming-up and the characteristic time of chemical reaction at the temperature of hot wall, on the rate of chain initiation and on the state of surface. With increasing rate of surface production of active centres or increasing total pressure of combustible mixture, the problem on SI passes on to the problem on ignition with heated surface, which can also catalyze chemical transformations. The results obtained should be taken into account in studies of SI at elevated pressures, *e.g.*, third self-ignition limit of H_2 oxidation,[1,3,8] because the dependence of τ_i on the diameter of reactor differs for the regime of heat explosion and the regime of ignition when the step of warming-up occurs.[23]

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