1448 Russian Chemical Bulletin, International Edition, Vol. 60, No. 7, pp. 1448—1451, July, 2011

Isothermal waves of hydrogen oxidation

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It is analytically shown that the chain ignition region is extended in the reaction of hydrogen oxidation due to the nonlinear interaction $H + HO_2 = 2\ OH$. As a result, the reaction propagates isothermally under the isothermal conditions outside the ignition region, which is calculated by the scheme taking into account only linear reactions with respect to radicals, if the reaction is initiated by additives of hydrogen atoms. The ignition limits were calculated with allowance for the above interaction, and the mathematical modeling of propagation of the hydrogen oxidation reaction under the isothermal conditions was performed.

Key words: oxidation of hydrogen, ignition limits, cold flame, nonlinear interactions, isothermal waves.

Isothermal flame implies the propagation of the reaction wave due to diffusion of active centers rather than heat propagation as in hot flames. The qualitative theory of this phenomenon is described in the monograph.[1] The first observations of isothermal (cold) flames are dated to the 1940s. The existence of cold flame of carbon disulfide oxidation has experimentally been proved for the first time and foundations for the theory of this phenomenon were formed.[2] At the content of CS_2 in the mixture equal to 0.03%, the adiabatic warming of the mixture did not exceed 15 K and the conversion wave observed by the luminescence of the mixture propagated along the tube with a rate of 0.02—0.4 $m\ s^{-1}$. The temperature of the surface of the tube and the flame zone was several degrees lower than the temperature of spontaneous ignition. Thus, the mixture in the cold flame during the process exists in the state lying outside the ignition peninsula. The mathematical modeling of the reaction wave in this system[3] on the basis of the kinetic scheme[4] revealed an important role of the quadratic interaction $CS + O \rightarrow CO + S$, which determines the wave propagation in the region of parameters lying outside the self-ignition region.

A series of experimental studies of cold flames in the low-temperature region of the reaction of fluorine with hydrogen[5] and in the decomposition of nitrogen trichloride[6] appeared in the 1970s.

In all these reactions the wave propagation is caused by diffusion to a fresh mixture of active particles, which initiate branching in the self-ignition region extended due to the positive interaction of the chains.

These studies concerned the low-temperature range of reactions in which the heat evolution is weak and the main reason for wave propagation outside the self-ignition region is the nonlinear interaction of active particles. In the case of hydrogen oxidation, the heat evolution is substantial even at low pressures and, hence, no cold flame was observed under natural conditions. However, for the artificial creation of isothermal conditions, the isothermal flame can be developed outside the self-ignition region using the fast removal of the isolated heat: there are all necessary kinetic prerequisites. The purpose of this work is the elucidation of these prerequisites and mathematical simulation of isothermal waves upon hydrogen oxidation.

Kinetic model and regions of linear and nonlinear ignition

The region determined by reactions linear with respect to concentrations of radicals is accepted below as the region of linear ignition, and the region of nonlinear ignition is obtained when reactions of radicals are additionally taken into account. To obtain self-ignition regions, it is enough to consider a model involving all linear and nonlinear reactions of branching and decay of active particles. The corresponding kinetic model is presented in Table 1.

To obtain boundaries of self-ignition regions, we use the procedure[7,8] that allows one to isolate fragments of the scheme (subgraphs) determining the critical conditions by an analysis of the graph corresponding to the scheme of reactions. The formulas for the boundary of the self-ignition region are obtained from the conditions where the determinant of the Jacobi matrix for the system of kinetic equations with respect to concentrations of active particles (H, O, OH, HO_2, H_2O_2) equals zero and the concentrations of the starting reactants are constant.[7,8] This condition corresponds to the equality to zero of one of the eigenvalues of the matrix of the linearized system. When

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1425—1428, July, 2011.

Table 1. Kinetic parameters of the reactions

Reaction	k^0_i *	n_i	E_i/kcal
$H_2 + O_2 \rightarrow 2\,OH$ (0)	$0.60 \cdot 10^{14}$	0	42.0
$O_2 + H \rightarrow OH + O$ (1)	$1.98 \cdot 10^{14}$	0	16.8
$H_2 + O \rightarrow OH + H$ (2)	$0.15 \cdot 10^{8}$	2	7.55
$H_2 + OH \rightarrow H_2O + H$ (3)	$1 \cdot 10^{8}$	1.6	3.3
$H + O_2 + M \rightarrow HO_2 + M$ (4)	$2.30 \cdot 10^{18}$	−0.8	0
$H_2 + HO_2 \rightarrow H_2O_2 + H$ (5)	$3.0 \cdot 10^{13}$	0	26.0
$H_2O_2 + M \rightarrow 2\,OH + M$ (6)	$1.2 \cdot 10^{17}$	0	45.4
$H + HO_2 \rightarrow 2\,OH$ (7)	$1.69 \cdot 10^{14}$	0	0.874
$H + HO_2 \rightarrow H_2O + O$ (8)	$3 \cdot 10^{13}$	0	1.721
$H + HO_2 \rightarrow H_2 + O_2$ (9)	$4.28 \cdot 10^{11}$	0	1.411
$H \rightarrow H^s$ (10)	–	–	–
$HO_2 \rightarrow HO_2{}^s$ (11)	–	–	–
$OH \rightarrow OH^s$ (12)	–	–	–
$O \rightarrow O^s$ (13)	–	–	–
$H_2O_2 \rightarrow H_2O_2{}^s$ (14)	–	–	–
$2\,H + M \rightarrow H_2 + M$ (15)	$1.98 \cdot 10^{18}$	−1	0

* In $cm^3\,mol^{-1}\,s^{-1}$ for reactions (0)—(3) and (5)—(9); in s^{-1} for reactions (10)—(14); in $cm^6\,mol^{-2}\,s^{-1}$ for reactions (4) and (15).

the parameters are beyond the boundary of the ignition region, this eigenvalue changes the sign and exponentially growing concentrations of active particles appear in the region where the eigenvalue would be positive.

The calculation of the determinant of the Jacobi matrix is reduced to the calculation of contributions from various subgraphs of the reaction graph and is performed by analytical computations.

Along with the classical branching cycles determined by reactions (1), (2), and (3) and the linear branching cycle

$$\mathrm{OH} \xrightarrow{(3)} \mathrm{H} \xrightarrow{(4)} \mathrm{HO_2} \xrightarrow{(5)} \mathrm{H_2O_2} \xrightarrow{(6)} 2\,\mathrm{OH},$$

Table 1 contains branching cycles proceeding *via* reactions (7) and (8)

$$\mathrm{HO_2} \xrightarrow{(7)} 2\,\mathrm{OH} \xrightarrow{(3)} \mathrm{H} \xrightarrow{(4)} \mathrm{HO_2},$$

$$\mathrm{H} \xrightarrow{(7)} 2\,\mathrm{OH} \xrightarrow{(3)} \mathrm{H},$$

$$\mathrm{OH} \xrightarrow{(3)} \mathrm{H} \xrightarrow{(8)} \mathrm{O} \xrightarrow{(2)} \mathrm{OH},$$

$$\mathrm{OH} \xrightarrow{(3)} \cup\ (\mathrm{H} \xrightarrow{(8)} \mathrm{O} \xrightarrow{(7)} \mathrm{H}).$$

The subgraph joining the indicated segment of the path of the reaction graph and the cycle is in the last row. The considered additional cycles determine the extension of the self-ignition region due to nonlinear interactions (7) and (8), although these reactions themselves are not branching.

The formulas are obtained by the procedure**[8]** described earlier as the equality $A = B$, where A is determined by the contributions to the determinant from the subgraphs (in this case, of the fifth order) corresponding to the branchings, and the value of B is determined by other contributions (involving the decay reactions). The inequality $A > B$ corresponds to the self-ignition region. For the scheme presented, the formulas for A and B take the form

$$A = \left\{\frac{2k_1}{k_4[\mathrm{M}]}\left(1 + \frac{(k_7 + k_8)[\mathrm{H}] + k_5[\mathrm{H}] + k_{11}}{k_9[\mathrm{H}]}\right) + \right.$$

$$\left. + \frac{(k_7 + k_8 + k_{13}k_7/k_2[\mathrm{H_2}])k_{11}}{k_9k_4[\mathrm{O_2}][\mathrm{M}]}\right\}\{1 + (k_{14}/\,(k_6[\mathrm{M}])\} +$$

$$+ \frac{k_5[\mathrm{H_2}]}{k_9[\mathrm{H}]}\left(1 + \frac{k_{13}}{k_2[\mathrm{H_2}]}\right),$$

$$B = \frac{k_8k_{12}}{k_4[\mathrm{O_2}][\mathrm{M}]k_3[\mathrm{H_2}]}\cdot$$

$$\cdot\left\{\frac{k_5[\mathrm{H_2}][\mathrm{HO_2}]}{k_9[\mathrm{H}]}\left(1 + \frac{2k_{13}}{k_2[\mathrm{H_2}]}\right) + \frac{k_{11}k_{13}}{k_9[\mathrm{H}]k_2[\mathrm{H_2}]}\right\} +$$

$$+ C + E\left\{\frac{k_8k_{13}}{k_9k_2[\mathrm{H_2}]}\left(2 + \frac{(k_5[\mathrm{H_2}] + k_{11})[\mathrm{HO_2}]}{k_4[\mathrm{O_2}][\mathrm{M}]}\right) + \right.$$

$$\left. + D\left(2 + \frac{k_{11}}{k_9[\mathrm{H}]} + \frac{2k_5[\mathrm{H_2}] + k_{11}[\mathrm{HO_2}]}{k_4[\mathrm{O_2}][\mathrm{M}]}F\right)\right\},$$

where

$$C = \frac{2k_1k_{12}k_{13}}{k_4[\mathrm{M}]k_2[\mathrm{H_2}]k_3[\mathrm{H_2}]}\cdot$$

$$\cdot\{k_5[\mathrm{H_2}] + (k_7 + k_8 + k_9)[\mathrm{H}] + k_{11}\}/(k_9[\mathrm{H}]),$$

$$D = 1 + \frac{k_{13}}{k_2[\mathrm{H_2}]},\quad E = 1 + \frac{k_{14}}{k_6[\mathrm{M}]},$$

$$F = 1 + \frac{k_{12}}{k_3[\mathrm{H_2}]}\left(1 + \frac{k_7}{k_9}\right) + \frac{k_{10}\mathrm{C}}{k_4[\mathrm{O_2}][\mathrm{M}]}\left(1 + \frac{k_{12}}{k_3[\mathrm{H_2}]}\right).$$

In the calculations of the limits by these formulas, the constant determined by diffusion of radicals was used for all constants of heterogeneous decay. For the decay of H atoms, the correction to square decay equal to $4k_{15}[\mathrm{H}]$ was added to the constant of linear decay. The ignition limits for two different compositions are given in Figs 1, *a* and *b* (50 and 10% of H_2 in air, respectively).

Curve *1* corresponds to the boundary of the linear ignition region, and curves *2* and *3* correspond to the additive of hydrogen atoms and HO_2 in an amount of $10^{-4}[O_2]$ and $10^{-5}[O_2]$. The contraction of region *2* compared to region *3* for high pressures and, on the contrary, extension for lower pressures are related to the competition of the quadratic decay of H atoms with the quadratic interaction of H and HO_2.

For modeling of the wave propagation under the isothermal conditions, we solved the system of nonstationary diffusion kinetic equations

$$\frac{\partial u_i}{\partial t} = \frac{\partial}{\partial x}D_i(T)\frac{\partial u_i}{\partial x} + \sum_j^M(\beta_{ij} - \alpha_{ij})W_j\ (i = 1, \ldots, N)$$

with the boundary conditions $\partial u_i/\partial x = 0$, at $x = 0$, $x = L$ and the initial conditions corresponding to the specified

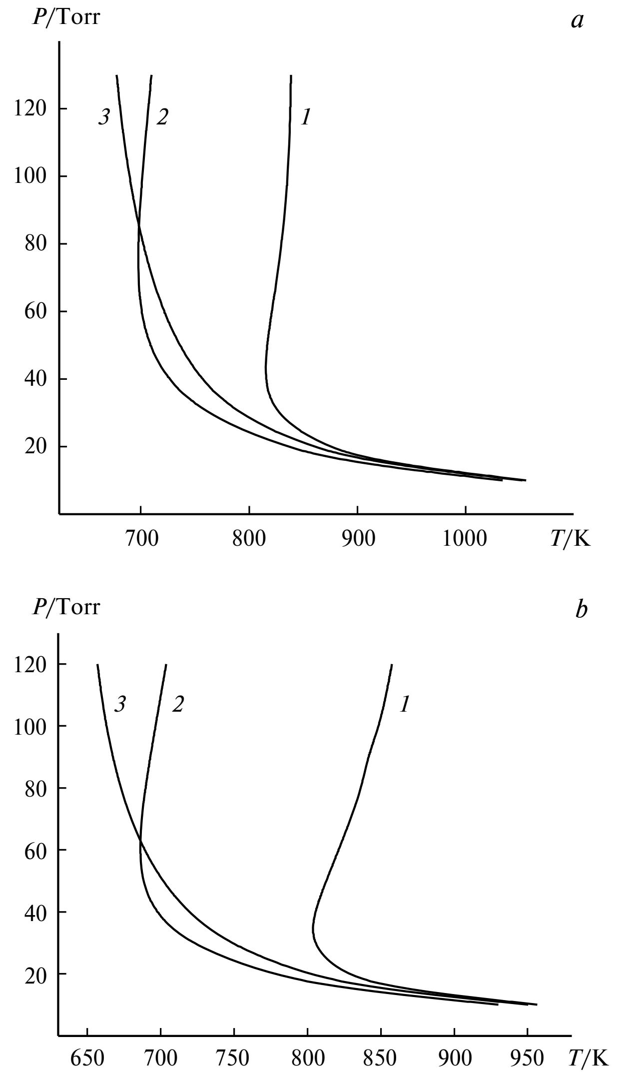

Fig. 1. Ignition limits of 50 (*a*) and 10% of H_2—air (*b*) mixtures: the boundary of the linear ignition region (*1*) and the boundaries at [H] = 10^{-4}[O_2] (*2*) and 10^{-5}[O_2] (*3*).

concentrations of the starting reactants along the whole reactor length and additives of atoms H and radicals HO_2 at the beginning of the reactor: $x < x_0$ at $t = 0$.

The wave rate was determined by the velocity of migration of the maximum H atom concentration after the wave was established; at L > 30 cm the rate was almost independent of L. The pressure and temperature for calculations were selected according to the calculated nonlinear ignition limits outside the region of linear ignition.

The profiles of O_2 and H concentrations for two different pressures (70 and 40 Torr) at T = 750 K and an H_2 content in air of 50% are shown in Figs 2 and 3.

The wave propagation was modeled in a wide range of the wave existence. Figure 4 shows the dependences of the wave rate on the pressure at the 50 and 10% of H_2 content in air and 700 and 750 K. At 700 K, the pressure region in

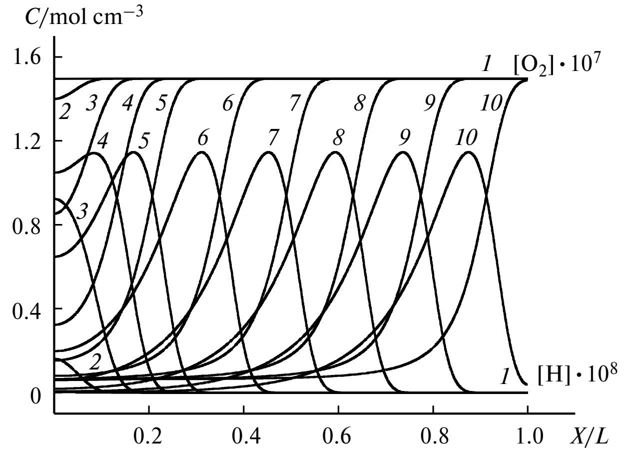

Fig. 2. Distribution of concentrations of oxygen and hydrogen atoms at t = 0 (*1*), 0.0194 (*2*), 0.0247 (*3*), 0.0298 (*4*), 0.035 (*5*), 0.0453 (*6*), 0.0556 (*7*), 0.0659 (*8*), 0.07663 (*9*), and 0.0866 s (*10*) for an H_2 (50%)—air mixture at 70 Torr and T = 750 K, L = 30 cm.

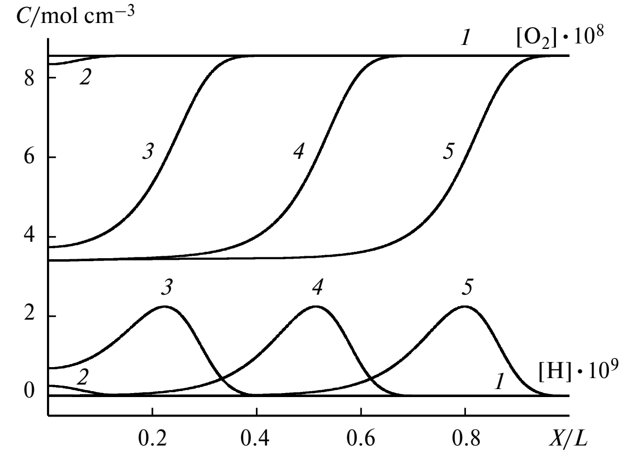

Fig. 3. Distribution of concentrations of oxygen and hydrogen atoms at t = 0 (*1*), 0.04 (*2*), 0.0612 (*3*), 0.0937 (*4*), and 0.1282 s (*5*) for an H_2 (50%)—air mixture at 40 Torr and T = 750 K, L = 30 cm.

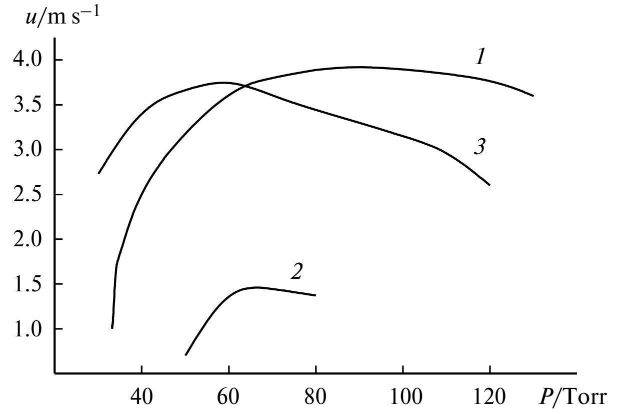

Fig. 4. Wave rate *vs* pressure: *1*, H_2 (50%)—air, T = 750 K; *2*, H_2 (10%)—air, T = 700 K; *3*, H_2 (10%)—air, T = 750 K.

which the waves exist is considerably reduced. Such a behavior is consistent with the existence of the nonlinear ignition region.

Thus, the study performed confirms once again the leading role of the chain branched kinetics in the propagation of the reaction wave during the oxidation of hydrogen, which determines the existence of the reaction wave outside the region of linear self-ignition due to diffusion of active particles under the isothermal conditions.

The authors are grateful to the Corresponding Member of the Russian Academy of Sciences V. V. Azatyan for discussion of the work.

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Received March 4, 2011;
in revised form June 3, 2011