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Investigation into spontaneous ignition of hydrogen–air mixtures in a heated reactor at atmospheric pressure by high-speed cinematography

Nikolai M. Rubtsov,*[a] Boris S. Seplyarskii,[a] Kirill Ya. Troshin,[b] Victor I. Chernysh[a] and Georgii I. Tsvetkov[a]

[a] *Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 495 962 8025; e-mail: nmrubtss@mtu-net.ru*
[b] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: troshin@chph.ras.ru*

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The spatial development of the chain ignition of hydrogen–air mixtures in the vicinity of the third combustion limit, investigated by means of quick gas transfer with the use of high-speed colour cinematography, has been demonstrated to be determined by the material and state of the reactor surface.

The spatial development of the spontaneous ignition of combustible gases at contact with a heated surface is of practical and scientific interest in the context of the use of hydrogen as fuel in engines and other power devices. The ignition of hydrogen (H_2) at low pressures (~1 Torr) in a heated reactor in the vicinity of the lower pressure limit is assumed to occur uniformly over the reactor volume.[1] The uniform ignition of a $2H_2 + O_2$ mixture can be observed[2] only at pressures of <10 Torr. With increase in total pressure of gas mixture under conditions of quick gas transfer, the time of warming up decreases because the velocity of gas flow must be increased to obtain larger pressure in the reactor. By the time of completion of gas transfer, the medium forms in the reactor in which different parts of the gas mixture have the different history of warming-up.[3] This serves to ignition of the gas mixture near the reactor surface. It means that, with pressure growth, the problem of the uniform ignition in a heated reactor transforms into a problem of ignition with a heated surface.[4–7] The ignition of stoichiometric and rich mixtures of propane and pentane with air at 1 atm in heated reactor begins with occurrence of ignition centre on the most chemically active site of surface, *i.e.* includes the steps of warming up, local ignition and flame propagation.[7]

Previously,[2] the spatial development of ignition in the stoichiometric mixtures of H_2, methane and isobutene with oxygen was studied at 10–100 Torr and T = 750–1000 K by means of high-speed colour cinematography. Numerical modeling[2] showed that the flow of active centres from the surface to the volume leads to non-uniform development of ignition over the reactor volume.

The promoting action of platinum coating of reactor surface on the rate of H_2 oxidation is known.[8] This action of Pt is caused by the heterogeneous development of reaction chains that enhances probability of ignition near surface.[9] Hence, another factor influencing uniformity of ignition is the material of reactor surface.

The area of spontaneous ignition of a $2H_2 + O_2$ mixture can be presented as follows.[10,11] The increase in the reactor temperature above 820 K causes a marked increase in the pressure of upper (second) pressure combustion limit and then to its disappearance. At pressures of about 1 atm, the third pressure limit of spontaneous ignition (P_3) occurs; in this case, the pressure of the third limit increases with decreasing temperature [Figure 1(*a*)]. P_3 has thermal nature over a Pyrex glass surface,[12] but if reactor walls are coated with potassium chloride (KCl), P_3 is of chain nature. According to reported data,[13] the third pressure limit of ignition in heated reactor has chain nature in all cases. The H_2 combustion at higher pressures and elevated temperatures was surveyed elsewhere.[14]

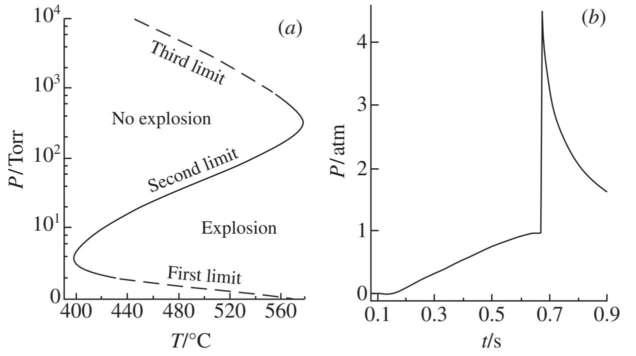

Figure 1 (*a*) Spontaneous ignition area of $2H_2 + O_2$ mixtures;[10] (*b*) the pressure dependence in the ignition of 40% H_2 in air (1 atm, 684 K).

This work was aimed at the experimental investigation of the spatial development of H_2–air ignition in the heated reactor over total pressures up to 2 atm by means of quick gas transfer with the use of high-speed colour cinematography, as well as at the establishment of the influence of both propene additives[15] and surface state on the temperature of the third pressure limit of ignition.

The experiments were performed with gas mixtures of 40% H_2 + + 60% air with 0–2% propene additive, 14% H_2 + 86% air, 12.5% H_2 + 87.5% air and 7% H_2 + 93% air at 1–2 atm and 500–800 K.[†] In a number of experiments, 1–2% carbon tetrachloride was added for visualization of H_2 flame. Note that a CCl_4 additive <5% does not influence the H_2 combustion.[11] The pumped and heated reactor was quickly filled with the gas mixture from a high pressure buffer volume to a necessary pressure. An electromagnetic valve was used to open and close gas communications. Because of a sharp pressure difference in the buffer

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[†] A heated cylindrical stainless steel reactor 25 cm in length and 12 cm in diameter equipped with demountable covers and an optical quartz window in one of the covers was used. The accuracy of temperature measurements was 0.3 K. Combustion was recorded by a Casio Exilim F1 Pro colour high-speed digital camera (30–1200 frames per second), sensitive over the spectral range of 420–740 nm through the optical quartz window.

volume and the reactor, there was a gas movement in the reactor that led to reduction of time of establishment of uniform temperature distribution.[3] The direct measurements of the dynamics of temperature change in the centre of the reactor by means of thin thermocouples was performed under similar conditions.[3] It has been shown that the time of warming up of gas mixture was no longer than 0.3 s. In this case, the formula considering only conductive heat exchange gives considerably greater value of about tens of seconds. Pressure in the course of bleeding-in and combustion was recorded by a pressure transducer. At the moment of the valve opening, a light-emitting diode was turned on, and its flash was recorded by the camera. It allowed us to determine a delay time of ignition τ from a shot sequence independently for each separate ignition.

To find out the influence of the reactor coating material on the value of P_3, the reactor surface was covered with a layer of potassium chloride. For this purpose, the reactor surface (except an optical window) was covered with a saturated water solution of KCl (5 ml) and then water was pumped out. In other series of experiments, Pt foil 12×6 cm and 0.3 cm thick was placed in the reactor. Before each experiment, the reactor was pumped out to 0.1 Torr. Total pressure in the reactor was controlled with a vacuum gauge, and the pressure in the buffer volume, with a manometer. Chemically pure gases and 99.99% Pt were used.

Experiments on thermal ignition of H_2–air mixtures over stainless steel and KCl have shown that, in the immediate vicinity of P_3, the pressure in the reactor reaches the expected value [Figure 1(*b*)], though the ignition delay period τ does not exceed 0.3 s, which is almost near certainty. These short values of τ can be explained by heterogeneous initiation occurring either on reactor surface or on the surface of artificial metal particles formed, *e.g.*, in the motion of electromagnetic valve details. The luminescence of Ni and Fe particles in H_2 flow was detected.[16] Ignition of H_2 at admission into heated reactor containing air really occurs on the surface of a radiating particle (Figure 2).

An increase in the temperature leads to ignition at early stages of gas transfer inside the ignition area. Data on the dependence of P_3 on pressure and on H_2 content in gas mixture are shown in Table 1. We considered that ignition had occurred, if the pressure transducer recorded sharp growth of pressure after filling the reactor with gas mixture and the camera recorded gas luminescence. Table 1 indicates that the ignition temperature of H_2–air mixture in the stainless steel reactor increases as H_2 content in the mixture diminishes. With increase in pressure the transition to ignition occurs in the narrower interval of temperatures (entries 7–10 in Table 1) making up less than 1 K. Temperature of ignition of H_2–air mixtures in the stainless steel reactor is ~20 K less than that in the reactor coated with potassium chloride and ~170 K less than that in the reactor containing Pt foil. This result means that P_3 depends on the reactor surface material. It is also seen in Table 1 that as propene additive is raised from 1 to 2%, 40% H_2 + + 60% air mixture does not ignite even at 733 K and 1.9 atm; *i.e.*, P_3 increases sharply. It means that H_2 combustion in the vicinity of P_3 is inhibited with a small chemically active additive.

All experiments performed on high-speed registration of ignition have shown that the primary centre of ignition occurs at reactor surface, irrespective of the surface material (Figure 3); the place of occurrence of the centre in a consecutive series of experiments changes from one experiment to another under the same initial conditions. Therefore, the chemical activity of various surface sites changes from one experiment to another.[7] Note that as distinct to initial stage of hydrocarbons combustion when the development of the primary single combustion centre leads to propagation of flame front of hemispherical shape,[7] the propagation of H_2 flame from the primary surface centre even in the presence of an inhibitor has a turbulent character (Figures 2, 3). Therefore, from the experiment it is possible to define only the average speed of flame propagation. The basic feature of processes observed implies that ignition occurs on separate surface sites at the same temperature of the reactor surface; these sites vary from one experiment to another (Figure 3) that corresponds to a mode of ignition with heated surface[4–6] rather than a uniform ignition mode.

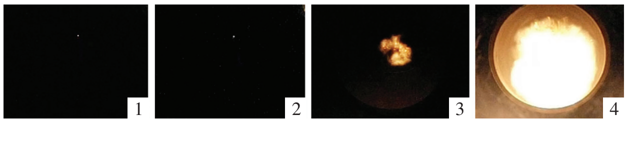

Figure 2 Sequences of video images of the spatial development of ignition on admission of H_2 to 1 atm of air at the reactor wall temperature 680 K, 600 shots s^{-1} to total $P = 2$ atm. Material of the wall, stainless steel. Ignition is initiated on the particle heated in H_2 flow.[16]

Table 1 Spontaneous ignition of H_2 in air at elevated pressures.

Entry	H_2 in air (%)	C_3H_6 (%)	T/K	Occurrence of ignition	Pressure/ atm	Surface material
1	40	1	691.1	–	1	Stainless steel
2	40	1	691.6	+	1	Stainless steel
3	40	1	711.3	–	1	KCl
4	40	1	711.8	+	1	KCl
5	7	–	623.4	–	1	Stainless steel
6	7	–	753	+	2	Stainless steel
7	14	–	743.4	–	1.4	Stainless steel
8	14	–	743.4	+	1.7	Stainless steel
9	14	–	753	+	0.8	Stainless steel
10	14	–	753	–	0.7	Stainless steel
11	12.5	–	755.6	–	1.7	Stainless steel
12	12.5	–	756.8	+	1.75	Stainless steel
13	40	2	733.1	–	1.9	Stainless steel
14	40	–	523.0	+	1	Stainless steel with Pt foil
15	40	–	521.5	–	1	Stainless steel with Pt foil

The data on the values of τ point to the same conclusion. Though over stainless steel and KCl τ does not exceed 0.3 s including the time of bleeding-in, the value of τ over Pt foil is 0.5–1.2 s. This

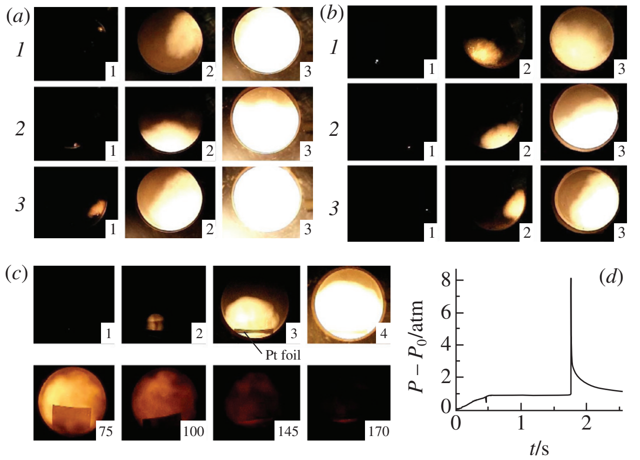

Figure 3 Sequences of video images of spatial development of ignition in (*a*) 40% H_2 + 60% air+ 1% C_3H_6 + 1% CCl_4 at the temperature of reactor walls (*1*) 698, (*2*) 710 and (*3*) 725 K; 600 shots s^{-1}; $P = 1$ atm; material of the wall is stainless steel; (*b*) 40% H_2 + 60% air + 1% C_3H_6 + 1% CCl_4 at the temperature of reactor walls (*1*) 715, (*2*) 725 and (*3*) 735 K; 600 shots s^{-1}; $P = 1$ atm; material of the wall is KCl coating; (*c*) 40% H_2 + 60% air mixture at the reactor walls temperature of 523 K; 600 shots s^{-1}; $P = 1$ atm. (Pt foil is placed in the stainless steel reactor. Its movement under explosion is clearly seen in shots 75, 100. As is seen from shots 145–170 Pt foil becomes incandescent under the action of reaction products.) Numbers in each frame correspond to consecutive number of the video image. (*d*) Time dependence of pressure change in the ignition for conditions (*c*).

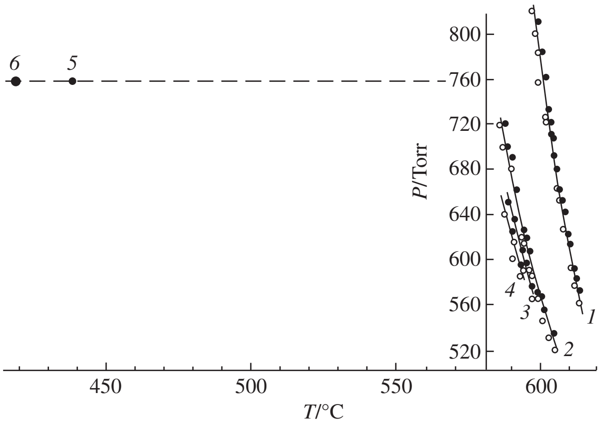

Figure 4 The temperature dependence of P_3 of $2H_2 + O_2$ (ref. 12): experiments (*1*) in reactors with KCl coating, (*2*) in pyrex glass reactors, (*3*) in pyrex glass reactors $2H_2 + O_2$ + 2% H_2O, (*4*) with the mixture addition during the reaction, reactor diameter of 4 cm; (*5,6*) the third pressure limits obtained in this work for 40% H_2 + 60% air + 1% C_3H_6 + 1% CCl_4 for KCl coating and stainless steel, reactor diameter d = 12 cm.

result means that over stainless steel and KCl the gas mixture does not warm up uniformly (a warming up period exceeds 0.3 s, see above), but uniform heating takes place over Pt foil [Figure 3(*c*)]. Note that for lack of ignition (P_3 is not reached) in immediate vicinity of P_3 the combustible gas in the reactor obviously warms up uniformly, *i.e.*, we obtain reliable P_3 values by measurement ‘from below’. In immediate vicinity of P_3, but above its value, ignition occurs locally over all surfaces investigated.

In Figure 4, the temperatures at P_3 = 1 atm are compared for mixtures of 40% H_2 + 60% air + 1% C_3H_6 + 1% CCl_4 (this work) and mixtures $2H_2 + O_2$ (published data[12]). The fact that the temperatures of ignition obtained with quick gas transfer method in the present work are ~160 K less than obtained previously[12] has engaged our attention. It is reasonable that both without inhibitor and at replacement of air by oxygen the temperatures at P_3 = 1 atm for our experimental conditions should be even lower than those presented in Figure 4. Observed distinctions in temperatures are obviously related to various experimental techniques used in this work when the heated reactor was filled with a preliminary prepared gas mixture, and in the reported process[12] (gas mixture was prepared in the heated reactor at temperatures close to that of ignition; the heated reactor was filled at first with H_2, and then with oxygen which was allowed to bleed in through a thin capillary for 4 s, thus the values of τ reached 30 s). It can be assumed that, in the published procedure,[12] oxygen could already react during bleeding-up in surface reactions, *i.e.*, the composition of gas mixture at the moment of ignition essentially differed from the initial one; therefore, the P_3 value obtained can be concerned with the mixture of some other composition.

Our results show that much as in hydrocarbons combustion[7] the process of H_2 combustion in the vicinity of P_3 is the ignition by a chemically active heated surface, which is accompanied by flame propagation into the reactor volume. It means that, in the mathematical modeling of ignition of H_2–air mixtures in the vicinity of P_3, it is impossible to restrict the consideration to the analysis of a uniformly distributed problem. It is also necessary to consider the formation of combustion centres on the reactor surface along with gas phase combustion kinetics, *i.e.*, heterogeneous processes.

Note that, within the framework of existing notions, the changeover across a critical condition of ignition should be accompanied by a substantial growth of the induction period τ. However, this is observed only over a Pt catalytic surface, probably, because of comparably low temperatures (~520 K) the reaction of chain origination (determining the value of τ)[1] on Pt has the lowest activation energy, as compared with stainless steel and KCl. As is seen from our experiments over stainless steel and KCl, the reaction rate in the vicinity of P_3 changes stepwise in a very narrow temperature interval of ~1 K; thus, ignition initiates at reactor surface. Really, the interval of 1 K is too small for a drastic change in the reaction rate. One can assume that it is connected with the sharp change of the reactivity of certain elements of reactor surface during the transition over a critical condition.

In conclusion, the temperatures at P_3 = 1 atm are experimentally defined for a number of H_2–air mixtures and for various materials of the reactor surface by quick gas transfer. The features of H_2 ignition in air in the area of P_3 depend not only on the mixture composition but also on the material of reactor surface and on the amount of chemically active additive. Comparably long delay times of 40% H_2 + air ignition at 1 atm were first observed over a Pt surface. It is established that the process of ignition of H_2–air mixtures at atmospheric pressure begins with primary centre occurrence on the most chemically active site of the surface, which initiates flame propagation.

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