Journal of Engineering Physics and Thermophysics, Vol. 83, No. 6, 2010

COMPRESSION IGNITION OF HYDROGEN-CONTAINING MIXTURES IN SHOCK TUBES

S. P. Medvedev, B. E. Gelfand,
S. V. Khomik, and G. L. Agafonov

UDC 541.126.2

The state of the art of the problem of discrepancy between the values measured in shock tubes and calculated for the delay of ignition of hydrogen-containing systems has been analyzed. It is shown that in the low-temperature region the off-design appearance of reaction sites leads to the propagation of a flame in a mixture heated by a reflected shock wave. The parameter of the time of mixture combustion in a deflagration regime has been introduced and the use of it together with the calculated delay in self-ignition for delimitation and classification of thermal and gas-dynamic phenomena on compression ignition of hydrogen-containing mixtures in shock tubes has been suggested.

Keywords: *hydrogen-containing mixture, delay in self-ignition, combustion regime.*

Introduction. The present paper is submitted for the jubilee issue of the Journal devoted to the 80th anniversary of the birth of Academician Rem Ivanovich Soloukhin. The authors did not pursue the goal of presenting a full review of the problem of self-ignition of hydrogen-oxidant mixtures. The aim of the work was to reflect on the contribution made by Soloukhin to the investigation of the delay in self-ignition of hydrogen-containing mixtures behind shock waves and to carry out an analysis of some aspects of the problem on the basis of recently developed approaches. The works published by Soloukhin are numerous and well-known to combustion and explosion experts all over the world. We have attempted to reveal the scientific significance of his ideas on the basis of the classical work [1] (the English-language version [2]) written in coauthorship with Academician V. V. Voevodskii.

The brilliant characteristic of works [1, 2] was noted by N. A. Fomin in [3]. Here are some excerpts from that work: ".. in 1964, the widely known paper by V. V. Voevodskii and R. I. Soloukhin [1], which summarized the results of the authors' long-term investigations on the kinetics of hydrogen ignition behind shock waves was published. The work is constantly cited, up to the present time, by all researchers in the field of combustion and detonation of hydrogen both in the CIS countries and abroad. It has become good form for publications in this field to compare new results precisely with [1], where measurements of ignition delay times were made up to pressures of about 3 atm. These data were recognized as the standard all over the world ... work [2] by Voevodsky (Voevodskii) and Soloukhin was their first publication abroad and it also contains these experimental data. The classical publication [1] was the first work (after the defense of his doctoral thesis) of the young Prof. R. I. Soloukhin from Novosibirsk together with the well-known specialist in this area, Associate Member of the Academy of Sciences of the USSR V. V. Voevodskii, who for many years investigated the mechanisms underlying the ignition of hydrogen."

The ideas suggested in [1, 2] served as the basis for subsequent investigations of the laws governing ignition of combustible gas mixtures behind reflected shock waves. In [1, 2], the notions of strong and mild ignition were introduced. For the first time it was attempted to connect the characteristic features of kinetic transformations (chain reactions) to gas-dynamical effects. The ideas were interpreted quantitatively in [4–9], where the results of experiments were analyzed and theoretical notions on the mechanism of strong and mild ignition in hydrogen-containing mixtures were developed, and also attempts at a mathematical description of the boundary between different regimes of ignition were made. Moreover, it turned out that the gas-dynamical characteristic features revealed for hydrogen-containing mixtures are also observed in ignition of hydrocarbon-oxidant systems [10].

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin Str., Moscow, 117977, Russia; email: detonation7@yahoo.com. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 83, No. 6, pp. 1104–1110, November–December, 2010. Original article submitted April 23, 2010.

The Problem of Delay in the Self-Ignition of Hydrogen-Containing Mixtures. In [1, 2], the results of measurements of the self-ignition of hydrogen–oxygen mixtures behind reflected shock waves are given. A comparison of experimental data with the results of kinetic calculations has revealed the following characteristic features:

a) in the temperature range $T > 1000$ K, the measured delay in self-ignition τ agrees with the theoretical value;

b) in the temperature range $T < 1000$ K, the parameter τ turns out to be substantially smaller than the calculated values; moreover, this difference at a temperature of about 800 K may attain three orders of magnitude.

It should be emphasized that precisely in [1, 2] was this characteristic feature in the behavior of the temperature dependence of measured delays in the ignition of hydrogen-containing mixtures first directly pointed out. Subsequent investigations [11–17] on various shock tubes fully confirmed this anomalous effect for the hydrogen–oxygen and hydrogen–air systems.

The problem of the discrepancy between experimental and theoretical values of the delay in self-ignition has evoked in recent years a wide response in connection with the increased interest in combustion of the so-called synthetic fuel (syngas) consisting of different mixtures of hydrogen with hydrocarbons, as well as with carbon monoxide. In [18], a review of more than 50 works pertaining to the self-ignition of hydrogen and synthetic fuel compositions is given. In the opinion of Dryer and Chaos [18], the generalized reason for the "off-design self-ignition" is the sensitivity of hydrogen-containing mixtures to different kinds of perturbations, especially in the range of relatively low temperatures corresponding to the regime of mild ignition. According to [18], such perturbations can be caused by admixtures in reagents, pollutants on the shock-wave tube, gas-dynamic effects, nonuniform mixing, catalytic processes on solid-phase inclusions and bounding surfaces. The list of reasons for the "off-design" ignition given in [18] (along with the list of the corresponding publications) can be easily enlarged. For example, in [13, 19, 20], the promoting influence of excited oxygen atoms is considered. In [21, 22], the contribution of mixture turbulization to the acceleration of chemical reaction is considered. The influence of the translational nonequilibrium of gases at the shock-wave front on the reaction of hydrogen with oxygen was investigated in [23, 24]. Finally, the joint outlook on the kinetics of ignition of hydrogen is presented in [25], where quantum corrections to the constants of the rates of exothermal processes are introduced.

At the moment it does not seem possible to obtain an unambiguous explanation of the effects discovered about 50 years ago in [1, 2]. The above-listed perturbing factors may exist simultaneously, which even further makes the interpretation of experimental data difficult. Thus, there remains a pressing need for carrying out further experimental and theoretical investigations of self-ignition of hydrogen-containing mixtures.

Self-Ignition and Propagation of a Flame. The analysis of the above-mentioned works shows that the greatest discrepancy between measured and calculated times of delay in ignition is observed in the region of temperatures that correspond to the mild regime of ignition. A detailed phenomenological description of this regime is given in [26] (for the English-language variant see [27]), which is devoted to investigation of the characteristic features of the ignition of hydrogen–oxygen mixtures behind a reflected shock wave. In view of the importance of the conclusions made as far back as in 1958, we will cite a quotation from [26]: "After a lapse of the induction period, at certain points of the volume conditions develop which lead to avalanche acceleration of the reaction in that part of the volume — the reaction center is formed. Further progress of the reaction from the center into the adjacent layers of the mixture is determined by the processes of *normal propagation of the flame front*" (italics added). Zaitsev and Soloukhin [26] cite the value 180–200 m/s for the velocity of the reaction-front motion at a temperature behind the reflected shock wave of about $T = 1170$ K.

In [26], it was not proposed to obtain systematic data on the dynamics of development of combustion sites under the conditions of gas heating by a reflected shock wave. On the other hand, a comparison of the measured (visible) velocity of reaction-front displacement with the calculated value for the conditions of normal propagation of a flame can appear useful for interpretation of the regime of mild ignition. To visualize the state of a reacting system and describe the dynamics of combustion sites under real and forced initial conditions, it is worthwhile to use frame photography with short exposures of individual stages of the transformations studied. The recommended range of the times of exposure is limited from above by a period of about 10^{-6} s. For an understanding of the dynamics of fast combustion, not less than 3 to 4 of its consecutive images (frames) are needed. To obtain a qualitative image and

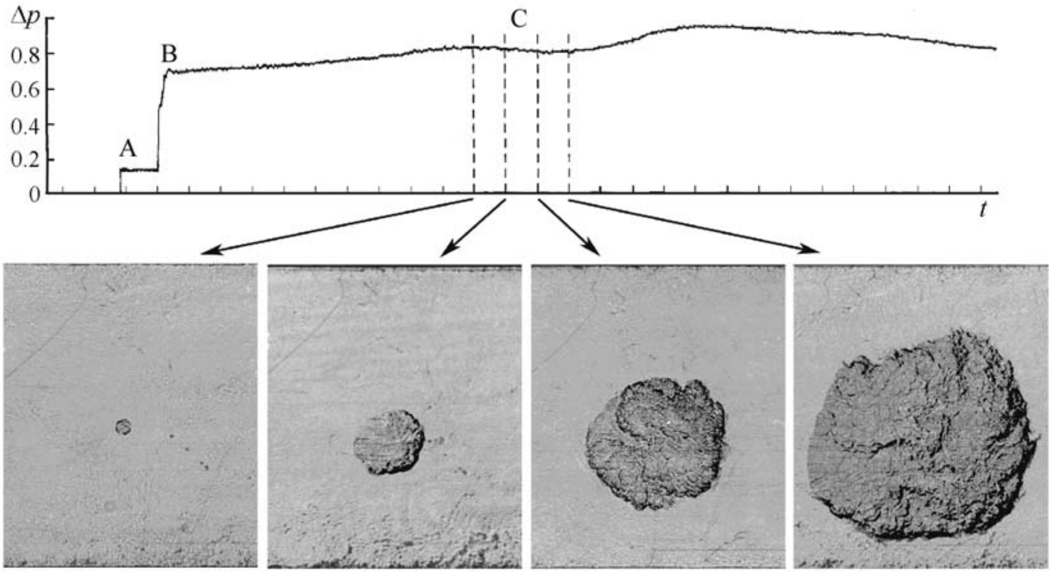

Fig. 1. Oscillogram of pressure recording and frames of flame propagation in the 15% H_2–air mixture. A, incident shock wave; B, reflected shock wave; C, phase of combustion. Δp, MPa; t, 200 μs/div.

overcome the proper glow of the combustion products a set of powerful pulsed illumination sources is required. For this purpose, it is very useful to employ combustible compositions with relatively transparent combustion products.

Among the well-known systems of rapid photorecording, as concerns their speed of response and off-duty ratio in application to observations of combustion under extreme initial pressure and temperature conditions, the most appropriate is a drum cine camera with a laser pulsed illumination source for exposure duration of 10 ns of each of the possible 100 frames [28, 29]. As an object of investigations it is recommended to take systems with the highest transparency of combustion products, say, lean mixtures of hydrogen with air or hydrogen with oxygen [28]. Also acceptable as to the informativeness is cine photography by means of the Cranz–Schardin camera with spark illumination with frame exposure of about 1 μs and number of frames of up to 24 [14, 29, 30]. The visualization of explosive processes in [14, 28–30] was conducted on shock tubes under the conditions of compression and heating of a combustible mixture by a reflected shock wave.

Photographic observations in [28–30] made it possible to reveal the dynamics with which the regime of mild ignition of hydrogen-containing mixtures develops. We will consider an example from the series of experiments partly described in [12, 30] that had been carried out in the course of the joint work of Prof. B. E. Gel'fand and Prof. G. Adomeit (see [10]) with coworkers at the RWTH Aachen University, Germany. The experiments were conducted on a shock tube with transverse cross section 54 × 54 mm^2 and low-pressure chamber 5.1 m long. Near the end-face portion of the tube a transparent section transilluminated by a multispark pulsed illumination source was mounted. The shadowgraph image of the object under observation was registered by a Cranz–Schardin camera. The test mixture consisted of 15% H_2 and 85% air; for this mixture, a sufficient number of initial data on determination of self-ignition delays was obtained from a set of pressure-time indicator diagrams in conjunction with pressure-time recordings and individual images of the phenomena discussed. The parameters of the incident and reflected shock waves were recorded by four piezoelectric pressure transducers (that located closer to the end-face was placed at a distance of 15 mm from it with the remaining ones placed further with a step of 50 mm). The choice of the mixture was determined by the moderate intensity of the light flux from the combustion products and by the presence of the mixture selected within the limits of combustion and detonation [28].

Figure 1 presents the pressure oscillogram at a distance of 115 mm from the end face, as well as a series of images made with a step of 200 μs in time in one of the experiments at the initial pressure P_0 = 25 KPa and incident shock-wave velocity 870 m/s. The vertical dashed lines indicate the instant of time of the filming of a respective frame. As is seen, approximately 2 ms after compression and heating of a mixture by a reflected shock wave, local ignition occurs, leading to the propagation of the reaction front with a shape close to a spherical one. The pressure

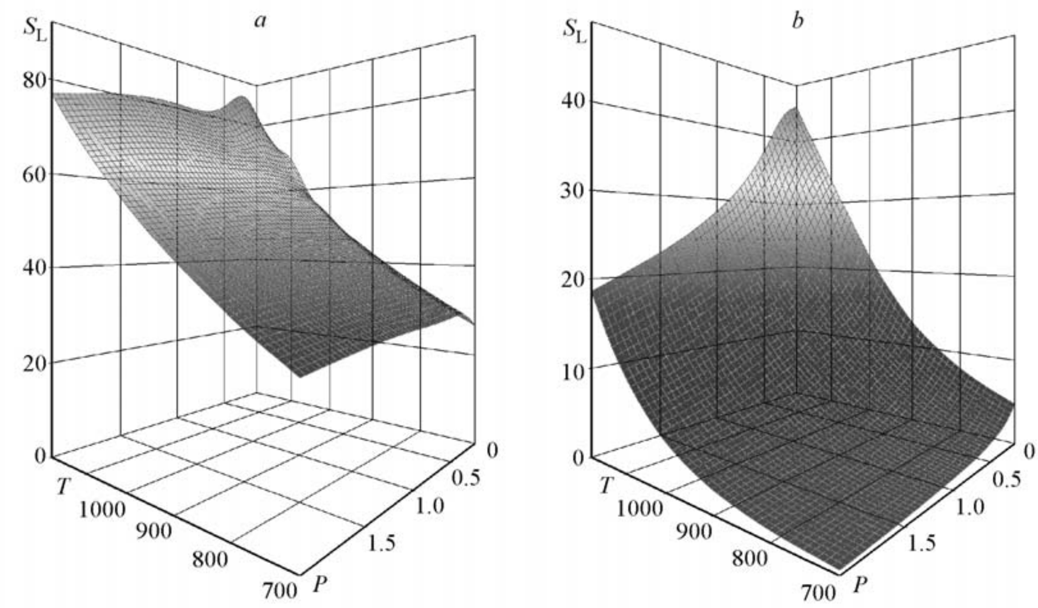

Fig. 2. Surfaces reflecting the dependences of the laminar combustion rate on pressure and temperature in hydrogen-containing mixtures: a) $H_2 + O_2$; b) 15% H_2–air. P, MPa; S_L, m/s; T, K.

behind the reflected shock-wave pressure considerably increases. As a result, at the phase of flame propagation the values of pressure P_{R1} and temperature T_{R1} differ from the values of P_R and T_R for the reflected shock wave. The value of P_{R1} is recorded directly, whereas for estimating the parameter T_{R1} it is admissible, according to [31], to use the approximation of isoentropic compression according to which $T_{R1} = T_R(P_{R1}/P_R)^{(\gamma-1)/\gamma})$, where γ is the adiabatic index of the gas mixture.

Under the conditions of the experiment presented in Fig. 1, combustion occurred at pressure $P_{R1} \approx 0.84$ MPa and temperature $T_{R1} \approx 1000$ K. The visible velocity of the reaction-front motion determined in both the vertical and horizontal direction was equal to $S_V = 25 \pm 5$ m/s. The expected expansion ratio of combustion products was $\sigma = 1.92$. Consequently, if we assume that in the given case we are dealing with flame propagation, then from the results of measurements we can estimate the level of the laminar combustion rate $S_L = S_V/\sigma = 13 \pm 2.6$ m/s. It will be recalled that under normal conditions in the mixture consisting of 15% H_2 + 85% air, $S_L \approx 0.8$ m/s [28]. Calculation by the model of [32, 33] yields $S_L = 11$ m/s at pressure $P = 0.84$ MPa and temperature $T = 1000$ K. The correspondence between the results of calculations and measurements shows that the focal ignition really leads to the propagation of a flame in the regime close to a laminar one.

An analogous approach applies to the analysis of the results of [26]. For an equimolar hydrogen-oxygen mixture at temperature $T = 1170$ K and pressure $P = 0.1$–0.3 MPa, the values of the laminar rate of combustion calculated by the kinetic scheme of [33] were equal to $S_L = 78$–80 m/s. Allowing for the fact that the parameter σ under these conditions is equal to $\sigma = 2.25$–2.32, the minimum visible flame velocity can be equal to $S_V = S_L\sigma = 177$–186 m/s. The values obtained correspond to the values 180–200 m/s measured by Zaitsev and Soloukhin in [26]. Thus, in this case, too, the assumption [26] on the normal (laminar) character of flame propagation is confirmed entirely.

Having obtained a detailed verification of the kinetic scheme of [32, 33], we can construct useful three-dimensional illustrations of the relation $S_L = f(P, T)$, as in Fig. 2, for the mixtures $H_2 + O_2$ (Fig. 2a) and 15% H_2–air (Fig. 2b). It is seen that with increase in temperature the velocity of the laminar flame increases. At a fixed temperature, the values of S_L for the equimolar hydrogen–oxygen mixture do not manifest a pronounced dependence on pressure. For the 15% H_2–air mixture, the parameter S_L changes in a wide range from the minimum value $S_L = 0.12$ m/s at $T = 700$ K and $P = 5$ MPa to the maximum value $S_L = 45.6$ m/s at $T = 1200$ K and $P = 0.1$ MPa.

Thus, it has been shown that the images of combustion seats obtained with the aid of contemporary methods of high-speed photorecording of hydrogen–air and oxygen–air mixtures on compression heating behind a reflected shock wave can be used to determine the visible velocity of a flame at the temperature and pressure of a combustible

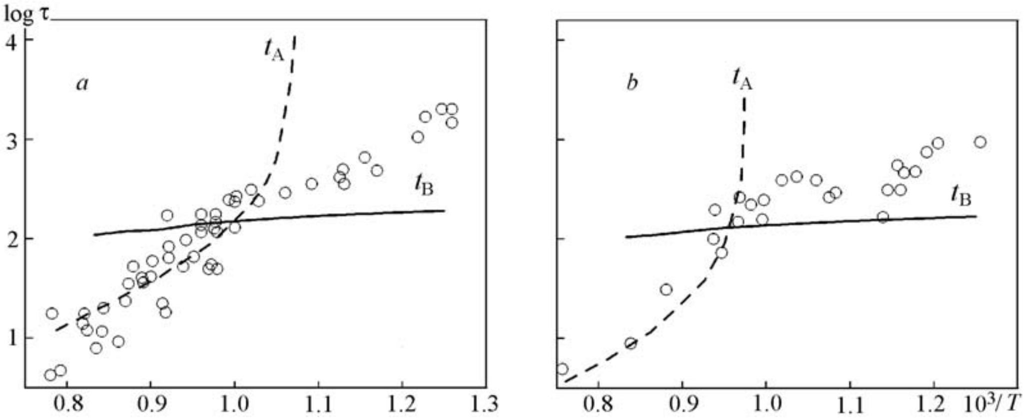

Fig. 3. Comparison of the results of experiments of [1] with calculated values of the parameters t_A and t_B at a pressure of 0.1 (a) and 0.3 MPa (b). T, K; τ, μs.

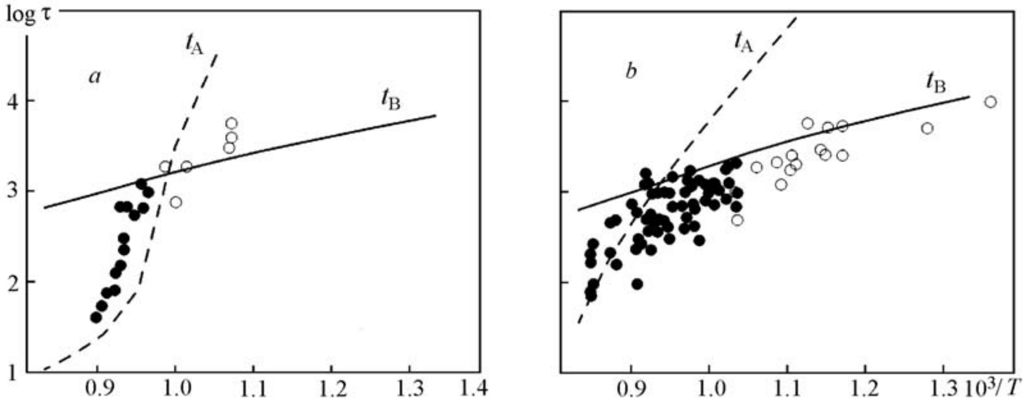

Fig. 4. Comparison of the results of experiments of [12] with calculated values of the parameters t_A and t_B at a pressure of 0.3–0.4 (a) and 1.2–1.8 MPa (b). Filled circles, strong ignition; open circles, mild ignition. T, K; τ, μs.

mixture near the ignition boundary. From the level of the visible velocity, one can evaluate the values of the normal rate of combustion expected on realization of promising means of ignition of combustible mixtures. The applicability of one of the well-known schemes of calculation of the rate of combustion of hydrogen-containing mixtures in application to the conditions near the ignition boundary has been proved. The conclusions thus drawn represent the development of the ideas advanced by R. I. Soloukhin and his coauthors from the late 1950 s to early 1960 s.

Interpretation of Experimental Data on Ignition Delay. Information on the characteristics of flame propagation at a relatively high temperature makes it possible to interpret some trends of the mild regime of ignition. The off-design ("earlier") focal self-ignition, irrespective of its reason, can serve as a source of ignition for the main mass of a gas heated behind a reflected shock wave. On appearance of the flame front, conditions for the competition of the process of self-ignition with deflagration combustion are created. Analytical solutions of such kind of problems are presented in [34–36]. In [37, 38], we suggested a simplified approach allowing one to carry out a direct comparison with experimental data on delays in self-ignition. In the majority of cases, the seats of self-ignition are located near the side walls of a shock tube, and a flame propagates from the periphery to the axis of the tube. The time of combustion in the deflagration regime t_B can be estimated as the ratio of the characteristic geometric dimension, e.g., tube radius r to the visible velocity of flame propagation as the first approximation we will assume that the flame is initiated immediately on shock wave reflection from the tube endface. We will also assume that the flame propagates at a constant velocity, with the pressure and temperature of the mixture ahead of the flame front not undergoing a change and corresponding to the values calculated from gas-dynamical relations for the reflected shock wave.

Following the procedure suggested in [38], the parameter $t_B = r/S_v$ thus introduced can be compared to both the experimentally determined delay in ignition τ, and to its calculated value t_A. In [38], such a comparison was made for hydrogen-air and syngas-air mixtures for the conditions of a high pressure $P = 1–2$ MPa. It is of interest to make such a comparison with the results of [1] on the delay in self-ignition of the H_2-O_2 mixture at P = 0,1–0,3 MPa.

Figure 3 presents a comparison of the experimental results of [1] with the calculated values of the parameters t_A, t_B in the temperature range $T = 700–1200$ K at $P = 0.1$ MPa (Fig. 3a) and 0,3 MPa (Fig. 3b). The delay in self-ignition t_A (dashed curve) is reproduced from the calculations in [1]. The time of combustion in the deflagration regime t_B (solid curve) was calculated from the relation $t_B = r/S_V$ ($S_V = S_L\sigma$) with allowance for the data of Fig. 2a at $r = 20$ mm and the fact that the parameter σ changes from $\sigma = 3.6$ at $T = 700$ K to $\sigma = 2.2$ at $T = 1200$ K. For comparison, Fig. 4 presents experimental results of [12] and, analogously, to Fig. 3, dependences for the mixture 15% H_2–air ($r = 27$ mm) at a pressure of $P = 0.3–0.4$ MPa (Fig. 4a) and 1.2–1.8 MPa (Fig. 4b). The values of t_B in Fig. 3 and t_A and t_B in Fig. 4 were calculated using the model of [32, 33].

Based on the comparison between experimental and calculated data (Figs. 3 and 4), we can make the following remarks:

1) the parameter t_A demonstrates a strong dependence on temperature, whereas the parameter t_B increases slightly with a decrease in temperature;

2) the values of the delay in self-ignition determined experimentally satisfactorily agree with the results of calculation of t_A in the high-temperature region at $T > 1050$ K;

3) in the low-temperature region at $T < 1000–1050$ K, the experimental results tend to the correspondence of the parameter t_B to the temperature dependence; this tendency increases with pressure.

Despite the simplifications, the analysis carried out allows one to differentiate the phenomena of self-ignition and flame propagation in a reacting gas heated by a reflected shock wave. Independently of the reason for the "earlier" formation of the self-ignition seats, the consequences of this event turn out to be different for different temperatures. In the region of *high* temperatures, the foci of the reacted gas have no time to produce appreciable perturbation of the main heated volume prior to the expiration, in it, of the self-ignition delay, exhibiting itself as a volumetric explosion (strong self-ignition regime). At relatively *low* temperatures, the focal ignition leads to the formation of flame fronts, and the delay in ignition, which corresponds to the temperature and pressure behind a reflected shock wave, does not manage to escape before the complete combustion of the heated gas in the deflagration regime. It should be emphasized that with the events developing in this way the self-ignition occurs only at local seats, where the temperature and pressure conditions and in some cases the mixture composition (e.g., the concentration of excited particles) are not known. The subsequent combustion in the deflagration regime cannot be identified as self-ignition and, consequently, the measurement of the parameter τ turns out to be impossible. In the *intermediate* temperature region (corresponding to the intersection of the functions $t_A(T)$ and $t_B(T)$), combinations of the regimes of self-ignition and deflagration can be observed up to the formation of shock and detonation waves. In outward appearance, such regimes are analogous to the phenomenon of transition of combustion into detonation, as was already noted in [12, 14].

Conclusions. An analysis of experimental data together with calculations of the delay in self-ignition and of flame propagation make it possible to differentiate and classify thermal and gas-dynamic phenomena in compression self-ignition of hydrogen-containing mixtures in shock tubes. The photographic methods suggested in the pioneering works [1, 26] for investigation of the processes of self-ignition must be used together with the recordings of pressure and radiation fluxes for identification of the self-ignition process and determination of the conditions of its progress.

The investigations carried out were realized within the framework of project No. 09-03-00487 of the Russian Fundamental Research Foundation.

NOTATION

P, pressure, Pa; r, radius (characteristic dimension) of a tube, m; S_L, laminar rate of combustion, m/s; S_V, visible velocity of reaction front propagation, m/s; T, temperature, K; t_A, calculated value of delay in ignition, s; t_B, time of combustion in deflagration regime, s; Δp, excessive pressure; γ, adiabatic index of a gas mixture; σ, degree of expansion of combination products; τ, measured delay in ignition, s. Subscripts: 0, initial value; R, calculated value in a reflected shock wave; RI, value in the phase of flame propagation.

REFERENCES

1. V. V. Voevodskii and R. I. Soloukhin, On the mechanism and limits of chain self-ignition of hydrogen with oxygen in shock waves, *Dokl. Akad. Nauk SSSR*, **154**, No. 6, 1425–1428 (1964).
2. V. V. Voevodsky and R. I. Soloukhin, On the mechanism and explosion limits of hydrogen–oxygen chain self-ignition in shock waves, in: *Proc. 10th Int. Symp. on Combustion*, The Combustion Institute, Pittsburgh (1965), pp. 279–283.
3. N. A. Fomin, Letter to the Editors, *Inzh.-Fiz. Zh.*, **78**, No. 1, 190–191 (2005).
4. J. W. Meyer and A. K. Oppenheim, On the shock-induced ignition of explosive gases, in: *Proc. 13th Int. Symp. on Combustion*, The Combustion Institute, Pittsburgh (1970), pp. 1153–1164.
5. E. Oran and J. Boris, Weak and strong ignition. Sensitivity of the hydrogen–oxygen system, *Combust. Flame*, **48**, No. 1, 149–161 (1982).
6. R. A. Yetter, H. Rabitz, and R. M. Hedges, A combined stability-sensitivity analysis of weak and strong reactions of hydrogen–oxygen mixtures, *Int. J. Chemical Kinetics*, **23**, 251–278 (1990).
7. A. M. Bartenev and B. E. Gelfand, Weak and strong ignition within the scope of spontaneous flame concept, in: *Proc. 25th Int. Symp. on Combustion*, The Combustion Institute, Pittsburgh (1994), pp. 61–64.
8. A. M. Bartenev and B. E. Gelfand, Spontaneous initiation of detonations, *Progr. in Energy and Combust. Science*, **26**, 29–55 (2000).
9. B. E. Gel'fand, S. P. Medvedev, A. N. Polenov, S. V. Khomik, and A. M. Bartenev, Basic regimes of self-ignition and conditions of their realization in combustible gas mixtures, *Fiz. Goreniya Vzryva*, **33**, No. 2, 1–10 (1997).
10. K. Fieweger, R. Blumenthal, and G. Adomeit, Self-ignition of SI-engine model fuels. A shock tube investigation at high pressure, *Combust. Flame*, **109**, No. 4, 599–619 (1997).
11. B. E. Gel'fand, O. E. Popov, S. P. Medvedev, S. V. Khomik, G. L. Agafonov, and A. Yu. Kusharin, Distinguishing features of the self-ignition of hydrogen–air mixtures at a high pressure, *Dokl. Ross. Akad. Nauk*, **330**, No. 4, 457–459 (1993).
12. R. Blumenthal, K. Fieweger, K. H. Komp, G. Adomeit, and B. E. Gelfand, Self-ignition of H_2–air mixtures at high pressure and low temperature, in: B. Sturtevant, J. E. Shepherd, H. Hornung (Eds.), *Proc. 20th ISSW, World Scientific*, **2**, 935–940 (1996).
13. B. E. Gel'fand, S. P. Medvedev, S. V. Khomik, O. E. Popov, A. Yu. Kusharin, and G. L. Agafonov, Self-ignition of hydrogen–oxygen mixtures at a high initial pressure, *Dokl. Ross. Akad. Nauk*, **349**, No. 4, 482–485 (1996).
14. B. L. Wang, H. Olivier, and H. Groenig, Ignition of shock-heated H_2–air–steam mixtures, *Combust. Flame*, **133**, No. 1/2, 93–106 (2003).
15. V. V. Martynenko, O. G. Penyazkov, K. A. Ragotner, and S. I. Shabunya, High-temperature ignition of hydrogen and air at high pressures downstream of the reflected shock, *Inzh.-Fiz. Zh.*, **77**, No. 4, 100–107 (2004).
16. G. A. Pang, D. F. Davidson, and R. K. Hanson, Shock tube ignition delay times for H_2–O_2–Ar mixtures at low temperature and elevated pressure, *Proc. WSS/CI*, Paper No. 07F-12 (2007).
17. B. E. Gel'fand, S. P. Medvedev, S. V. Khomik, and G. L. Agafonov, Self-ignition of hydrogen–oxygen mixtures behind reflected explosion waves, *Teplofiz. Vys. Temp.*, **48**, No. 3, 458–462 (2010).
18. F. L. Dryer and M. Chaos, Ignition of syngas–air and hydrogen–air mixtures at low temperatures and high pressures: Experimental data interpretation and kinetic modeling implications, *Combust. Flame*, **152**, No. 2, 293–299 (2008).
19. N. G. Dautov and A. M. Starik, Investigation of the influence of vibrational excitation of molecules on the kinetics of H_2–O_2 mixture combustion, *Teplofiz. Vys. Temp.*, **32**, No. 2, 222–229 (1994).
20. N. A. Popov, Influence of nonequilibrium excitation on the ignition of hydrogen–oxygen mixtures, *Teplofiz. Vys. Temp.*, **45**, No. 2, 296–315 (2007).
21. S. Tsuge and K. Sagara, Arrhenius' law in turbulent media and an equivalent tunnel effect, *Combust. Sci. Technol.*, **18**, 179–189 (1978).

22. S. Tsuge, Rate increase in chemical reaction and its variance under turbulent equilibrium, *Combust. Sci. Technol.*, **162**, 303–330 (2001).
23. S. V. Kulikov, Evolution of the tails of velocity distributions for gas mixtures at the shock wave front and the influence of the nonequilibrium state on the reaction of H_2 and O_2, *Mat. Modelir.*, **11**, No. 3, 96–104 (1999).
24. O. G. Divakov, V. S. Ziborov, A. V. Eremin, and V. E. Fortov, Nonequilibrium self-ignition of oxygen-hydrogen mixtures at the front of a weak shock wave, *Dokl. Ross. Akad. Nauk*, **373**, No. 3, 487–490 (2000).
25. A. V. Eletskii, A. N. Starostin, and M. D. Taran, Quantum corrections for equilibrium velocity constants of inelastic processes, *Usp. Fiz. Nauk*, **175**, No. 3, 299–313 (2005).
26. S. G. Zaitsev and R. I. Soloukhin, On ignition of an adiabatically heated gas mixture, *Dokl. Akad. Nauk SSSR*, **112**, No. 6, 1039–1041 (1958).
27. S. G. Zaytsev and R. I. Soloukhin, Study of combustion of an adiabatically heated gas mixture, in: *Proc. 8th Int. Symp. on Combustion*, The Combustion Institute, Pittsburgh (1962), pp. 344–347.
28. B. E. Gel'fand, O. E. Popov, and B. B. Chaivanov, *Hydrogen: Parameters of Combustion and Explosion* [in Russian], Fizmatlit, Moscow (2008).
29. B. E. Gelfand, S. V. Khomik, S. P. Medvedev, H. Groenig, and H. Olivier, Visualization of self–ignition regimes in hydrogen–air mixtures under shock waves focusing, in: *Proc. SPIE*, **4183**, 688–695 (2001).
30. R. Blumenthal, K. Fieweger, K. H. Komp, and G. Adomeit, Gas dynamic features of self–ignition of nondiluted fuel–air mixtures at high pressure, *Combust. Sci. Technol.*, **123**, 1–30 (1997).
31. E. L. Petersen and R. K. Hanson, Nonideal effects behind reflected shock waves in a high-pressure shock tube, *Shock Waves*, **10**, 405–420 (2001).
32. A. Yu. Kusharin, O. E. Popov, and G. L. Agafonov, Normal flame velocities in mixtures of a detonating gas with steam, *Khim. Fiz.*, **14**, No. 4, 179–189 (1995).
33. A. Y. Kusharin, G. L. Agafonov, O. E. Popov, and B. E. Gelfand, Detonability of H_2–CO–CO_2–air mixtures, *Combust. Sci. Technol.*, **135**, 85–98 (1998).
34. Ya. B. Zel'dovich, *Propagation of a Flame over a Mixture Reacting at an Initial Temperature*, Preprint of the Joint Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka (1978).
35. P. K. Senachin and V. S. Babkin, Self-ignition of a gas in front of a flame in a closed vessel, *Fiz. Goreniya Vzryva*, **18**, No. 1, 3–8 (1982).
36. L. A. Gussak and B. V. Novozhilov, Frontal and volumetric regimes of gas mixture combustion, *Khim. Fiz.*, **1**, No. 11, 1551–1556 (1982).
37. S. P. Medvedev, G. L. Agafonov, S. V. Khomik, and B. E. Gelfand, Competition between self-ignition and deflagrative burnout in hydrogen–air mixture heated by reflected shock wave, in: *Proc. 22nd ICDERS*, Minsk, Belarus (2009), CD ROM, Paper 251.
38. S. P. Medvedev, G. L. Agafonov, S. V. Khomik, and B. E. Gelfand, Ignition delay in hydrogen–air and syngas–air mixtures: Experimental data interpretation via flame propagation, *Combust. Flame*, **157**, No. 7, 1436–1438 (2010).