Autoignition of Flowing Hydrogen-Air Mixtures

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A shock tube was used to determine the cause of autoignitions occurring at low temperatures in flowing hydrogen-air mixtures. For flow speeds above 750 m/sec, ignitions were observed at temperatures 400K below that established in static mixtures by the thermal explosion limit method. Gasdynamic processes which can produce high local static temperatures were absent. Therefore, the classical concept of "ignition temperature" does not seem to apply to these spontaneous ignitions. The onset of ignition has been experimentally correlated to the flow speed, the density in the boundary layer, the wall temperature, and the stagnation temperature of the flow. It has been concluded that the low temperature ignition originates in the boundary layer and is caused by friction induced ionization of the hydrogen molecule at the surface of the tube. When the boundary layer is turbulent, the low temperture ignitions do not occur.

Nomenclature

M = Mach number relative to tube wall
$[O_2]$ = concentration of oxygen
P = pressure
Re = Reynolds number
T = temperature
u = speed of shocked gas
$w_{a,2}$ = speed of sound in shocked gas
W_{12} = wave speed in buffer gas section
W_{34} = wave speed early in test section
W_{56} = wave speed at end of test section
ρ = density
τ = ignition delay time

Subscripts

1 = unshocked test gas
2 = shocked test gas
o = total or stagnation conditions
r = reflected shock conditions
w = conditions of shocked gas near wall

Introduction

SEVERAL investigations of the combustion process occurring in subsonic and supersonic flows of hydrogen-air and hydrogen-oxygen mixtures have been performed in recent years because of its importance to the hypersonic ramjet combustor. Spontaneous ignitions of these flowing mixtures at static and total temperatures below the normally accepted ignition temperatures (thermal explosion limits)[5] have been frequently reported.[1-4,6-8,12-14] In some cases these ignitions have resulted in unexpected and destructive explosions. Low temperature ignitions have been observed in mixing chambers, in lines leading to test apparatus, in shock tubes, and in combustion chambers.

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Index categories: Shock Waves and Detonations; Combustion Stability, Ignition, and Detonation.

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Low temperature ignitions of hydrogen-air mixtures were observed by Walker[7] in a shock tube behind incident waves but not behind reflected waves (Fig. 1). Ignition temperatures obtained by Walker for methane-air and ethylene-air mixtures were found to be the same behind both incident and reflected waves and also in agreement with thermal explosion limits.[5] Walker also reported similar low temperature ignitions behind weak shock waves propagating through flowing hydrogen air mixtures (Fig. 1). Furthermore, the slope of the curve of ignition delay time vs inverse temperature (Fig. 2) was observed to change abruptly for ignitions occurring below the thermal explosion limits. Recently, a study was conducted by Hopkins et al.[14] in which an attempt was made to ignite hydrogen-oxygen mixtures behind reflected shock waves for the purpose of conducting rocket plume simulation studies. The studies were hampered when the gas mixtures could not be prevented from igniting behind the incident wave until the shock strengths were reduced to such a point that ignition would not even occur behind the reflected wave. Diehl[8] has shown that under certain conditions spontaneous ignitions in mixing chambers are caused by aerodynamic resonance.

Various phenomena such as friction-induced ionization or static charge accumulation, test section surface irregularities, boundary-layer effects, aerodynamic resonance, ther-

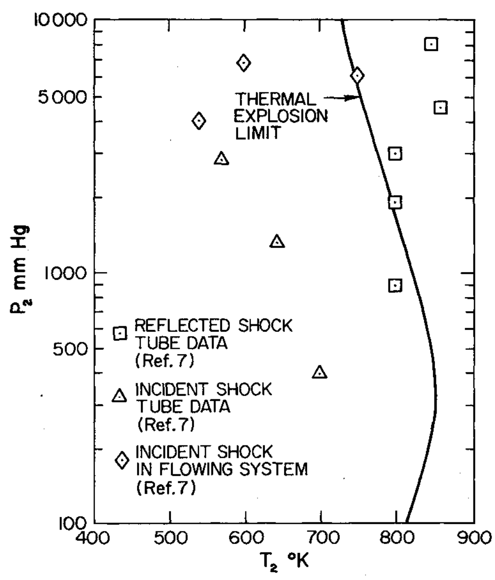

Fig. 1 Previously reported ignition conditions in static and flowing hydrogen-air mixtures.

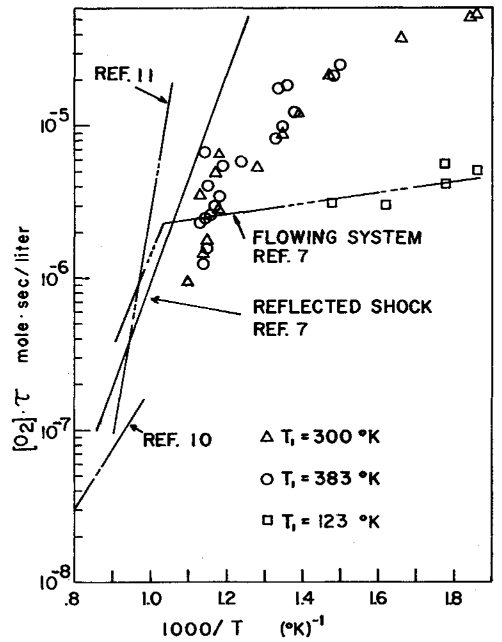

Fig. 2 Ignition delay times for hydrogen-air mixtures.

modynamic nonequilibrium, and diaphragm rupture have been considered as the cause of the low temperature ignitions. While most of these phenomena may lead to low temperature ignitions, it is not known which one of them or combination of them is actually responsible. It is evident however that the low temperature ignitions occur only when the gas mixture is moving with respect to a surface.

A systematic investigation into the origins of these low temperature ignitions has been undertaken in a manner such that the effects of various phenomena can be isolated. Maximum energy release mixtures of hydrogen and air were shocked to various temperatures, pressures, and flow speeds in a shock tube. The shock tube has been designed and built to minimize ignitions due to: diaphragm rupture, unsteady effects associated with shock formation, and stagnation or wave reflection due to obstacles in the flow such as mismatched surfaces, orifices, and instrumentation.

To obtain various shocked gas speeds P_2 or Mach numbers for given shocked gas pressures P_2 and temperatures T_2, it was necessary to vary both the initial pressure P_1 and the initial temperature T_1 of the unshocked gas. The onset of ignition was correlated to the various parameters involved.

Description and Operation of Shock Tube

A stainless steel shock tube[9] slightly more than 12 m long and with an i.d. of 7.5 cm (Fig. 3) was used for the measurements. The internal surfaces of the 6 m long test section were carefully matched and honed with fine grindstones to avoid any disturbance being produced in the flow behind the shock wave. The heat transfer gages and their holders were also ground to match the i.d. of the tube. The 3 m long buffer gas section was separated from the test section by a tightly stretched rubber diaphragm that virtually disappeared into a 0.002-in. clearance space upon mechanical rupture. The driver section was also 3 m in length and was separated from the buffer gas section by carefully selected thicknesses of mylar diaphragm. The tightly stretched rubber diaphragm was broken only a few seconds before the mylar diaphragms were ruptured with high pressure helium.

The desired gas mixtures were produced by mixing according to partial pressures in sufficient quantities for several experiments. The intial temperature of the buffer and test gas sections (Fig. 3) were controlled by circulating hot antifreeze or liquid nitrogen around the tube's periphery. The heating or cooling channel was surrounded by a layer of fiberglass for

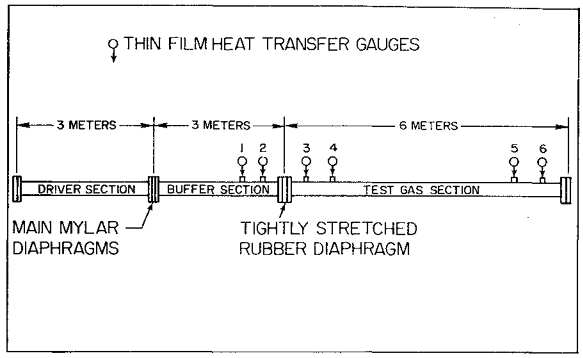

Fig. 3 Schematic of shock tube geometry and location of heat transfer gages.

insulation. The temperature of the shock tube was thermostatically controlled and was monitored at several points with copper constantan thermocouples imbedded in the tube wall. Six thin-film heat transfer gages were mounted in the tube wall to monitor the speed of the shock wave, turbulence in the boundary layer, and the onset of ignition. The speed of the shock wave was measured by pairs of heat transfer gages as it left the buffer gas, after it had entered the test gas, and also at the end of the test section. The hydrogen gas was 99.8% pure commercial grade with a dew point of $-75°F$. The air contained no oil and had a dew point of $-140°F$. The shock tube was thoroughly cleaned before each experiment.

The onset of ignition was determined by the nature of the heat transfer gage responses and by the acceleration of the incident shock wave as it reached the end of the tube. The voltage across the heat transfer gages was observed to decrease sharply[9] when a flame front passed by as opposed to the voltage increase associated with a passing shock wave. Under conditions near the ignition limit, the onset of ignition did not occur until the incident wave approached the end of the tube, in which case the ignition behind the reflected wave obscured the interpretation of the gauge response. In these cases, which were of greatest interest in the present study, the speed of the shock wave measured at the end of the tube was compared with that of experiments in which no ignition had occurred. To obtain these comparisons, a nonreacting mixture of hydrogen (26.9%) and nitrogen (73.1%) was used instead of the usual hydrogen (29.6%) and air 70.4%), so that both mixtures had the same molecular weights. When ignition occurred in the hydrogen mixture, the wave speed at the end of the tube was higher than in the nonreacting case.

Experimental Results

The experiments were conducted at initial temperatures of 123K, 300K, and 383K. For a shocked gas temperature of 600K, the shocked gas speeds u_2 corresponding to these initial temperatures are 933, 655, and 510 m/sec, respectively. Initial pressures ranged from 22.5 mm Hg-813 mm Hg. The shocked gas pressures ranged from 200-6000 mm Hg while the shocked gas temperatures varied from 350-1000K. The shocked gas speeds ranged from 200-1100 m/sec. Nitrogen was used as the buffer gas for all experiments. An example of the technique by which an individual ignition limit was determined is shown in Fig. 4, which shows wave speeds measured just inside the test section (W_{34}) and at the end of the test section (W_{56}) as a function of the wave speed measured in the buffer gas (W_{12}). All points shown in Fig. 4 were obtained with an initial pressure of 100 mm Hg and an initial temperature of 300K. The dashed lines represent data obtained in the nonreacting hydrogen-nitrogen mixture at the same initial conditions. The speed of the shock wave (W_{34}) for which the wave speed at the end of the tube begins to show some acceleration is 1155 m/sec which corresponds to a pressure of 870 mm Hg and a temperature of 711K for the shocked gas. Altogether, 15 in-

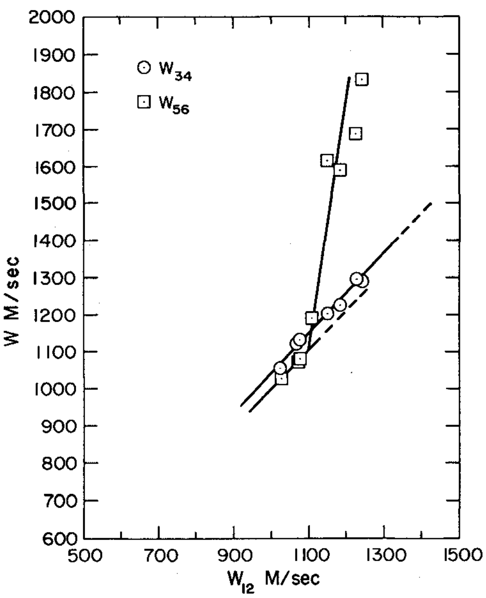

Fig. 4 Wave speeds for $T_I = 383K$, $P_I = 300$ mm Hg.

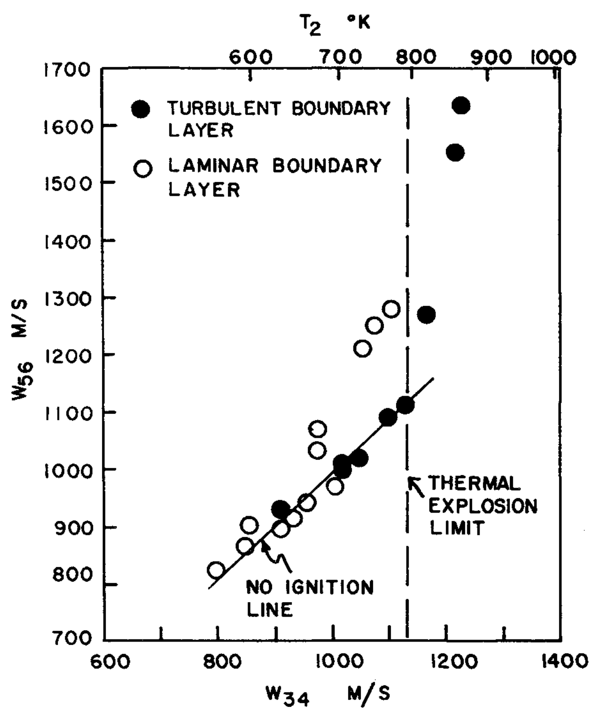

Fig. 5 Wave speeds for $T_I = 300K$, $P_I = 100$ mm Hg.

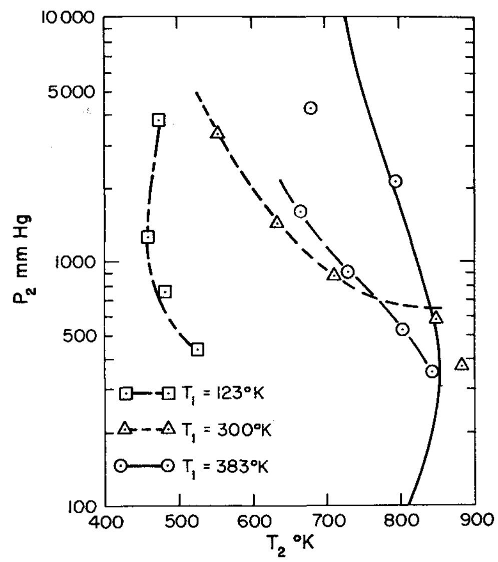

Fig. 6 Ignition conditions obtained for the fourteen sets of initial conditions.

dividual points of the ignition limits were obtained in this manner and are shown in the pressure-temperature plane of Fig. 6. Table 1 gives the initial conditions and important flow properties associated with these ignition limits; $w_{a,2}$ is the speed of sound, T_{TEL} is the thermal explosion limit temperature, and T_r is the reflected shock temperature. The ignition limits obtained from initial pressures below 50 mm Hg and initial temperatures of 300K agreed with the thermal explosion limits in concurrence with the observations of Belles and Ehlers.[6] For initial temperature of 383K and initial pressure of 300 mm Hg, two distinct ignition limits were obtained. Ignition first occurred for shocked gas temperatures in the vicinity of 665K as shown in Fig. 5. As successively stronger shock waves were produced, the ignitions became erratic occurring for one experiment and not for the next, until the shocked gas temperature reached the thermal explosion limit of 795K (see Fig. 6). At first, it was felt that this erratic behavior was due to either an error in the mixing of the gases or reflected expansion waves from the end wall of the driver section. The data was reproducible however and even the most conservative calculations showed that reflected expansion waves could not reach the test gas during the available test time. Upon careful examination of the heat transfer gage responses for these experiments, it was found that the boundary layer had become turbulent in experiments above 665K in which no ignition occurred. In other words, the transition from a laminar to a turbulent boundary layer apparently prevents the low temperature ignitions.

Table 1 Flow parameters and ignition characteristics for 15 ignition limits

P_I mm Hg	T_I K	T_2 K	P_2 mm Hg	u_2 m/sec	$w_{a,2}$ m/sec	M_2	ρ_2 g/m³	R_e (10⁶/m)	T_{TEL} K	T_o K	T_r K	$[O_2]$ 10^{-3} Moles Liter	τ msec
44.1	383	845	346	858	685	1.25	138	2.90	854	1110	1415	0.965	3.47
73.5	383	804	526	808	668	1.21	220	4.61	848	1040	1319	1.54	3.64
152.0	383	724	889	700	633	1.11	414	7.86	828	901	1134	2.89	4.04
320.0	383	665	1568	615	607	1.01	794	14.0	802	802	998	5.56	4.39
298.0	383	795	2086	796	664	1.20	884	1.80	790	1024	1300	6.18	3.69
813.0	383	677	4105	632	613	1.03	2042	3.66	758	821	1021	14.3	4.32
30.0	300	886	372	1019	701	1.45	141	3.45	854	1261	1621	0.990	3.19
50.0	300	850	585	978	686	1.43	232	5.57	845	1195	1543	1.62	3.30
100.0	300	711	870	812	628	1.29	412	9.19	830	949	1239	2.88	3.80
200.0	300	642	1440	723	597	1.21	756	16.0	808	831	1053	5.29	4.30
610.0	300	556	3325	596	555	1.07	2014	38.7	770	684	855	14.1	4.85
22.5	123	525	446	845	539	1.57	286	8.11	852	783	1029	2.00	4.16
42.3	123	481	746	790	516	1.53	522	14.7	835	706	936	3.66	4.41
75.6	123	463	1270	770	507	1.53	924	26.0	812	677	894	6.47	4.54
215.0	123	474	3713	782	513	1.54	2639	74.0	765	695	920	18.5	4.47

Turbulent boundary layers were observed for all experiments conducted at an initial temperature of 383K and an initial pressure of 870 mm Hg. The ignition temperature observed for these initial conditions was 690K which is only 70K below the thermal explosion limit. Apparently the turbulence in the boundary layer had at least interfered with the onset of the low temperature ignitions for these initial conditions.

As can be seen from Fig. 6, 5 of the 15 experimentally determined ignition limits agree with thermal explosion limits, while the remaining 10 are considerably lower. In agreement with Walkers observations (Fig. 2), the slope of the curve representing the ignition delay time as a function inverse temperature is quite steep for ignitions occurring at temperatures above the thermal explosion limits and quite shallow for ignitions occurring below these limits. For temperatures above the thermal explosion limits, the ignition delay times agreed with those in Fig. 2 while those of the low-temperature ignitions showed the same abrupt change in slope but different magnitudes for various initial temperatures.

Discussion of Results

The utilization of a buffer gas showed that the unsteady effects of the diaphragm rupture and the shock formation are not responsible for the low temperature ignitions. When the platinum thin film gauges in the first 5 m of the test section were replaced with glass blanks, no changes were observed in the ignition limits. The possibility that the static temperatures in the boundary layers might exceed the thermal explosion limit temperature has been ruled out for several reasons. The stagnation temperatures for several experiments in which ignition occurred were as much as 100K below the thermal explosion limit temperature. Also, according to boundary-layer calculations performed for all experiments in which ignition occurred, the static temperatures throughout the boundary layer were less than the freestream temperature.

The possibility that the low temperature ignitions were due to reflected shock waves occurring somewhere in the flow due to surface irregularities was ruled out for 2 reasons. The interior shock tube surfaces of the various sections were carefully matched and honed to avoid such irregularities. Also, the ignition limits which occurred for initial temperatures of 300K are in close agreement with those found by Walker[7] in a shock tube which had no buffer gas, very rough surfaces, and relatively large protruberances and orifices.

The possibility that standing or traveling waves were responsible for the low temperature ignitions was also ruled out. Traveling waves, strong enough to raise the temperature of the gas by 400K would have been easily detected by the heat transfer gages. Resonance waves which were too weak to be detected by the gages would not have had time to raise the temperature by 400K. A set of standing oblique waves could not have raised the temperature by such large amounts without greatly decreasing the shock speed. Nonequilibrium effects were also ruled out because at such low temperatures the upper vibrational modes were not excited, and the ignition delay times were several orders of magnitude longer than the rotational relaxation time.

Ignition Mechanism Originating in the Boundary Layer

Most of the mechanisms mentioned in the previous section were based on the assumption that somewhere in the flow, the local temperature of the gas actually reached the thermal explosion limit temperature. The other possibility was that the ignitions were not initiated thermally but rather through some different type of mechanism such as friction induced ionization, sparks, or catalytic phenomena.

Strong evidence was found to show that the low temperature ignitions were originating in the boundary layer. The outputs of the heat transfer gages in the test section indicated reactions of increasing strength occurring in the boundary layer between the time the shock wave passed and the time the buffer gas arrived. As the shocked gas passed over gages further down the tube, the reaction rates appeared to increase in magnitude although the speed of the shock wave remained constant. Finally, ignition occurred and the shock wave rapidly accelerated to detonation speed. The reactions in the boundary layer were indicated by small voltage decreases[9] across the heat transfer gages, similar to the large decreases observed when ignition occurred. These voltage decreases were observed only for the experiments in which low temperature ignitions occurred. The magnitudes of the voltage decreases were generally proportional to the temperature of the tube walls, indicating that colder walls tended to quench the reaction. Since the phenomena responsible for the low temperature ignitions were apparently occurring in the boundary layer, it was not surprising that the transition to turbulent boundary layers prevented the ignitions.

It was obvious from Fig. 6 that the onset of ignition for the various initial temperatures (and therefore various flow speeds) did not correlate in the pressure temperature plane. The ignition limits could be correlated however using the density in the lower regions of the boundary layer, the temperature of the wall and the shocked gas speed in the freestream. This correlation is shown in Fig. 7 for the 10 measurements of the ignition limits which did not agree with the thermal explosion limits. As can be seen in Fig. 7, the onset of ignition was favored by increasing the density near the wall (which is calculated from the equation of state based on the temperature of the wall). Likewise, an increase in the shocked gas speed or an increase in the ratio of wall temperature to stagnation temperature also favored ignition. Thus, a very dense gas mixture moving with a high speed next to a warm wall was more likely to ignite than a low density mixture moving slowly over a cold wall. To demonstrate the sensitivity of the correlation shown in Fig. 7, both the thermal explosion limits and points representing a shocked gas tem-

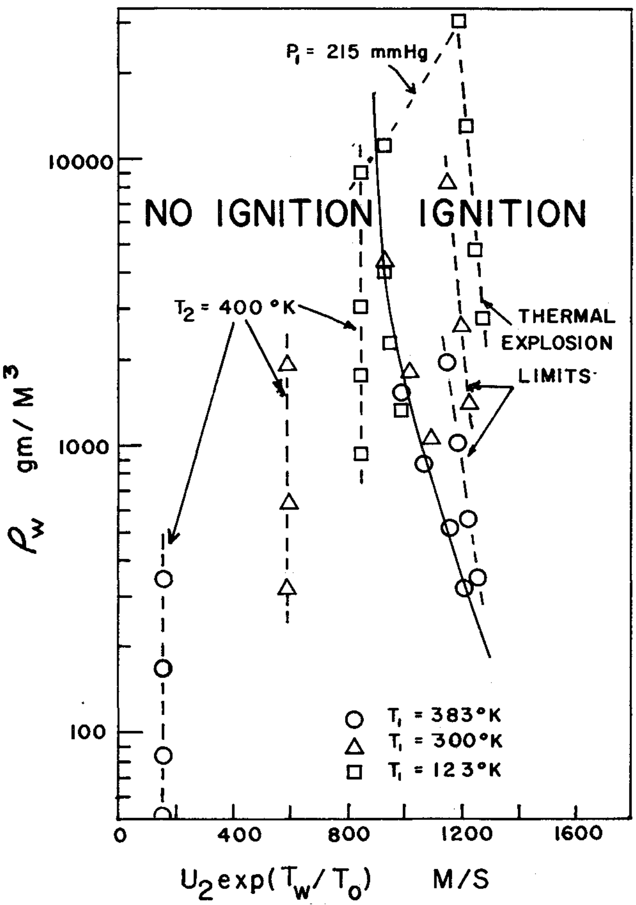

Fig. 7 Correlation of data with wall density.

perature of 400K have been included for each initial temperature.

It might be postulated, based on the previous observations, that ionization was occurring due to the high-speed flow over the wall. The same conditions that apparently favor the onset of ignition are also likely to enhance friction induced ionization. The buildup of static charge associated with the flow over solid walls is well known. As early as 1918, Pothman[1] observed a charge buildup on a wire which had been placed within a flowing hydrogen-air mixture. Fay[3] suspended a steel probe along the axis of a shock tube containing a hydrogen air mixture and observed large negative charge accumulations as incident shock waves passed along the probe. Once charged particles are produced in the flow, ignition would be easily obtained. If for example H_2^+ were formed due to friction induced ionization, then active radicals would be produced very quickly by way of the following reactions,

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

and

$$H_2^+ + O_2 \rightarrow HO_2^+ + H$$

both of which have activation energies below 100 joules/mole and are therefore relatively fast. It is possible that the accumulation of these charged particles in the boundary layer could result in sparks jumping back to the tube wall, thus initiating the combustion. The concentration of active radicals, however, would become high enough to initiate the combustion before sufficient charge could accumulate to result in a spark. The rates of the previous reactions are not very sensitive to temperature as a result of the relative low activation energy and therefore the apparent independence of the ignition limits on shocked gas temperature as depicted in Fig 7 can be explained.

Another phenomenon which can be explained by the previous mechanism is the abrupt change in slope of the curve of ignition delay time as a function of temperature (Fig. 2) which occurs in the region of the thermal explosion limits. If there are 2 completely different mechanisms leading to ignition, then the change in slope merely represents the intersection of the two mechanisms. Thus, at any given temperature, ignition will occur by whichever mechanism has the shortest ignition delay time.

The reaction by which H_2^+ is formed at the tube surface, namely

$$H_2 \rightarrow H_2^+ + e^-$$

is most likely the one which produces the negative charge which Fay observed. While the reaction $O_2 \rightarrow O_2^+ + e^-$ also involves the formation of a negative charge, it would not take into account the fact that the low temperature ignitions are observed only when hydrogen is a constituent. It is therefore postulated that the low temperature ignitions which originate in the boundary layer are caused by the formation of H_2^+ ions on the tube surface due to the high speed flow over the wall.

Additional experiments were conducted with similar results with hydrogen-oxygen instead of hydrogen-air mixtures. Experiments were also conducted in which the hydrogen-air mixtures were saturated with water vapor. The addition of the water had no apparent effect on the ignitions temperatures.

Conclusions

The low temperature ignitions observed in the past behind incident shock waves in hydrogen-air mixtures were also observed in the present study with good agreement for the cases reported. The results show that the low temperature ignitions were not due to phenomena such as: 1) diaphragm rupture, 2) unsteady shock formation, 3) overshoot of static temperature in the boundary layer, 4) stagnation in the boundary layer, 5) wave reflection on interior tube surfaces, or 6) traveling or standing waves. Attempts to explain the low temperature ignitions, on the premise that the static temperature was locally higher than it appeared to be, have proven to be fruitless.

The concept of an "ignition temperature" does not appear to be valid in this case. The onset of ignition has been correlated to flow speed, density near the wall, and wall temperature. In general, with higher speeds, denser gas mixtures and warmer walls, the gas was more likely to ignite. Reactions were observed to originate in the boundary layer for some time before ignition occurred. The low temperature ignitions do not occur when the boundary layer is turbulent. It is postulated that H_2^+ ions are formed at the tube wall which react very quickly with neutral molecules to form sufficient active radicals to initiate the combustion.

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