Determination of Induction Times in One-Dimensional Detonations (H_2, C_2H_2, and C_2H_4)

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Induction time is determined for the reactions $2H_2 + O_2 + 3.76N_2$, $2H_2 + O_2 + 4A$, $C_2H_2 + 0.75 O_2 + 4N_2$, and $C_2H_4 + 1.5 O_2 + 4N_2$. The one-dimensional detonations were established in a converging-diverging nozzle in a shock tube. For many of the experiments, pulsed-light schlieren photography displays the shock wave and the density gradient, which signals the exothermic recombination reaction proceeding to a significant extent after the induction period. In the range of conditions $1000° \leq T \leq 1600°K$, $8 \leq p_1 \leq 40$ mm Hg, $3.5 \times 10^{-4} \leq [O_2] \leq 1.4 \times 10^{-3}$ moles/liter, and $14 \leq t_i \leq 92$ μsec (gas time), it was found for all four detonable mixtures that $\log_{10}([O_2]t_i)$ mole-sec/liter $= -10.0 + 14,650/4.58T$. Further substantiation is thus found for the $[O_2]t_i$ temperature dependence in H_2-O_2 and C_2H_2-O_2 reactions determined by other shock-tube techniques. These experiments indicate that induction time in C_2H_4-O_2 detonations can also be explained in terms of a branching chain mechanism controlled by the reaction $H + O_2 \rightarrow OH + O$.

I. Introduction

A recent survey article[1] describing research on the formation, structure, and stability of detonation waves stated the general conclusion that the motion of the gas in the vicinity of the reaction zone, and probably in the vicinity of the shock wave, was never rigorously one-dimensional. It was also noted in Ref. 1 that there iss ome evidence obtained interferometrically by White[2,3] that a one-dimensional detonation could be established as a transient. The new technique due to White utilized a convergent-divergent channel as a flow passage for a detonation wave. For low initial pressures (25-mm-Hg range), the detonation was approximately one-dimensional, and the flow behind the front appeared to be laminar as the shock wave left the nozzle. The fluid dynamics of the complex flow pattern with a chemical reaction is an interesting problem in itself and deserves further study. In the present experiments, pulsed-light schlieren photography has been used to investigate the induction time in one-dimensional detonations formed by the nozzle geometry. Good agreement was obtained in comparing the induction-time measurements in H_2-O_2 detonations with the frequently quoted work of Schott and Kinsey[4] and also with that of White, although the gas mixtures, shock tubes, and experimental techniques were different in each case.

II. Experimental

The stainless-steel shock-tube driver, 10-cm i.d. and 1.6 m long, was separated from the 7.6-cm i.d., 8-m-long driven section by a carefully scored aluminum diaphragm. Cold hydrogen driving with pressure breaks at 6.5 to 10 atm was used to ignite the detonable mixture in the driven tube using the incident shock wave. At the end of the circular cross section driven tube, 8 m away from the driver, a transition piece adapted it to a 90-cm-long square test section. The square section contained a two-dimensional converging-diverging nozzle, and a $\frac{1}{2}$-mil mylar diaphragm separated it from the dump chamber.

Two pressure transducers were located near the window at the end of the converging-diverging nozzle (Fig. 1) for shock velocity measurement. The first pressure transducer provided a signal through a variable delay circuit, amplifier, and pulse-forming network to fire the trigger gap on the short-duration (fraction of microsecond) light source. The vertical knife-edge schlieren system was conventional except for the use of a dydymium glass filter to reduce luminosity due to sodium impurities in the reaction zone. The lead-zirconate/lead-titanate pressure transducers near the window section were made by us from a design[5] that emphasized short response time and high sensitivity. For this application the rise time was about 1 μsec. The wave, moving from left to right, accelerated to a throat section 0.36×6.4 cm², and then decelerated as it approached the window.

The detonations observed here were actually cylindrical rather than one-dimensional. However, the observations could be related to the chemistry within a hypothetical one-dimensional laminar detonation wave if the channel flow were laminar, the induction zone thin with respect to the curvature, and the propagation velocity constant. A shallow angle nozzle (10°) was used to keep the propagation velocity gradient small near the region of the window. The typical velocity attenuation curve shown in Ref. 2 is representative of the present experiments. If the shock were attenuating, the temperature characterizing the induction zone would be somewhat higher than that used, and the temperature dependence of the data would have to be corrected to take this limitation of the technique into account.

The gases for detonation experiments were taken from commercial cylinders through a cold trap at $-80°C$ and then admitted to stainless-steel storage containers. Compositions were obtained from pressure readings without correcting for gas nonideality. The combustible gas was stored for several days to insure thorough mixing. The shock-tube driven section, when evacuated to the low micron range, had a leak rate of 10 μ/hr. The time interval between filling the
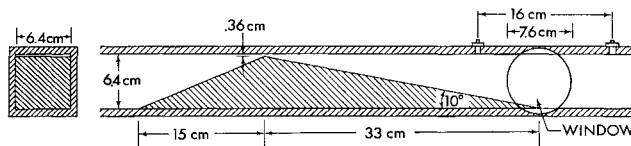

Fig. 1 Two-dimensional converging-diverging nozzle. Wave moves from left to right.
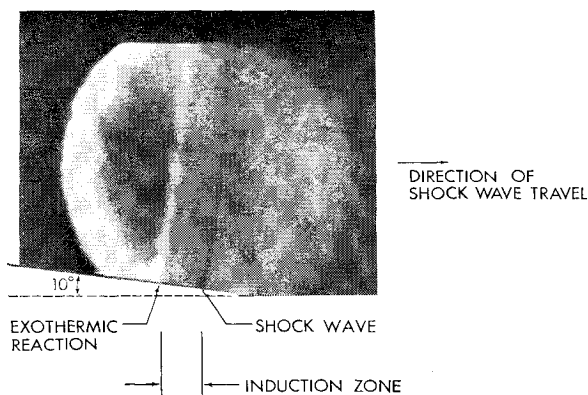
Fig. 2 Typical schlieren photograph showing induction zone for $2H_2 + O_2 + 3.76N_2$. Detonation is propagating to the right. $p_1 = 25$ mm Hg, shock velocity $= 1.9$ mm/ μsec.

Fig. 3 O_2t_1 vs $1/T$, p_1 varies from 8 to 40 mm Hg.

driven tube with test gas and the pressure break with cold hydrogen driven was about 5 min.

To obtain quantitative information on the induction zone, several measurements were made in each experiment. These included 1) a schlieren photograph, which gave the physical length of the density plateau; 2) the shock velocity at the window region; and 3) the initial pressure of the detonable mixture. A computer program was set up to provide state-of-the-gas information for the induction zone of H_2-O_2-inert gas detonations using initial conditions of interest in the shock-tube experiments. Later it was extended to include detonable mixtures of C_2H_2 and C_2H_4. The density ratio in the induction zone was calculated assuming that the gas passed over by the shock was vibrationally equilibrated but unreacted. In the shock velocity range of the experiments, vibrational equilibration reduced the temperature and increased the density ratio across the incident shock wave about 10%. Dissociation lowered the temperature still further but would not be significant at temperatures below $2500°K$. This was considerably beyond the range of temperatures reached in the induction zones of these experiments ($1000°$–$1500°K$). It cannot be stated with certainty that the vibration relaxation times for the mixtures used in all of these experiments were short as compared to the induction times relative to the moving system (10–100 μsec). However, there is evidence from the extensive measurements of Millikan[6] and White[7] that this is indeed the case.

Figure 2 is a typical schlieren photograph from which the length of the density plateau is measured. This plateau, a region of high pressure and high density at the front of the detonation wave, is usually referred to as the von Neumann "spike." The shock wave is moving to the right and shows some curvature. The induction zone lies between the shock front (dark line) and the light line, which signals the density decrease due to exothermic reaction. This is the distance d. The induction time relative to the moving gas behind the shock front is given by

$$t = (d/v_s)(\rho_2/\rho_1)$$

where v_s is the shock velocity and ρ_2/ρ_1 is the calculated density ratio across the shock wave assuming vibrational equilibration of the unreacted combustible gas mixture. The calculated density ratio also permitted a determination of the oxygen concentration in the shocked but unreacted combustible mixture of the induction zone.

Measurement of induction time by schlieren photography with hydrocarbon-oxygen mixtures was less satisfactory than with hydrogen. The density gradient, which indicated that exothermic recombination reactions were proceeding to a
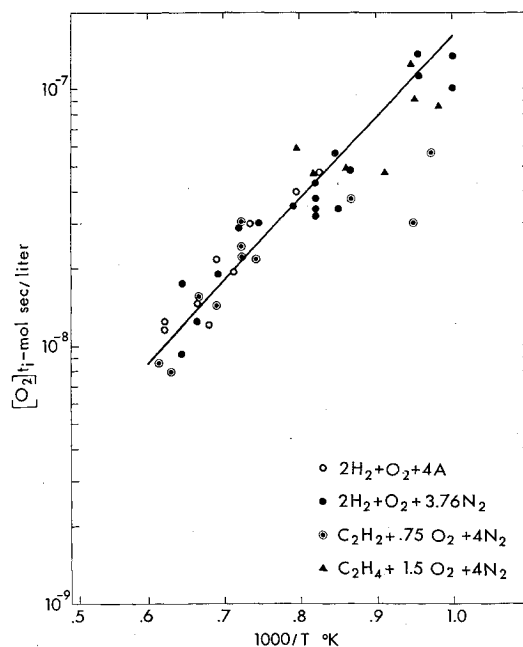
significant extent, was often nonuniform, thus making the induction distance difficult to measure.

III. Results and Discussion

Figure 3 summarizes the results of the induction time study by schlieren photography. The equation of the least-squares line is

$$\log_{10}([O_2]t_1)(\text{mole-sec/liter}) = -10.0 + 14{,}650/4.58T \qquad (1)$$

where O_2 is the initial molecular oxygen concentration in the shocked but unreacted gas, and T is the vibrationally relaxed temperature in $°K$. It is interesting to compare these results with several other shock-tube experiments. Schott and Kinsey[4] found for H_2-O_2-argon mixtures that

$$\log_{10}([O_2]t_1) = -10.65 + 18{,}200/4.58T \qquad (2)$$

White and Moore[8] conclude that interferometric measurements in a H_2-O_2 induction time study can be represented by

$$\log_{10}\{([O_2][H_2])^{1/2}t_i\} = -9.8 + 14{,}200/4.58T \qquad (3)$$

in experiments in which $[H_2]/[O_2]$ was varied by a factor of 10^4.

Researchers at Harvard[9-11] have investigated various aspects of acetylene-oxygen reactions. Depending on the method of measurement, they either showed close agreement with the results of Ref. 4, or expressed C_2H_2-O_2 induction time by

$$\log_{10}([O_2]t_i) = -10.57 + 17{,}100/4.58T \qquad (4)$$

A sample calculation at $T = 1250°K$ and assumed concentrations of O_2 and H_2 of 8×10^{-4} and 1.5×10^{-3} moles/ liter, respectively, show a factor of 3.5 between the induction times, using formulas (1–4).

Recently reported experimental and theoretical work[12, 13] has shown that two chain branching reactions are of equal importance during the induction period in the H_2-O_2 reaction for the temperature range of interest. These are

$$H + O_2 \rightarrow OH + O \qquad (5)$$

$$O + H_2 \rightarrow H + OH \qquad (6)$$

In general, induction times in the H_2-O_2 reaction in shock waves will depend on concentration of both hydrogen and oxygen. It is recognized now that the use of equations for induction time involving only O_2 t_1, such as presented here, have value only for comparison purposes except in the limit of very rich mixtures. The activation energy for (5) is about 16.9 kcal. The apparent activation energy from the data of the present experiments (14.7 kcal) is anomalously low for the ratio of hydrogen to oxygen used. Reaction (5) is the rate-controlling reaction in acetylene oxidation, and a proposed chain branching mechanism for the acetylene oxidation is given in Ref. 14. The experimental results indicate that the same rate-controlling process holds for ethylene.

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