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THERMODYNAMICS AND DISTRIBUTION OF EQUILIBRIUM COMPOSITIONS IN LPG–O_2 DETONATION BEHIND AN INITIAL SHOCK WAVE

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ABSTRACT

We have measured pressures and induction times of the detonation in liquefied petroleum gas–oxygen (LPG–O_2) mixtures behind an initial shock wave. Induction times of the detonation in the stoichiometric mixture show an activation energy of about 43 kJ mol^{-1}. Theoretical calculation of thermodynamic parameters and the distribution of the equilibrium compositions at the Chapman–Jouguet detonation of LPG–O_2 mixtures were also performed. A comparison of the calculated and experimental results is made in terms of the pressure.

INTRODUCTION

In recent years, a great deal of shock-tube investigations of hydrocarbon–oxygen mixtures have been reported [1–4]. However, the progress has not been satisfactory due to the complicated reaction mechanism of hydrocarbon oxidation [5]. In general, thermal decomposition and oxidation of hydrocarbons have been employed to elucidate the chemical process of the detonation of a hydrocarbon–oxygen mixture. As an example, on the basis of the oxidation reaction mechanism of methane suggested by Olson and Gardiner [6] and that of ethane put forward by Westbrook et al. [7], Westbrook [8] proposed detailed chemical kinetics of the LNG detonation behind a reflected shock using a model. He studied ignition delay times (or induction times) as a function of temperature and concentration of reactants with or without any inert diluent such as Ar. It is very difficult to deduce a

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reaction mechanism and to determine individual rate constants from ignition delay times. Ignition delay times, however, are very useful to determine if the proposed model is reasonably correct [9,10].

In the shock-tube investigation of a detonation in an explosive gas mixture, the calculation of complex equilibria at the Chapman–Jouguet (CJ) plane is an interplay of thermodynamic fundamentals and the product distribution [11,12]. A detailed description of the chemical equilibria in a complex system could be very useful for evaluating theoretical thermodynamic properties and for examining some main reaction steps in the CJ detonation. Although an atmospheric gaseous detonation of LPG is the most dangerous hazard, the detonation characteristics relating to the ignition delay time and the chemical equilibrium at the CJ detonation have not been reported. In this work, pressures and density profiles behind an initial shock wave in the liquefied petroleum gas–oxygen (LPG–O_2) mixture have been measured as a function of an initial pressure of the mixture and an equivalent ratio of LPG. These results are compared with theoretically computed ones using the method of complex chemical equilibria for the CJ detonation.

EXPERIMENTAL

Equipment and samples

A single-pulse stainless steel shock tube 37.5 mm in diameter consisting of 1 m driver and 4 m driven sections was used. A 25 l dump tank was connected to the end of the driven section. Each section was separated by a mylar thin diaphragm (Lookwood). The detonation was established in the driven section by a shock wave produced by bursting the diaphragm between the driver and the driven sections. The N_2 gas (purity, 99.99%) was used as a driver gas. The detonation pressure was measured over 30 cm intervals with two piezotype pressure transducers (PCM, 102M24) mounted at the end of the driven section. The signals produced by the wave were amplified by two dual-mode amplifiers (Sundstrand 504E) and were displayed on a storage oscilloscope (Tektronix 100 MHz), or alternatively they were acquired by using a combination of a digital oscilloscope (Sony) and a personal computer. The signal detected by the first transducer was used as an external trigger source. The laser-schlieren method was employed to measure the ignition delay time. As shown in Fig. 1, an He–Ne laser beam (Spectra Physics, 4 mW) traversing the shock tube passes through a monochromator (Bausch–Lamb) with two 0.1 mm slits and is detected by an npn phototransistor (Fair Child) with a time resolution of 2.8 μs.

The LPG (Al 40 propane liquefied petroleum gas) used in this work consists of 0.9 vol.% ethane, 98.5 vol.% propane, 0.5 vol.% isobutane and 0.1

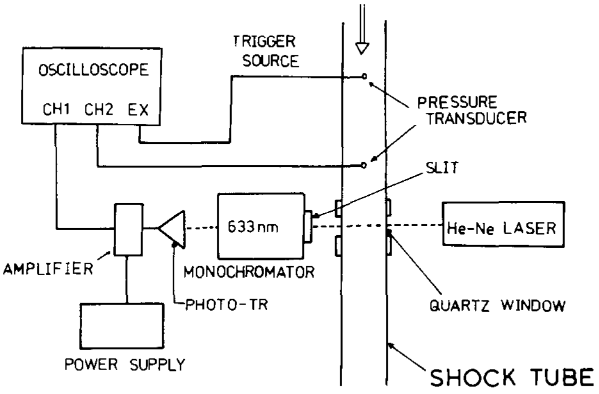

Fig. 1. Block diagram of the laser-schlieren measurement used in this work.

vol.% n-butane. The mixture of LPG and O_2 (purity, 99.9%) was prepared manometrically in a stainless steel gas sampler and allowed to mix at least overnight before use.

Theoretical calculation

A thermodynamic study of the detonation products at the CJ plane was undertaken by computing detonation parameters such as detonation pressure, temperature, velocity and their derivatives. The program used in this work, originally written by Gordon and McBride [12], has been modified to accommodate it to IBM 370/148. The theoretical framework of the chemical equilibrium in this calculation is the Gibbs free energy minimization method subject to the mass balance constraints. A descent Newton–Raphson method with an iteration procedure is employed to acquire the equilibrium composition and the partial derivatives of the volume (with respect to the pressure and temperature) in logarithmic form. The calculated thermodynamic properties of products at the chemical equilibrium are linked to the evaluation of the CJ detonation parameters in terms of the conservations of continuity, momentum and energy. Thermochemical properties were computed from polynomial fits to JANAF [12] and other published data [13].

RESULTS AND DISCUSSION

Figure 2 shows a typical schlieren profile. Initial positive deflection attributed to vibrational relaxation appears at the shock wave front, followed by a negative gradient. Behind the shock wave front, the chemical reaction begins and the heat of the reaction is given off. The chemical reaction and the liberation of the heat behind the wave front are accompa-

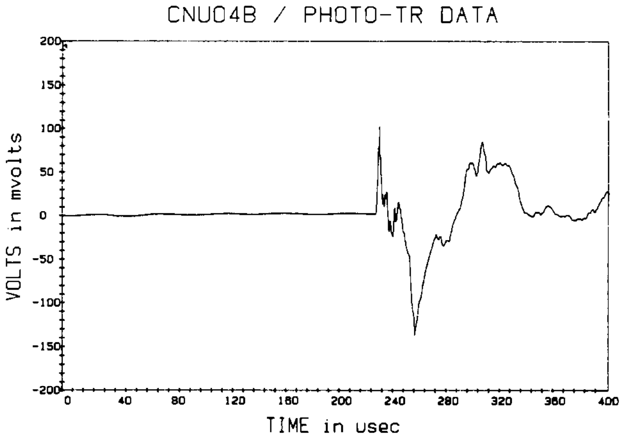

Fig. 2. Typical oscillogram of phototransistor laser-schlieren in LPG–O_2 detonation.

nied by the rarefaction. It results in a diminution in density. In the region where the reaction has been consummated, the free propagation of the detonation wave is established without additional compression. Accordingly, at the CJ detonation, the density gradient reaches a minimum and then increases gradually. The induction time of the CJ detonation was calculated as the oscillographic time elapsed between incident shock arrival and the minimum gradient. The calculated induction time τ_2 in the stoichiometric LPG–O_2 mixture ($\phi = 1.0$, 16.67 mol.%) are listed in Table 1. In Table 1, the temperature T of the shocked but unburned mixture was calculated from

$$\frac{T}{T_1} = \frac{\left(\gamma M_1 - \frac{\gamma - 1}{2}\right)\left(\frac{\gamma - 1}{2} M_1^2 + 1\right)}{\left(\frac{\gamma + 1}{2}\right)^2 M_1^2} \tag{1}$$

with an assumption that, in the case of the well-established detonation, the detonation front is fundamentally regarded as the shock front, where T_1 is the initial temperature, γ is the ratio of heat capacities for the unburned mixture, and M_1 is the measured Mach number.

The induction time could be expressed in terms of an activation energy and concentration as follows

$$\tau = A \exp(E_a/RT)[\mathrm{LPG}]^a[\mathrm{O_2}]^b \tag{2}$$

where A is a proportionality factor. At the given concentrations, the induction time is only dependent on the temperature, so that the equation can be written in the following conventional manner

$$\ln \tau = \left(\frac{E_a}{R}\right)\frac{1}{T} + \text{constant} \tag{3}$$

TABLE 1

Induction times of the detonation of the stoichiometric LPG–O_2 mixture (ϕ = 1.0, 16.67 mol.%)

Initial pressure P_1 (lbf in^{-2})	Mach number M_1	T_2 (K)	τ (μs)
0.98	7.52	2718	37
0.98	7.52	2718	40
1.97	7.92	2988	25
1.97	7.92	2988	30
1.97	8.03	3063	22.5
1.97	8.03	3063	27.5
3.93	7.72	2848	30
3.93	7.72	2848	35
3.93	7.72	2848	30
5.90	8.14	3140	25
5.90	8.03	3063	22.5
5.90	8.03	3063	22.5

As shown in Fig. 3, the slope of the plot of log τ as a reciprocal of the shock temperature gives $E_a = (43.1 \pm 0.5)$ kJ mol^{-1}. This value is smaller than literature values for hydrocarbon oxidations. According to the results reported previously [9,14], the activation energies of small hydrocarbons (C_1–C_5) with Ar diluent, initiated by the reflected shock wave (1200–1600 K), range from 120–209 kJ mol^{-1}. In this work, we have used a much higher shock temperature and no diluent gas.

Figure 4 shows measured detonation pressures for the fuel-lean (ϕ = 0.48, 8.04 mol.%), stoichiometric and fuel-rich (ϕ = 1.45, 24.14 mol.%) mixtures. The experimental results indicate that the detonation pressure could be dependent on the initial pressure. In the figure, the detonation pressure increases proportionally with the initial pressure. In addition, the detonation

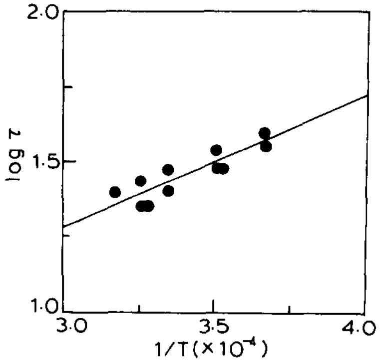

Fig. 3. A plot of log τ vs. $1/T$ in LPG–O_2 detonation (ϕ = 1.0).

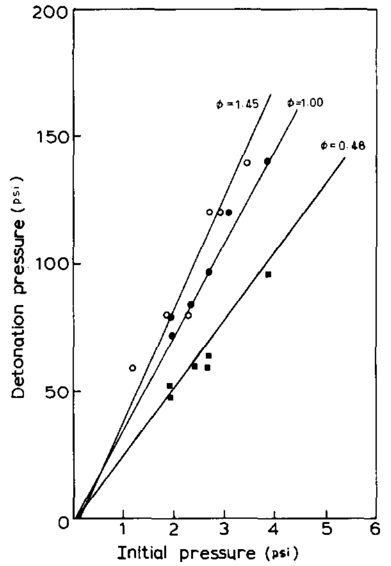

Fig. 4. A plot of detonation pressure vs. the initial pressure P_1 for the fuel-lean (■, $\phi = 0.48$), stoichiometric (●, $\phi = 1.0$) and fuel-rich (○, $\phi = 1.45$) mixtures. The solid lines represent calculated values for each mixture.

pressure, as a function of the equivalent ratio of the fuel, was investigated in the detonable concentration limits. Figure 5 shows that the detonation pressure also increases with increasing concentration of the LPG.

Finally, we have attempted to evaluate the equilibrium composition and thermodynamic properties at the CJ detonation since it has been used in a

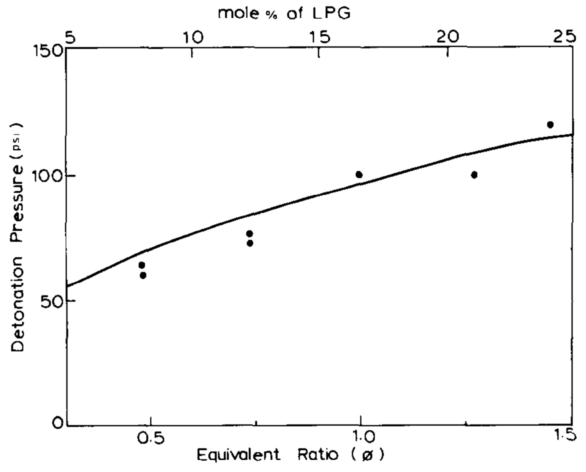

Fig. 5. A plot of detonation pressure vs. ϕ for the LPG–O_2 mixture ($P_1 = 2.71$ lbf in^{-2}). The solid line represents calculated values.

TABLE 2

Detonation properties of the stoichiometric LPG–O_2 mixture ($T_1 = 298.15$ K)

Unburned gas						
P_1 (lbf in^{-2})	0.98	1.93	2.46	2.95	3.93	4.91
Burned gas						
P (lbf in^{-2})	32.54	67.72	87.09	105.14	141.55	178.30
T (K)	3392	3511	3555	3589	3643	3685
ρ (g cm$^{-3}\times10^4$)	1.729	3.401	4.334	5.195	6.917	8.639
H (cal g^{-1})	461.6	473.3	477.6	480.9	486.0	490.1
S (cal g^{-1} K^{-1})	3.133	3.070	3.048	3.031	3.005	2.985
$(\mathrm{d}\ln V/\mathrm{d}\ln P)_T$	−1.095	−1.092	−1.091	−1.090	−1.088	−1.087
$(\mathrm{d}\ln V/\mathrm{d}\ln T)_P$	2.722	2.606	2.565	2.535	2.488	2.452
C_P (cal g^{-1} K^{-1})	3.427	3.123	3.019	2.944	2.828	2.741
u (m s^{-1})	2284.1	2315.3	2326.6	2335.1	2348.6	2356.1
Mole fraction [a]						
CO	0.21951	0.22001	0.22011	0.22016	0.22018	0.22015
CO_2	0.09060	0.09268	0.09355	0.09424	0.09535	0.09639
H	0.08216	0.07575	0.07346	0.07175	0.06906	0.06699
HCO	0.00001	0.00002	0.00003	0.00003	0.00004	0.00004
HO_2	0.00005	0.00007	0.00008	0.00009	0.00011	0.00012
H_2	0.07407	0.07294	0.07248	0.07211	0.07151	0.07101
H_2O	0.23970	0.24575	0.24806	0.24984	0.25274	0.25506
H_2O_2	0.00000	0.00001	0.00001	0.00001	0.00001	0.00001
O	0.07706	0.07351	0.07219	0.07118	0.06954	0.06823
OH	0.11742	0.12087	0.12203	0.12288	0.12417	0.12513
O_2	0.09941	0.09839	0.09800	0.09771	0.09734	0.09686

[a] Additional products which were considered but whose mole fractions were less than 0.50×10^{-5} for all assigned conditions are C(s), C, CH, CH_2, CH_2O, CH_3, CH_4, C_2, C_2H, C_2H_2, C_2H_4, C_2H_4O, C_2H_6, C_3H_8, C_4H_{10}, C_2O, C_3, C_3O_2, C_4, C_5, H_2, H_2O(l), O_3.

wide variety of practical applications in shock-tube chemistry. The calculated numerical data for the detonation of the stoichiometric mixture are listed in Table 2. The usefulness of theoretical thermodynamic properties in predicting actual results are examined by comparing calculated detonation pressures with the measured values. In Figs. 4 and 5, the solid lines present the calculated values. The comparison suggests that the assumptions used in the theoretical calculations closely approximate the physical reality of the detonation. The distribution of equilibrium compositions is very useful for predicting some key reaction steps in the detonation. The mole fractions of products in the detonation of the stoichiometric LPG–O_2 mixture are also listed in Table 2. The results show that the initial pressure has little effect on the mole fraction of the equilibrium composition at the CJ detonation in the LPG–O_2 mixture. As shown in Fig. 6, the product distribution presents some characteristic features in the curves of the O, OH, H and CO_2 products: the H species has a maximum mole fraction in the fuel-rich mixture, whereas the others have maximum values in the fuel-lean mixture.

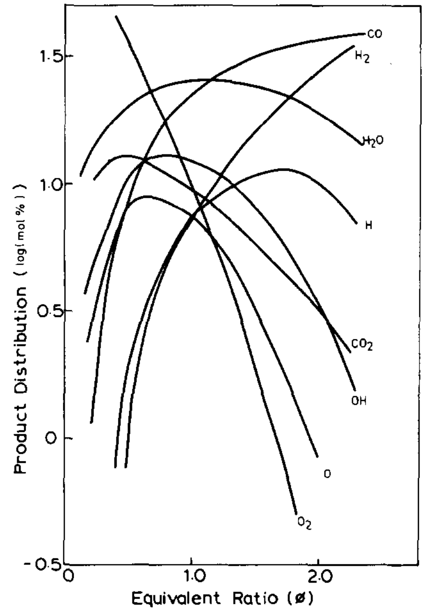

Fig. 6. Product distribution of equilibrium compositions at the CJ detonation of the LPG–O_2 mixture as a function of ϕ.

These features could be attributed to particular steps depending on the equivalent ratio of the LPG. According to the hydrocarbon oxidation reported by Khandelwal and Skinner [15] and the pyrolysis of propane studied by Koike and Gardiner [16], the rate of the pyrolysis and the product distribution are almost the same with or without oxygen. The pyrolysis of propane is initiated by the decomposition of propane itself

$$C_3H_8 \rightarrow C_2H_5 + CH_3 \qquad (4)$$

Subsequent reactions following reaction (4)

$$CH_3 + C_3H_8 \rightarrow CH_4 + \text{i,n-}C_3H_7 \qquad (5)$$

$$\text{i,n-}C_3H_7 \rightarrow C_3H_6 + H \qquad (6)$$

$$C_2H_5 \rightarrow C_2H_4 + H \qquad (7)$$

mainly contribute the H concentration to the distribution of the equilibrium components. Minor constituents sensitize the H production kinetically. On the other hand, the oxidation reaction of hydrocarbon is mainly propagated by

$$H + O_2 \rightarrow OH + O \qquad (8)$$

The OH radical plays a very important role in the oxidation of the system producing the H and O radicals. Each species could be dependent on both the nature of the reactants and the concentration. The above reactions could account for the main effects on the product distribution: in the fuel-rich mixture the pyrolysis of propane occurs mainly producing the H radical, whereas in the fuel-lean mixture the chain branching procedure of eqn. (8) is predominant. In addition, the production of CO_2 occurring through excited $CO_2^\star$ as

$$O + CO \rightarrow CO_2^\star \tag{9}$$

$$CO_2^\star + O_2 \rightarrow CO_2 + 2O \tag{10}$$

is related to the O product distribution and these reactions are predominant in the fuel-lean mixture rather than in the fuel-rich mixture.

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