Oxy-Acetylene Detonations*

(1st Report, The Transition Phenomena Associated with Soot Formation)

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This paper describes a study of peculiar phenomena in fuel-rich oxy-acetylene detonations. The detonation wave and the accompanying soot-formation were observed by a high speed streak camera. The pressure and particle velocity changes in the expansion wave were measured and compared with theoretical predictions. The effect of an additive which is thought to accelerate the soot-formation was investigated. The following results were obtained:

1. Introduction

The detonation wave constitutes one type of the self-sustaining propagation of combustion reaction in a combustible mixture along with the "flame" (deflagration wave). In contrast with the latter, which has as its driving force the heat conduction from the reaction zone to the unburned gas and is accompanied by a slight pressure drop, the former has a strong plane shock wave in front of its reaction zone and an expansion wave in the rear and propagates at a supersonic speed. Generally, a flame propagating in a mixture with large calorific value readily makes a transition to detonation. And once a detonation wave is established, it has a very nearly constant propagation velocity (D), and one is able to assign a regular propagation velocity to a fixed mixture. The propagation velocity D can be calculated on the basis of the "Chapman-Jouquet condition", and it has been shown that the calculated values are very close to the experimental values(1).

Assume, for simplicity, that the mixture is a perfect gas with gas constant R and specific heat ratio \( \gamma \) throughout the unburned and burned states, and denote the initial temperature with \( T_0 \) and ratio of detonation velocity D to the initial sound speed in the mixture \( a_0 \) (D/\( a_0 \): detonation Mach number) is represented in the following form

\[
\frac{D}{a_0} = f(q/RT_0, \gamma),
\]

namely, D serves as a representation of the calorific value q.

Acetylene has the largest calorific value among the hydrocarbon fuels, and has been used frequently as the source of high temperature in industrial applications, thus constituting an important industrial material. The mixture of this fuel with oxygen can easily detonate in a very wide range of mixture ratios, and detonations may develop even in extremely fuel-rich mixtures(2). In such cases, large amounts of soot are formed within the gas phase, and this phenomenon can be used for the production of uniform fine-sized soot. As for the physico-chemical mechanism of the soot formation by the combustion of hydrocarbons, there have been proposed various hypotheses(3). Among them there is the "acetylene theory" proposed by Porter, according to which the fuel hydrocarbon is thermally decomposed into acetylene and soot is then formed through the latter. The study of the be-
haviour and nature of oxy-acetylene detonations is of basic importance from various aspects described above.

When the detonation propagates in a fuel-rich mixture, it has been shown that some peculiar phenomena occur, as studied by G.B. Kistiakowsky et al. (4)(5). It is expected from the equilibrium calculation that the excess acetylene is thermally decomposed in the high temperature atmosphere, and the cracking products form soot particle by condensation and releases large latent heat. Therefore one can adopt two distinct values for the calorific value $q$, namely the one which is associated with the oxidation reaction (A), and the other which is the sum of (A) and the heat of condensation of soot. Kistiakowsky et al. described the relation between the measured detonation velocity (D) and the two kinds of the theoretical detonation velocities (A), (B) as follows. When the measurement was done at a constant distance from the ignition point, D decreased with the ratio of acetylene to oxygen along the curve (A), but from a certain mixture ratio upward, the propagation velocity D switches from (A) to (B). They also observed a double wave structure during the transition (A) $\rightarrow$ (B), and this is composed of two waves, one sustained by oxidation reaction alone, and the other by soot formation. The latter travels after the former, propagating at a higher speed and when it catches up with the former the propagation velocity (B) is attained.

The object of this study is to investigate the foregoing peculiar nature of oxy-acetylene detonations and to find a key to the elucidation of the soot formation process. To accomplish this purpose, the propagation of detonation and the accompanying soot formation were observed by a streak camera. The pressure changes and particle velocities in the expansion region were also measured and compared with theoretical values. Furthermore, the effect of additive which promotes the soot formation was investigated.

Nomenclature

A : detonation velocities calculated on the assumption that the calorific value is decided by the oxidation reaction alone
a : sound speed (m/s)
B : detonation velocities calculated on the assumption that the calorific value is decided by the oxidation reaction and the soot formation
C : specific heat at constant pressure ($\text{Kcal/kg}^o\text{K}$)
P : detonation velocity (m/s)
m : mass-flow rate (kg/s)
P : pressure (atm or mmHg)
Q : Riemann's invariant
q : specific value ($\text{Kcal/kg}$)
R : universal gas constant ($\text{Kcal/kg}^o\text{K}$)
T : temperature ($^o\text{K}$)

Subscripts

CJ : at the Chapman-Jouguet plane
e : equilibrium
f : frozen
g : gas phase or gas
m : measured
s : solid state
1 : initial or upstream state
2 : downstream state

2. Experimental apparatus

Figure 1 shows the experimental apparatus. The main part of the apparatus is composed of the detonation tube (I.D.= 25.4mm) and the dump tank (volume=50 l). The test mixture is prepared in the mixing tank, and is introduced into the detonation tube which has been evacuated. An oxy-acetylene equinomolar mixture is introduced into the ignition section, where it is ignited to produce a strong detonation wave. This detonation wave breaks the diaphragm at the left end of the ignition section, and ignites the test mixture. A detonation wave then develops in the detonation tube and propagates through the test section, breaking the diaphragm as it is transmitted into the large-volume dump tank. Using this method, a rapid establishment of the detonation is assured even in extremely fuel-rich test mixtures, and the detonation wave travels as if the detonation tube extends to infinity. The detonation wave is not altered by the change of the initial pressure of the igniting mixture, so that the detonation in the test mixture is considered to be self-sustained. The x-t diagram which shows the wave patterns is presented in Fig.2. The detonation velocity was measured by a high speed streak camera which records the emission from the three 100mm-wide slitlike windows which were located axially. The pressure changes were measured by pressure transducers which were located at several fixed stations. Acetylene mole fraction of test

![Fig.1 Experimental apparatus.](image-url)
mixture was varied from 50 to 85%, and the initial pressure from 200 to 500 mmHg. In the extremely fuel-rich region a steady detonation was not obtained, while at lower pressures the emission from the detonation was so weak that the measurement by the streak camera was difficult.

![Fig.2 x-t diagram showing the wave patterns.](image)

3. Propagation velocity

3.1. Theoretical calculation of propagation velocity

In a detonation wave, the unburned mixture is compressed and heated through a shock wave and then completes a combustion reaction within a thin reaction zone. Provided that the propagation velocity is constant and the reaction zone does not change with time, the flow between the shock front and the rear end of the reaction zone is rendered one-dimensional and stationary when observed in the coordinate system fixed to the shock front. In the following analysis, the Chapman-Jouguet condition (6) which states that the flow speed is equal to the sound speed at the rear end of the reaction zone is assumed to be valid.

In a combustion wave, generally, the upstream condition (state 1) is related to the downstream condition (state 2) by the Rankine-Hugoniot curve with heat release, which is shown in Fig. 3. The C-J condition corresponds to the case where the downstream condition is represented by the point of contact of a tangent drawn from state 1 to this R-H curve, and the propagation velocity becomes minimum at this point. The ratio of the pressure at state 2 to the pressure at state 1 is represented as a function of the quantities at state 1 and the temperature, enthalpy and gas constant at state 2 by means of mass, momentum and energy conservation equations for steady, one dimensional, constant-area flow. In the following equilibrium calculation, the pressure at state 2 is assumed to be known and the pressure at state 1 to be unknown. If the temperature at state 2 is assumed and the chemical equilibrium in this state is postulated, the equilibrium concentration of chemical species, the enthalpy and gas constant, at state 2 can be calculated. The propagation velocity is determined from the quantities at state 2 in this way. The C-J detonation velocities can be determined if the temperature at state 2 is corrected until the propagation velocity becomes minimum.

In the equilibrium calculation, $C_2H_2$, $CO$, $H_2O$, $CO_2$, $H$, $OH$, $O$, $H_2$, $O_2$ and gas phase $C$ (Cs) or solid phase $C$ (Cg) were taken into account as products. The enthalpy and the specific heat at constant pressure were taken from the JANAF thermodynamic tables (7). The case (A) in which Cs is considered as the product corresponds to the case where calorific value is determined by the oxidation reaction alone, and the case (B) incorporating Cg as the product corresponds to the case where calorific value is determined by the condensation of extricated carbon and the oxidation reaction.

3.2. Measurement of detonation velocity

The emission from the detonation is recorded on the film by a high-speed streak camera and the detonation velocity is determined from the slope of the emission trace on the film. Figure 4 shows an example of streak camera record.

![Fig.4 Streak camera record.](image)

Acetylene mole fraction 60%, initial pressure 300 mmHg.
Here acetylene mole fraction $X=60\%$, initial pressure $P_1=300\text{mmHg}$, propagation velocity $D=2500\text{m/s}$; time increases from left to right and detonation propagates downward. Figure 5(a) represents the measured propagation velocities at initial pressure of $500\text{mmHg}$. The thin line (A) represents the theoretical value based on the assumption that the carbon produced is in gas phase, and the thin line (B) is the one that is based on the solid-phase carbon. The pressure at the C=J plane of detonation is assumed to be $15\text{atm}$ in calculating the theoretical propagation velocity. The open circles represent the measured velocity and the vertical bars on the circles represent the fluctuation of the propagation velocity in single measurements. When the acetylene mole fraction $X$ is less than $65\%$, the detonation velocity is constant and highly reproducible in the test section. When $X$ becomes greater than $70\%$, however, the detonation velocity fluctuates and loses reproducibility. Such fluctuation becomes more remarkable with increasing $X$ up to $X=75\%$, and with decreasing initial pressure. The solid line in the figure represents the mean propagation velocity, and it is seen that the transition begins at $X=73\%$. This mole fraction corresponds to the point where a change appears in the emission from the detonation wave and an increase of the soot deposited on the wall is detected.

The measured propagation velocities at various initial pressures are shown in Fig.5(b). Each of the symbols represents the measured mean velocity at various initial pressures, and the curves link the mean propagation velocities at respective initial pressures. From this figure it is seen that the transition of the detonation velocity (A) + (B) is delayed by lowering the initial pressure.

4. Soot formation

Figure 6 shows the representative streak camera records of soot formation in the rear of the detonation front. The time $t$ increases from left to right, and the detonation propagates downward. Figure 6(a) corresponds to $X=71\%$, $P_1=300\text{mmHg}$, $D=2100\text{m/s}$, and shows a striped pattern of soot-particle trajectories behind the wave front. In this case, detonation velocity $D$ still stays on the curve (A). If $X$ is increased a little more, the shock wave which follows the main wave is formed as an accumulation of compression waves originating from the soot-formation heat release as shown in Fig. 6(b). This figure corresponds to $X=72\%$, $P_1=500\text{mmHg}$, $D=2050\text{m/s}$ and shows a double wave structure composed of the main front and the wave due to soot-formation ($D'=2090\text{m/s}$) appearing in upper right-hand part of the figure. $D'$ can be either greater or smaller than $D$. Figure 6(c) with $X=76\%$, $P_1=200\text{mmHg}$ shows an explosive soot-formation process near the main wave.
wave front, and it is seen from the figure that shock waves travel both upstream and downstream. Figure 6(d) represents the case where $X=84\%$, $P_1=500$ mmHg, $D=2160$ m/s, and shows that a large amount of soot is formed just behind the wave front with $D$ approaching the curve (8), the wave front appearing unstable and fluctuations in emission being observed.

Figure 7 illustrates the velocity fluctuation in detail in one case with $X=75\%$, $P_1=300$ mmHg. Figure 7(a) is a streak-camera record, and the propagation velocities at respective points are shown in Fig. 7(b). The highly luminous region seems to represent that of soot formation. It is seen from this figure that the detonation wave propagating at a speed of 2030 m/s (1) is accelerated to $D=2510$ m/s by the accompanying soot formation (i), decelerated then to $D=2010$ m/s (ii), and accelerated again to $D=2430$ m/s (v). The detonation velocity calculated on the assumption of soot formation is 1976 m/s, and the values (i) and (iii) are only slightly greater than this. The theoretical detonation velocity for the soot-formation case is 2350 m/s, and the values (i) and (v) exceed this. This latter situation can be attributed to an over-driven state of the detonation. The reverse transition from (ii) to (iii) seems to indicate that a certain mechanism, which prevents the soot formation from contributing to detonation propagation, is working.

5. Expansion region

5.1. Pressure change in the expansion region

Provided that the expansion waves behind the C-J plane of detonation wave constitute a centered simple wave system originating from the diaphragm position shown as in Fig. 2 and the gas undergoes an isentropic change in the expansion region, then along the characteristic curve:

$$\frac{dx}{dt} = u - a$$

Riemann's invariant:

$$Q = u - \frac{2}{\kappa - 1} a$$

becomes constant(8). The sound speed at the C-J plane can be calculated if the temperature is assumed to be equal to the value obtained in the propagation velocity calculation. From the Chapman-Jouguet condition:

$$u = D - a$$

the gas particle velocity $u$ at the C-J plane may be calculated and thus Riemann's invariant $Q$ is determined. If one specifies the slope of the characteristic curve through a point $(x,t)$ in the expansion region, the sound speed and gas particle velocity at this point are determined from Eq. (1) and (2) combined. One can also determine the temperature from the sound speed, thence the pressure by use of the isentropic relation. The specific heat ratio $\kappa$ and the gas constant $R$ are assumed to be constant throughout the expansion region, and equal to the value at the C-J plane. When the acetylene mole fraction is about 50% at which no soot formation is considered to occur, the measured pressure $P_m$ does not coincide with the theoretical pressure $P_{CJ}$, the former being about 85% of the latter. However, when the theoretical and measured pressures are normalized by their respective maximum values $P_{MAX}$, a fairly good agreement with each other is obtained as shown in Fig. 8.

\[ \text{Experimental} \quad \text{Theoretical} \]

Fig.8 Pressure profile in the expansion region. Acetylene mole fraction 50\%, initial pressure 500mmHg.
When soot is formed and the momentum and energy exchanges at finite rates between soot particle and gas are taken into account, two sound speeds, i.e., the equilibrium and frozen sound speeds, are defined at the C-J plane, which are expressed as follows:

$$a_f^2 = \frac{\kappa RT}{\gamma}, \quad \frac{a^2}{\gamma} = \frac{\gamma e}{1+(\gamma-1)\frac{\dot{m_s}}{\dot{m}_g}}$$

$$\kappa_e = \frac{1+(\gamma-1)\frac{\dot{m}_g}{\dot{m}_s}}{1+(\gamma-1)\frac{\dot{m}_g}{\dot{m}_s}}$$

where $\dot{m}_s$ is mass-flow rate of solid particles and $\dot{m}_g$ is that of gas.

Two kinds of theoretical pressure waveforms in the expansion region are obtained according as one adopts $a_e$ or $a_f$ as the sound speed at the C-J plane.

Figure 9 shows a typical pressure change for $X=70\%$ and $P_J=500$ mmHg. Three sets of theoretical curves, namely (1) adopting $a_f$ as the sound speed at the C-J plane and assuming soot formation, (2) adopting $a_e$ and assuming soot formation, (3) assuming no soot formation are shown in Fig. 9. The lower and upper solid lines in this figure represent the measured pressure changes at points 2.84 m and 3.33 m from the ignition source respectively. A pressure bump is seen at about 240 μsec after the main shock front in the upper curve, and this second wave is considered to be the pressure wave due to soot formation observed in the streak camera record.

At $X=50\%$, measured peak pressure does not coincide with the theoretical value at the C-J plane ($P_{CJ}$), and $P_m$ is about 85% of $P_{CJ}$. At $X=70\%$ on the other hand, $P_m$ is greater than the calculated value of $P_{CJ}$ with no soot formation, and is almost equal to that with soot formation. This is probably caused by the presence of the compression wave formed by the soot formation behind the detonation wave. The steep expansion closely behind the wave front supports this explanation.

5.2. Gas velocity in the expansion wave region

The gas velocity change in the expansion region can be calculated in the same way as the pressure change. Again, two kinds of gas velocity profiles can be obtained according as one adopts $a_e$ or $a_f$ as the sound speed at the C-J plane when soot formation is assumed. For the detonation velocity, the measured value was used.

Figure 10 shows the measured soot particle velocity (open circles) obtained from the streak records, together with the theoretical gas velocity. The experimental conditions are $X=69\%$, $P_J=500$ mmHg for Fig. 10(a), $X=73\%$, $P_J=400$ mmHg for Fig. 10(b), $X=75\%$, $P_J=500$ mmHg for Fig. 10(c). In Fig. 10(a), the measured detonation velocity is 2250 m/s, while the theoretical C-J detonation velocity is 2200 m/s with no soot formation and 2450 m/s with soot formation. Thus the nature of the detonation wave is considered to be close to that with no soot formation. It is seen that the measured soot particle velocity is 150 m/s less than the theoretical value with no soot formation. Figure 10(b) represents the case where the measured detonation velocity is 1990 m/s, initial pressure 500 mmHg.

![Fig.9 Pressure profiles in the expansion region. Acetylene mole fraction 70%, initial pressure 500 mmHg.](image)

![Fig.10 Particle velocity in the expansion region.](image)
and the theoretical values without and with soot formation are 2050 m/s and 2390 m/s, respectively. In this figure an abrupt increase in soot particle velocity is observed at a point about 85 µsec behind the detonation wave, and this corresponds to the pressure increase observed in Fig. 9. Figure 10(c) shows the case where the measured detonation velocity is 2090 m/s, and the theoretical values are 1960 m/s and 2350 m/s, respectively. The measurement of detonation velocity suggests that soot is formed in the reaction zone, but does not reach its equilibrium concentration. Since theoretical curves (1) and (2) are based on the assumption that soot is formed to its equilibrium concentration, the temperature at the C-J plane is overestimated in relation to the actual temperature, and in calculating the curve (2) the amount of soot formed is also overestimated. Thus, it is not clear whether $\omega_{f}$ or $\omega_{s}$ is attained at the C-J plane.

6. Effect of benzene

As shown in Sections 4 and 5, a double wave structure, composed of oxidation-supported wave and the second wave sustained by soot formation, is observed and a fluctuation appears in propagation velocity in fuel-rich acetylene detonations. The double wave structure seems to be attributed to the delay of nucleus formation in the soot formation process. To study the effect of the delay in soot formation and to clarify whether or not the soot formation is completed in the reaction zone, measurements were made of the detonation waves in acetylene-methane mixtures in which benzene was added. The effects of additives on hydrocarbon diffusion flame were studied by Tesmer et al. (10), who reported that the number of soot particle increased drastically when small amounts of aromatic hydrocarbon were added. In the present experiment, the amount of benzene added was about 0.5 mole% so that the thermal effect of benzene was very small.

The method of adding benzene is as follows. Benzene is introduced into a glass container and the inlet valve made of teflon is shut. Then the mixing tank and the piping between the needle valve and the mixing tank is evacuated. Subsequently, the needle valve is controlled to introduce the vapor of benzene into the mixing tank.

Figure 11 shows the streak-camera records. Figure 11 represents a case where $X=75\%$, $P_{1}=300\text{mmHg}$. Figure 11(a) and Fig. 11(b) are records without and with benzene, respectively. Whereas in Fig. 11(a) a double wave structure and a fluctuation in propagation velocity are observed, these phenomena disappear in Fig. 11(b) and in consequence the propagation velocity becomes constant and reproducible within good accuracy in the test section. This trend prevails in the entire range of experimental parameters, and it is indicated that the addition of small amounts of benzene shortens the delay of nuclei formation considerably.

Figure 12 shows the effect of benzene addition on the detonation velocity for $P_{1}=500\text{mmHg}$. The open circles denote the measured velocities without benzene and the broken line shows the same with benzene. Whereas without benzene, the propagation velocity fluctuates and the transition (A) $\rightarrow$ (B) begins at about $X=73\%$,

![Fig.10](image1)

![Fig.11](image2)

![Fig.12](image3)
the transition begins at a lower acetylene mole fraction and more gradually with small amounts of benzene.

Figure 13 shows the results for various initial pressures. The solid line represents the mean propagation velocity obtained without benzene, and the open circles and other symbols show the same with benzene at respective initial pressures, the broken line connecting the values at P1=500mmHg. A discrepancy exists between the broken and the solid lines in the region X=60-76% at P1=500 mmHg, which may be attributed to the delay in nucleation. The discrepancy between the detonation velocities with and without benzene is not observed from X=76% upward, and the probable reason is that the induction times for soot formation and acetylene oxidation without benzene do not differ from those with benzene. The discrepancy between the solid and the broken lines at X=85% is attributed to the unsteady propagation of detonation.

As the heat of reaction per unit mole of mixture, one can adopt two-fold values, namely (A) taking into account the oxidation reaction alone and (B) taking into account both the oxidation reaction and the soot formation. Figure 14 shows these heats of reaction vs. acetylene mole fraction. The former were calculated based on the equilibrium concentration at the C-J plane obtained in the calculation of propagation velocity in Sec. 3.1. It is clear from the measurement of propagation velocity that all of the heat of condensation of soot does not contribute to the propagation of detonation.

To show to what extent the heat of soot formation contributes to the propagation of detonation, the ratio of D1-Dg (the difference between the measured propagation velocity D1 and the theoretical value taking into account the oxidation reaction alone) to Dg-Dp (the difference between the theoretical propagation velocity taking into account the oxidation reaction and soot formation and Dp) is plotted against X in Fig. 15. In this figure the solid line shows the case where benzene is not added and the broken line the case where benzene is added. It is seen that the nature of the propagation velocity changes drastically at X=75%, and even at X=85%, Dg is not attained. The difference between the solid and the broken lines below X=75% is attributed to the delay in nucleation, and the drastic change at X=75% may be explained by an increase in the degree of supersaturation of the thermal-cracking products.

Two explanations may be presented for the difference between D1 and Dg at X=85%, one being that in the calculation of Dg the heat of sublimation of graphite was used in place of the heat of sublimation of soot. The chemical structure and the composition of soot are not the same as those of graphite and the heat of sublimation of the former may differ from that of the latter. It may also be argued that the soot formation is not completed in the so-called reaction zone between the shock wave and the C-J plane.

7. Conclusions

The following features have been
made clear about the peculiar phenomena which occur in the fuel-rich region of oxy-acetylene detonations. (1) The propagation velocity exhibits a fluctuation in the region where acetylene mole fraction X is high (X ≥ 70%) and this is enhanced as X increases and as the initial pressure P₁ decreases. The mean value of the propagation velocity undergoes a transition from (A) to (B) and this transition is delayed by lowering the initial pressure. (2) A shock wave is formed behind the main detonation wave as an accumulation of compression waves generated by the soot formation. The propagation velocity of the second wave can be either greater or smaller than that of the main detonation wave. (3) The peak pressure in the detonation wave does not coincide with the theoretical prediction, and at X=50% the measured value is about 85% of the predicted value. When the pressure waveform is normalized by the peak pressure, however, it coincides with the theoretical curve, which is calculated under the assumption that the expansion waves form a centered simple-wave system and changes are isentropic. (4) The soot particle velocity was measured by the streak camera. The change of measured soot particle velocity is almost consistent with the prediction based on the same assumption as above. (5) By adding small amounts of benzene, the fluctuation in the detonation velocity is eliminated and the transition (A) → (B) is made to occur at lower acetylene mole fraction. This is attributed to the fact that the delay in nuclei formation is shortened by the presence of benzene.

References

(7) Hult, D. R., JANAF Thermochemical Tables, (1965), Dow Chemical.