

STUDIES ON THE EXPLOSIONS UNDER HIGH PRESSURES, II

The Explosions of Acetylene mixed with Oxygen or Air
and the Effects of Added Substances

BY RYO KIYAMA, JIRO OSUGI and HIROSHI TERANISHI

Introduction

With the development of acetylene chemistries, it is indispensable to prevent explosions of acetylene for handling it under high pressures. Owing to its endothermic nature and to its severe propagation when exploded, acetylene has been considered to be one of the most dangerous substances for handling, and therefore, many works have been reported in literature on the combustion or explosion of the mixtures of acetylene with oxygen or air.^{1,2)} These have been, however, measurements under atmospheric pressure, and the temperature of explosion limits reported have been distributed over 335~700°C because of the differences of initial pressures, temperatures, and compositions of the reaction gases, velocities of the gases flowing into the reaction vessels, the materials and width of the reaction vessels, and the ways of determining the explosion limits employed in these measurements. It is, therefore, difficult to determine the accurate limits of the explosions, and as a matter of course, it is impossible to surmise the condition of the explosion of acetylene under high pressures.

On the explosions of acetylene under high pressure, W. Reppe³⁾ has performed the experiments over wide range employing the fusions of metallic wires as the ignition plugs, and has given basic data for engineering procedures on the maximum pressures and temperatures and the propagating velocities when exploded, and on the prevention of the propagations. It is true that his works have attained the purpose for preventing the propagation of explosions, but are not satisfactory as the data for the occurrence of the explosion, because in his works sufficient conditions of ignition have locally given for acetylene.

In the previous paper,⁴⁾ the authors reported preliminarily on the explosion of acetylene and oxygen mixtures (owing to the mechanical stimulus caused) by the rapid

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- 1) W. Rimarski and M. Kanschak, *Acetylen in Wiss. und Ind.*, **31**, 24 (1928)
 - 2) V. Meyer and A. Münch, *Ber.*, **26**, 2430 (1893)
H. Le Chatelier, *Compt. rend.*, **121**, 1144 (1895)
H. B. Dixon and H. F. Coward, *J. Chem. Soc., London*, **95**, 514 (1939)
M. Taffanel and Le Floch, *Compt. rend.*, **157**, 469 (1913)
H. Fiesel, *Z. phys. Chem.*, **97**, 158 (1921)
 - 3) W. Reppe, *Chem.-Ing.-Technik*, **22**, 273 (1950)
J. W. Copenhaver and M. H. Bigelow, *Acetylene and Carbon Monoxide Chemistry*, p. 310 (1949)
 - 4) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, **23**, 43 (1953)

compression. In the present paper the authors will mention on the conditions of explosions of the acetylene mixed with oxygen or the air when rapidly heated by letting them flow into the reaction vessel heated at the experimental temperature, on the effects of added substances, and on preliminary experiments on the behavior of the mixtures at elevated temperatures.

Experimentals

Apparatus The layout of experimental apparatus is shown in Fig. 1. A is an oxygen or air bomb and B is a reservoir containing compressed acetylene (about 30 kg/cm²). The reservoir C for mixing the reaction gases is 5cm and 2cm in outer and inner diameter and 55cc in capacity. The reaction vessel D is made with mild steel, 4cm and 1cm in outer and inner diameters respectively, and 9.42cc in capacity. D is covered by electric heater and heated to a given temperature, and the temperatures are measured by means of two alumel-chromel thermocouples which are inserted into holes E in the wall of the reaction vessel. V₁~V₇ are high pressure valves of which V₆ and V₇ are connected to a vacuum pump and G is a Bourdon type pressure gauge which is used for measuring the initial pressure of reaction gases. The membrane pressure gauge F is constructed by a spring steel membrane and a mirror rotating by the deflection of the membrane.⁵⁾ The pressure changes are measured by the displacements of light spot on a scale which is about 1m distant from the mirror. The pressure sensitivities of the membranes of 0.8, 1.0, and 1.5mm in thickness, which are employed in this experiment, are 2.0, 1.5, and 1.0cm in the displacement of the light spot per 1kg/cm² respectively. K is a safety-wall.

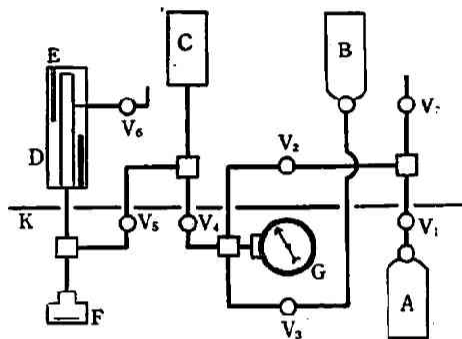


Fig. 1 The layout of experimental apparatus

Materials Acetylene gas is prepared with calcium carbide and is purified through refining reagents. The purity of acetylene gas used is 99.4~99.6%. Commercial compressed oxygen is used, and carbon tetrachloride used is the distillate at 76.8~77.0°C.

Experimental Procedures Every part of the apparatus is evacuated by means of a vacuum pump. Then the vessel C is filled with oxygen or air at a given pressure from A through valves V₁, V₂ and V₄, and acetylene is poured into C from B through valves V₃ and V₄ and mixed at a given total pressure and V₄ is shut. The high pressure gases, being under such conditions as those of the present experiment, require more than 10 minutes for the mixing. In the experiment measuring the behaviors

5) R. Kiyama, J. Osugi and H. Teranishi, *This Journal*, 24, 81 (1954)

of the mixtures where the temperature is elevated slowly (Exp. 1), the gas mixtures are poured through valve V_5 into the reaction vessel D, and the pressure changes when the temperature is elevated at the rate of 1°C per minute are measured by means of the membrane pressure gauge F at every 10 minute. In the experiments measuring the limits of the explosion (Exp. 2~4), the gas mixtures are poured by rapid opening of valve V_5 into D which is previously heated to a given temperature. In the preliminary test, it has been confirmed by the observation of light spot that by quick opening of valve V_5 the gas contained in the vessel C at a pressure of $12\text{kg}/\text{cm}^2$ has been poured into the reaction vessel D to a final pressure of $10\text{kg}/\text{cm}^2$ within about 1 second. When the explosions of acetylene-oxygen mixtures take place, their occurrences, of course, accurately perceived by their sounds, are observed by the very rapid and discontinuous displacements of the light spot, and furthermore are confirmed by the carbon produced. By these manner the explosion limits of acetylene-oxygen mixtures are determined. On the other hand, the explosions of acetylene-air mixtures under such conditions as those of the present experiments, are very weak,¹⁾ and it is impossible to be perceived neither by their sounds nor by the displacements of the light spot. In the latter cases, a wire resistance strain gauge* is cemented on the membrane of the pressure gauge F, and the changes of electric resistance of the strain gauge due to the pressure changes are amplified and recorded with time by an electromagnetic oscillograph. The recorded correction curves are linear to the pressure changes.⁵⁾ The explosions are confirmed by the discontinuities of the pressure change curves recorded on the oscillographic papers.

Experimental Results and Considerations

1. The behaviors of the acetylene mixtures with the temperature elevated slowly As preliminary tests for determining the explosion limits of the mixtures of acetylene and oxygen or the air, the behaviors of the acetylene mixtures with temperature elevated slowly are observed. The results of the measurements on the pressure changes of the mixtures with various compositions caused by the temperature elevation to 310° at the rate of 1°C per minute are shown in Fig. 2. In Fig. 2, the initial total pressures of the mixtures are $7.8\sim 8.2\text{ kg}/\text{cm}^2$ at 100° or 200°C , and curve a shows the pressure changes for the air only, and may be regarded as the standard line where no reaction takes place. Comparing with curve a, every curve for the mixtures of acetylene and oxygen (curves b~h) shows that some reaction with the decrease of total moles of the mixtures should take place at the temperatures of $160\sim 180^\circ\text{C}$ and above, and that the deviation from striking the standard line becomes evident as the C_2H_2 content becomes richer and more striking at the ratio where the partial pressure ($\text{C}_2\text{H}_2/\text{O}_2$) is between 4 and 7 (curves e and f). That is, as the abscissa of

* Type S_{24} ($4\times 4\text{ mm}$, 120 Ω , G. F. 1.82) made by Shinkoh Communication Ind. Co. Ltd.

Fig. 2 may be regarded as the time axis, it is recognized that the rate of such reaction may be rapid in these compositions. In the cases where the contents of acetylene become more richer (curves g and h), however, such tendency becomes more indistinct and the forms of the curves become similar to that of pure C_2H_2 (curve i). It may be surmised that the knicks in curves e and f would be not due to the polymerization of C_2H_2 , but due to the reaction of C_2H_2 with O_2 which decreases the numbers of mole of the mixtures, probably forms peroxide, and that the rate of formation would be most rapid at the compositions

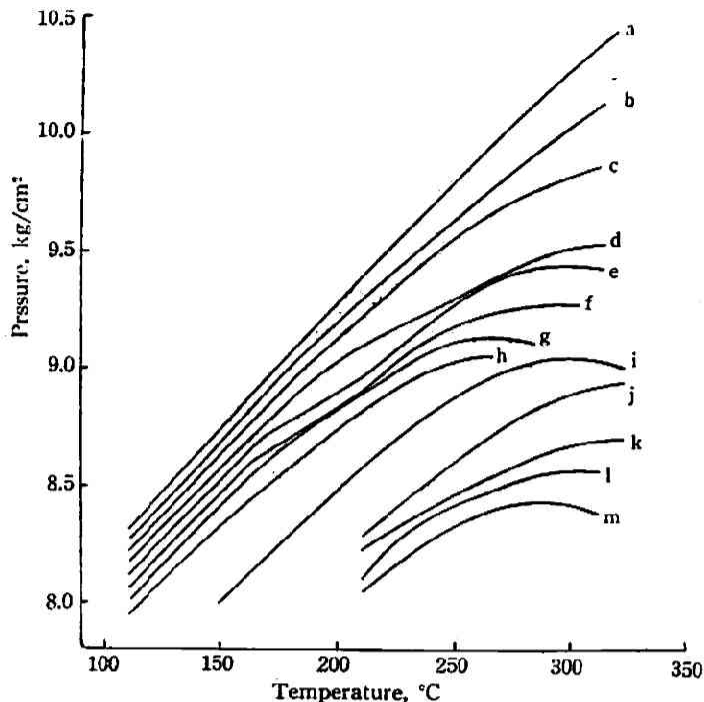


Fig. 2 The behaviors of the gases when heated at the rate of 1°C per minute

a : air	h : $C_2H_2 : O_2$ 13 : 1
b : $C_2H_2 : O_2$ 1 : 1	i : pure acetylene
c : " 2 : 1	j : $C_2H_2 : \text{air} = 1/5 : 1$
d : " 3 : 1	k : " 1 : 1
e : " 4 : 1	l : " 2 : 1
f : " 7 : 1	m : " 10 : 1
g : " 10 : 1	

$C_2H_2/O_2=4$ and 7. The inclination of the pressure-temperature (time) curves increase at about 210°C , as shown most evidently in curves e and f, and such a reaction as the decomposition of peroxide may take place. Acetylene and air mixtures show qualitatively similar behaviors, with the increase of C_2H_2 content (curves j~m), to those of the acetylene and oxygen mixtures. The decreases of the inclinations of the curves which are found at about 250°C and above are considered to be due to the polymerization of C_2H_2 . The inner wall of the reaction vessel after the reactions is covered with yellow or brown products which look like cuprene, and the deposits like carbon are not found.

In such experiments that the acetylene mixture is heated slowly to 310°C , neither explosion nor rapid pressure change does occur, but if the knicks of the curves shown in Fig. 2 are due to the formation of peroxide, those would have some relations to the explosion limits.

2. Explosion limits of the mixtures of acetylene and oxygen When the

mixtures of C_2H_2 and O_2 at definite compositions are rapidly poured (within about 1 second) into the reaction vessel which is previously heated at given temperatures, whether the explosion does occur or not is observed. By the rapid pouring the total pressure of the mixture decreases from 12 kg/cm^2 to 10 kg/cm^2 , and the results obtained are shown in Fig. 3. It is evident in Fig. 3 that the explosion limits can be determined clearly and become smooth line. The fact that the minimum temperature of the explosion limits lies in such composition that the partial pressure ratio C_2H_2/O_2 is between 4 and 7, and that the explosion temperatures corresponding to such partial pressure ratios are $220\sim 230^\circ\text{C}$, is relevant to the results of Exp. 1, that is, the knicks of the curves (curves e and f in Fig. 2) are most evident between such partial pressure ratios, and the formation of peroxide which initiates the explosion takes place at these temperatures, so it is probable that the explosion limits appear, by such rapid heating as these experiments, at $220\sim 230^\circ\text{C}$. In such a wide range of the compositions as 15~90% of C_2H_2 , the explosion limits lie between $220\sim 270^\circ\text{C}$. These temperatures are more than 100°C below those reported by Rimarski and Konschak.¹⁾ These facts would be due to the following reasons, that is, in Rimarski and Konschak's experiment, the gas mixtures were let flow at the rates of $12\sim 15\text{ cc/sec}$, through the reaction vessel of 230 cc in capacity at the pressures of slightly above 1 atm, while in this experiment, the mixtures of high pressure gas are poured into the reaction vessel of 9.42 cc at the rate of about 100 cc/sec , so the present experimental conditions are much severer than those of the former and would be sufficient for the initiation of explosion.

For each explosion in this experiment, it is impossible to determine quantitatively the initial pressure and the maximum pressure. On the whole, however, for O_2 rich mixtures, the sounds and propagating ranges of explosions are large but the amount of carbon produced is small, while for C_2H_2 rich mixtures the sounds and propagating range are relatively small, but a larger amount of carbon is produced. Both explosions under the conditions of $C_2H_2/O_2=1/1$, 260°C and $1/3$, 250°C (sign $\odot$ in Fig. 3) were especially violent, being propagated to the mixing reservoir C through the spiral pipe

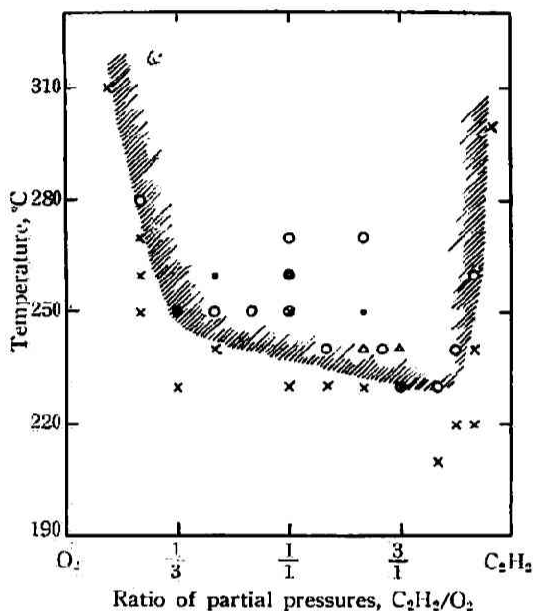


Fig. 3 The explosions of acetylene-oxygen mixtures

- : exploded
- ⊙ : exploded and propagated to reservoir C
- △ : exploded very weakly
- × : not exploded
- : not exploded with the rusty vessel

of 1 mm in inner diameter and 1 m in length, and caused 6 mm plastic deformation at its center of the spring steel membrane (dia. 44 mm and thickness 0.8 mm) of the pressure gauge F. Considering from the results, the maximum pressure of the explosions is to be about 1,200 kg/cm²,⁶⁾ and is of a similar order in violence to that reported in the previous paper.⁴⁾ On the other hand, the explosion under such conditions that $C_2H_2/O_2 = 3/1$, 240°C and 2/1, 240°C (sign Δ in Fig. 3), were very weak and could scarcely be perceived by the sounds.

In this experiment the pressure vessel and pipe lines were washed and the polymers and carbon produced were taken away after several runs, and, however, no effect was observed on the explosion limits, even if the pressure vessel containing carbon produced in the preceding explosion was employed. In cases where the vessel covered with rust was used, no explosion was observed even under the conditions clearly above the explosion limits (sign $\blacksquare$ in Fig. 3), and, however, the reversibility of the limits was obtained by using the vessel of fresh surface drilled. The explosion of acetylene is generally influenced by the materials, capacities and diameters of the vessels.³⁾ The conditions of the surfaces of the mild steel reaction vessel produce influence on the explosion limits in this experiment.

3. The effects of added substances on the explosion limits As the effect of added substance on the explosion limits of C_2H_2 and O_2 mixtures, the measurements have been done in cases where carbon tetrachloride and water added, and the results are shown in Figs. 4 and 5 respectively. About 10~15 cc of these substances are kept in the reservoir C and their vapors are mixed with the reaction gases. The partial pressures of CCl_4 and H_2O , under the present experimental conditions are 0.15 and 0.02 kg/cm² respectively. With the addition of CCl_4 , as shown in Fig. 4, the temperatures of explosion limits have been elevated more than 25°C at every composition of $C_2H_2-O_2$ mixture and the minimum of the limits, being found at the composition that $C_2H_2/O_2 = 4 \sim 7$ without added substance (Exp. 2), has disappeared. On the other hand, in cases of adding H_2O , though the vapor pressure of H_2O is one-seventh of that

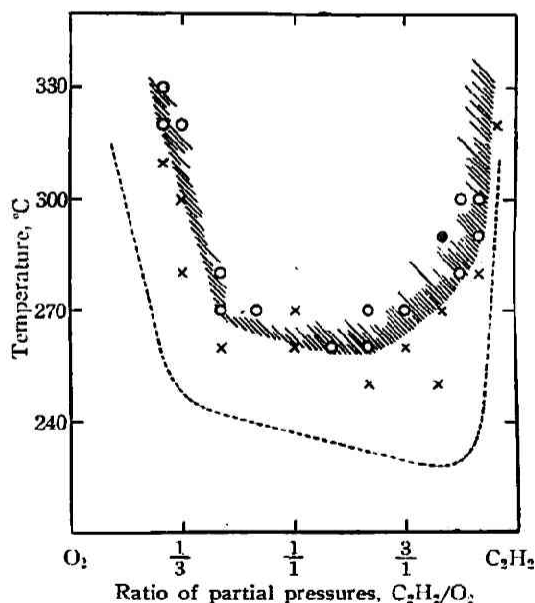


Fig. 4 The explosions of acetylene-oxygen mixtures when added CCl_4

$\circ$: exploded
 $\odot$: exploded and propagated to reservoir C
 $\times$: not exploded

6) A. Gleyzal, *J. App. Mech.*, 15, 288 (1948)

of CCl_4 , the temperatures of explosion limits, as shown in Fig. 5, have elevated still more about 15°C than that of the cases adding CCl_4 at the composition whose C_2H_2 contents are 33~66%.

Generally speaking, the temperatures of explosion limits are elevated by adding these substances, but the violence of explosion seems to become severer when exploded. In the cases signed as $\odot$ in Fig. 4, the explosions propagated to the reservoir C, and CCl_4 in reservoir C was decomposed, and stimulating gases and cohesive polymer were produced. In the case of adding H_2O , the explosions were still more severer, and all of them propagated to reservoir C. Hence these added substances are considered to have some effects upon the initiation of explosion reactions, and H_2O , at the high temperatures, seems to accelerate the propagations.

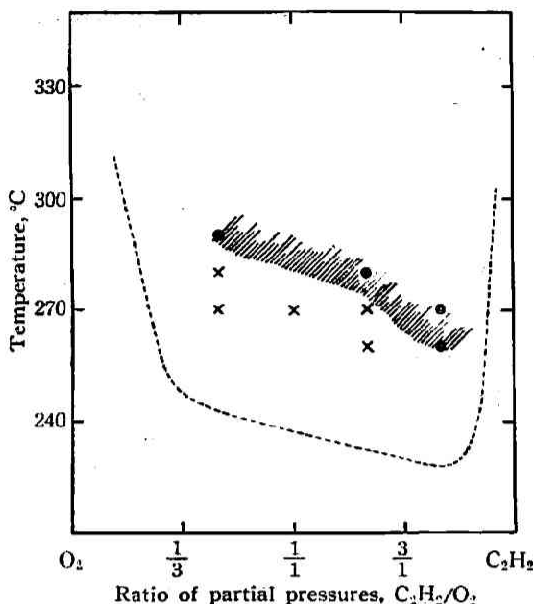


Fig. 5 The explosions of acetylene-oxygen mixtures when added H_2O

$\odot$: exploded and propagated to reservoir C
 $\times$: not exploded

4. The explosion limits of acetylene and air mixtures The results of the measurements on the explosion of acetylene-air mixtures are shown in Fig. 6. As shown in Fig. 6, the temperatures of explosion limits are about 150°C higher than those of O_2 - C_2H_2 mixtures, and are in much the same degree as those of Rimarski and Konschak's measurements at atmospheric pressure (sign $\blacksquare$ in Fig. 6). The temperatures of explosion limits have not distinctively influenced by the change of the initial pressures, i. e. 2.8, 5.6 and 11.5 kg/cm^2 (flowing velocities are 80, 160 and 300 cc/sec respectively), and hence the pressure effects on the explosion limits have not been observed in the range of these experiments.

As the explosions of acetylene-air

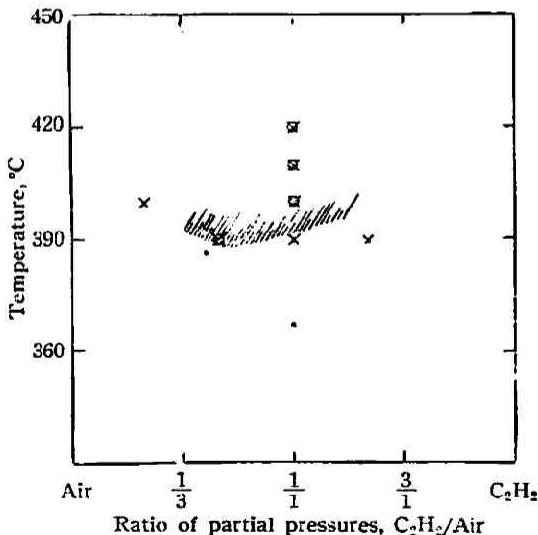


Fig. 6 The explosions of acetylene-air mixtures

$\circ$: exploded
 $\times$: not exploded
 $\blacksquare$: exploded in Rimarski and Konschak's measurements

mixtures were very weak, it was impossible to perceive the occurrence of the explosion by the sound, and, therefore, the explosion limits were determined from the discontinuity of pressure change curves on the oscillographic papers which were recorded by means of a wire resistance strain meter and an electromagnetic oscillograph. The maximum pressure of the explosion, for example, has been 13kg/cm^2 and the magnitude of pressure change due to explosion is of the same order as those reported by Rimarski and Konschak. From the oscillographic records, it has been observed that, in some cases, as shown by r and s in Fig. 7, small explosions within $1/50\text{sec}$ have taken places a few times repeatedly, and considering from the results, the explosions are initiated heterogeneously at the surfaces of the reaction vessel.

As mentioned previously, it is much more difficult to determine the explosion limits of acetylene-air mixtures than acetylene-oxygen mixture,⁷⁾ and the explosion limits of the former mixtures have not yet been determined clearly by the present experiment. This may be considered to be due to the fact that the explosion is greatly influenced both on its initiation and propagation, the former by the conditions of the surfaces of the vessel, and the latter by nitrogen in gas phase.

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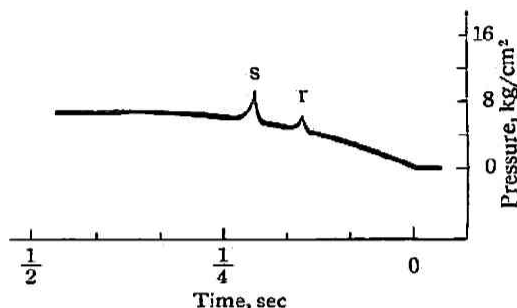


Fig. 7 The pressure-time curve in explosions of C_2H_2 -air mixture

*The Laboratory of Physical Chemistry,
Kyoto University*

7) H. Holm, *Z. angew. Chem.*, **26**, 273 (1913); A. G. White and T. W. Price, *J. Chem. Soc., London*, 115, 1462 (1919)