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STUDIES ON THE EXPLOSIONS UNDER HIGH PRESSURES, I

The Preliminary Experiments on the Compressions of Acetylene and Its Mixtures with Other Gases

By RYO KIVAMA, JIRO OSUGI and HIROSHI TERANISHI

Introduction

With the progresses of chemical industries, many chemical processes are carried out under high pressures. Thus it is indispensable for preventing disasters to research the explosion phenomena under high pressures.

In the present work the authors will mention preliminarily on the experiments on the compressions of acetylene and its mixtures with other gases which have been done in taking into consideration the progresses of the chemical reactions of acetylene under high pressures.

On the explosion of acetylene many works have been reported in literature, and owing to its endothermic nature, acetylene has been considered to be one of the most dangerous substances. W. Reppe¹⁾ has performed the experiments on the explosion phenomena of acetylene over wide range and developed the engineering procedures of handling acetylene. In his works, however, the fusions of metallic wires have been employed for the ignitions of explosions, so his works would be taken for the studies on the conditions of preventing propagation by supplying the sufficient ignition in the explosion process which may be considered to consist of ignition, propagation and termination, in other words, the studies on determining the surely safe regions.

In the practical cases, however, there would be various causes for ignitions of explosions and so the studies in which only one method of ignitions was employed would not be sufficient for elucidating the essential nature of explosion.

In the present work, the authors have studied the behaviours of acetylene and its mixtures with air or oxygen which is caused by compression, in connection with the problem of the compression of acetylene and that of decomposition or autoxidation of acetylene by compression.

Experimentals

Apparatus The layout of experimental apparatus is shown in Fig. 1. The differential manometer based on electric capacity change (A) consists of an electric condensor which has a movable membrane as one electrode plate, an oscillator, and an amplifier.

1) J. W. Copenhaver and M. H. Bigelow, *Acetylene and Carbon Monoxide Chemistry*, p. 310 (1949); W. Reppe, *Chem.-Ing.-Technik*, 22, 273 (1950)

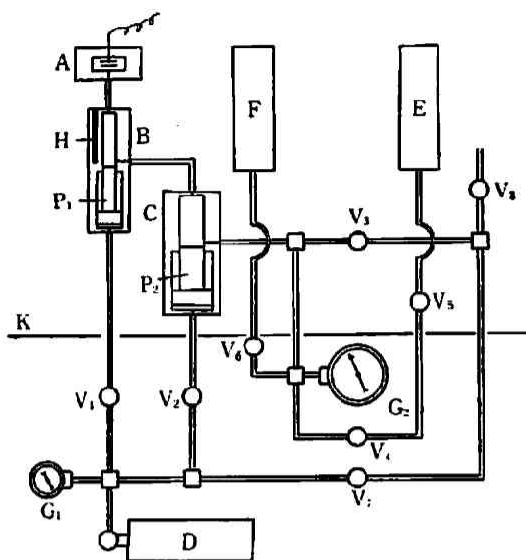


Fig. 1 The layout of experimental apparatus

The out-put power of the amplifier changes according to the capacity change of the electric condenser which are caused by pressure change, and are recorded with time by means of an electromagnetic oscillograph. The oscillator and amplifier can be used for any pressure by employing the proper movable membrane²⁾. The reaction vessels (B) used are made with mild steel and are 5 mm (vessel I) and 10 mm (vessel II) in inner diameters at each piston head (P_1) respectively. The vessel (B) is heated electrically from its outside to a given temperature and the temperatures are read by means of alumel-chromel thermocouple which is inserted into a hole (H) in the wall of the vessel. The diameters of the piston (P_2) in the intensifier (C) are 20 and 40mm in front and rear parts respectively, and the reaction gases, when required, are intensified by means of the piston which is driven by compressed air in a bomb (D). Acetylene reservoir (E) is filled with compressed acetylene (about 30 Kg/cm²) which is used for the reaction. The safety-wall (K) is made with steel plate which has 3 mm in thickness and 75 cm in height.

Materials Acetylene gas is prepared with calcium carbide and is purified through refining reagents. The purity of acetylene gas used is 99.5 ~ 99.6 %. Commercial compressed oxygen stocked in reservoir (F) is used.

Experimental procedures Every parts of the apparatus are evacuated by means of a vacuum pump, and then B, which is heated previously to a given temperature, is filled with the reaction gases at a given pressure from E through C. This pressure of the gases is read by means of a Bourdon type pressure gauge (G_2) and is also recorded by means of the differential manometer (A) whose pressure sensitivity is determined from the displacement of the light spot caused by the pressure.

For the mixing of oxygen or air with acetylene, the valves V_6 or V_3 and V_7 are opened and oxygen in F or air in D is mixed with acetylene in B respectively at desired pressures. High pressure gases, being under such conditions as those of the present experiment, require about 10 minutes for complete mixing, and in the preliminary test, however, it has been confirmed by chemical analysis that if, in the present experiment, the gas mixture in B has been compressed at 3 minutes or less after the mixing for convenience of the differential manometer (A), the deviation of composition of the gas

2) J. Osugi, *This Journal*, 21, 86 (1951)

mixture from that of complete mixing has been about 10%*. When, particularly, a specified composition is required, the component gases are preliminarily mixed at the desired composition in vessel F as used for the completely mixed gases. The gas sample which is filling vessel B is intensified, if necessary, by means of C, and then, when the valve V_1 is quickly opened, the gas is compressed by means of the piston driven, and the pressure change is recorded. For consideration of the result, air is compressed in B under the same conditions as those where the results is obtained, and from the comparison of both pressure change curves whether the chemical reaction of acetylene or its mixtures by the compression occurs or not is determined.

The time interval necessary for the compression by means of the piston driven by compressed air in bomb (D) is read from the pressure change curve. To make the compression fast, the method destroying a metallic membrane which has a proper thickness and has been set at the rear part of B is also taken. The time intervals necessary for the compression by means of the piston are also changed by the quickness of opening the valve V_1 . In the present experiment the time interval required for compression is in the range $1/5 \sim 1/10$ sec.

Experimental Results and Considerations

The typical form of the pressure-time curve is shown in Fig. 2. In the figure, a is

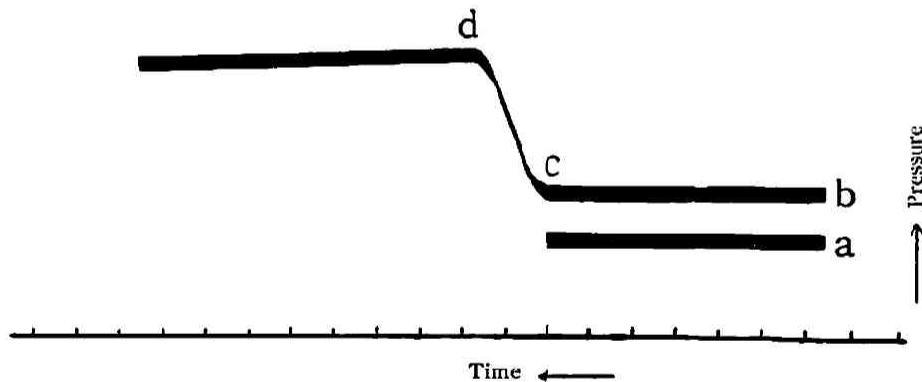


Fig. 2 Pressure-time curve

the standard line and b the compression curve. The compression starts at c and finishes at d and the time interval between c and d is the compression interval. The time axis recorded below is graduated at every $1/12$ sec.

The time interval for compression, the form of the pressure-time curve and so the maximum pressure attained depend on the driving of the piston and the change owing to the degree of the clearances of the piston and the cylinder. The higher the temperature, the more the degree of the friction between the piston and the cylinder and so the curve

* In the present procedure acetylene in B has been richer than its equilibrium composition.

becomes flatter and the compression interval becomes longer (referring to Table I). Therefore, in order to consider the form of the curve, it is necessary to compare the curve with that of air under the same condition. Of course even if the same initial pressure and the same driving pressure are used in both cases of acetylene and air, the maximum pressure attained in the compression of air is higher than that in acetylene because the latter is more compressible than the former, nevertheless so far as the forms of the curves by the moving of the piston are similar, it may be decided that no chemical reaction (explosion etc.) occurs.

Table I

Exp. No.	Temperature (°C)	Composition	Initial pressure (atm)	Maximum pressure (atm)	Compression interval (sec)	Reaction vessel	Remarks	
31	97.5	pure C ₂ H ₂	15.6	97.3	0.25	I	—	
34	84	C ₂ H ₂ air	50 % 50 %	16.5	155.5	0.1	I	—
35	84	C ₂ H ₂ air	64 % 36 %	41.4	118.1	0.12	I	—
36	84	C ₂ H ₂ air	50 % 50 %	34.7	118.1	0.1	I	—
38	26	pure C ₂ H ₂	14.9	120.5	0.2	I	—	
39	83	C ₂ H ₂ air	93 % 7 %	16.6	131.2	0.12	I	—
40	115	C ₂ H ₂ O ₂ N ₂	56 % 39 % 5 %	26.7	82.4	0.1	I	—
41	150	C ₂ H ₂ O ₂ N ₂	45 % 51 % 4 %	24.1	110.4	0.08	I	—
4	200	pure C ₂ H ₂	5.84	36.6	0.12	II	—	
5	200	C ₂ H ₂ air	50 % 50 %	4.48	38.3	0.12	II	—
6	200	C ₂ H ₂ air	37 % 63 %	10.7	43.1	0.14	II	—
7	250	pure C ₂ H ₂	3.13	66.2	0.25	II	—	
9	150	C ₂ H ₂ air	37 % 63 %	5.84	26.3	0.12	II	—
10	270	pure C ₂ H ₂	5.84	199.7	0.7	II	—	
11	270	C ₂ H ₂ air	25 % 75 %	20.0	67.2	0.5	II	—
13	270	C ₂ H ₂ air	50 % 50 %	5.84	53.8	0.6	II	—
14	270	C ₂ H ₂ O ₂	54 % 46 %	10.9	56.1*	0.7	II	+ **

The sign + in the remarks column shows the occurrence of explosion and the sign — shows no explosion.

* The value before the explosion.

** The reaction gases were left for 2 minutes before the compression, and during this time the initial pressure decreased to 10.4 atm.

The experimental results are shown in Table I. Considering the forms of the curves obtained, pure acetylene and its mixtures with air show no change by the compression at the temperatures up to 250°C.

The oxidation of acetylene is observed at about 200°C and higher³⁾, and the polymerization of pure acetylene is observed at about 250°C and higher⁴⁾.

As, in the present experiment, the reaction gases are quickly compressed, the temperature elevation due to the compressions must be taken into consideration. If the compression be adiabatic, the temperature elevation will be 1.4 ~ 1.6 times in absolute scale at the compression ratios 5 ~ 10 times respectively.

In some of the experiments, the reaction gases are poured into the reaction vessel being at high temperature and are compressed at 30 sec or so after pouring. In this method of compression it is evident that the gas mixtures of acetylene and oxygen are able to be compressed to several ten atm even at 270°C.** It is noticeable that the maximum pressure of pure acetylene compressed at 270°C attains abnormally high value.

Explosion Under the conditions listed at the last line in Table I (Exp. No. 14), the explosion was observed. In this experiment the gas mixture (54% C₂H₂, 46% O₂) was poured into the reaction vessel B (270°C) shown in Fig. 1 and was left for 2 minutes. On this occasion, the pressure shown by the pressure gauge G₂ decreased from 10.9 to 10.4 atm abs. Considering the capacities of B, C and the pipes, the pressure drop in B would be considerably much in amount and would be considered to be in connection with the explosion. The pressure change curve by the compression in this case are shown in Fig. 3, and at d the explosion occurred and the trace of the light spot disappeared owing to the destruction of the electric condenser.

On the observation of every part of the apparatus after the explosion, a small amount of carbon was observed between B-V₁-G₁, the more amount between C-V₂ and the especially large amount between C-G₂. It has been considered from the results that in B, having been at high temperature,

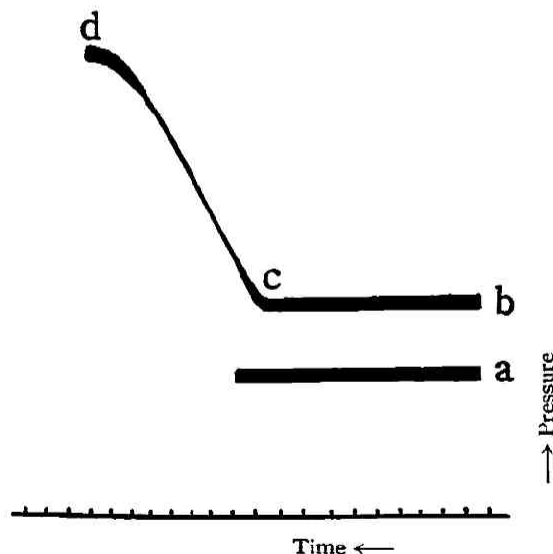


Fig. 3 Pressure-time curve

3) E. W. J. Mardles, *Trans. Farad. Soc.*, **27**, 718 (1931)

4) R. Kiyama and H. Kinoshita, *Unpublished*

** Referring to the report of W. Reppe¹⁾, pure acetylene can be compressed up to 60 ata at 18°C and to 50 ata at 97°C without any decomposition.

the combustion explosion would have principally occurred and, on the other hand, in C, having been at room temperature, the decomposition explosion would have taken place. Considering that the pipe connecting between B and C is 1 mm in inner diameter and carbon is observed at both the front and rear sides of the piston (P₂) in C, the propagation of the explosion would be considered to be due to the shock waves. Calculating from the observed value of plastic deformation of the reaction vessel B after the explosion⁵⁾, the internal pressure at the instance of the explosion is estimated to be about 4,500 atm, calculating from the plastic deformation of the piston P₂ in C, the pressure is about 3,500 atm, and also estimating from the plastic deformations of the movable membrane of the electric condenser in A⁶⁾, the pressure is found to be higher than 1,200 atm.***

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Kyoto University.*

5) A. Nadai, *Theory of Flow and Fracture of Solids*, P. 436 (1950)

6) A. Gleyzal, *J. App. Mech.*, 15, 288 (1948). The estimation does not include the factors due to bendings of the materials, so the calculated value will be much lower than the real one.

*** In these calculations, the factor of explosion time was neglected.

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