The Reaction of Hydrogen and Oxygen through a Silent Electric Discharge. III. The Ignition of the Hydrogen-Oxygen Gas by Silent Electric Discharge

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The ignition of a detonative gas mixture can be actuated by an electric spark with sufficient strength[1,2]. Usually there is a threshold value of the strength above which the initiation of the detonation is realizable. Very few investigations have, however, been reported on the silent electric discharge which is involved in the initiation of the detonation.

In the present paper, the problem of the initiation of the detonation of a hydrogen-oxygen mixture is dealt with mainly from the view-point of the electrical energy necessary to cause any detonation. The electrical energy is expressed as pulse current estimated from an oscillogram pattern.

Experimental

The oxygen and hydrogen gases taken from each cylinder were dried over calcium chloride and silica gel and then stored in the desired composition for several hours before use.

The electrical circuit system of the silent discharge and a brief diagram of the detonation bomb are shown in Fig. 1. The cylindrical bomb, made of mild steel, has an inside diameter of 6 cm. and a depth of 9 cm. A kind of safety diaphragm to prevent a dangerous pressure rise is attached to the bomb. A silent discharge electrode, composed of ordinary glass plates 5×6 cm. and 1 mm. thick, was mounted in the center of the bomb. The area of the electrode and the gap length are 7.5 cm^2 and 2 mm. respectively. The whole system is air-tight, and the measuring gas can be introduced through a tap just before each measurement. Direct current is supplied from a system of storage batteries of 120 V. and 250 amp. hr. As can be seen in Fig. 1, the voltage of direct current from the storage batteries was potentiometrically regulated and was supplied to the transformer via the throwing switch S. In the secondary coil of the transformer, an inductive high tension is induced according as the switch S is "on" or "off". In the present experiment, the shock current which is induced by the "on" position was used exclusively.

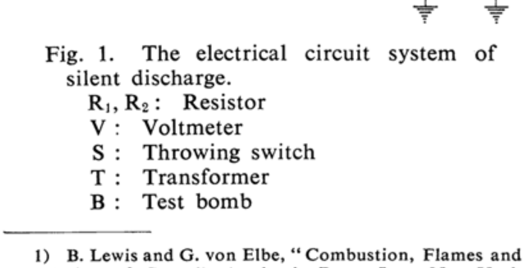

Fig. 1. The electrical circuit system of silent discharge.
R$_1$, R$_2$: Resistor
V : Voltmeter
S : Throwing switch
T : Transformer
B : Test bomb

The pulses of the silent electric discharge were observed by an oscilloscope synchronized with the switch S. The time constant of the C–R circuit for observing the pulse current was 5.2×10^{-6} sec.

Whether or not the gas is ignited can easily be detected by a distinct cracking noise of the safety bursting diaphragm, or by the sudden fall of the pressure gauge.

Several shots of the oscillographic pattern of the explosion just above the explosion limit of the primary voltage and of the non-explosion just under the limit were taken. In the experiments the scope of the primary voltage of the explosion and non-explosion patterns could be set within 2.5 V. or, in the worst case, within 5 V.

The composition of the gas mixture covers a range of 8.5∼75% oxygen. The ignition is actually observed in gas mixtures of more than 9.9% oxygen.

Results

An oscillographic pattern of the induced high tension which appeared in the secondary coil simultaneousely with the primary circuit being closed by switch S is shown in Fig. 2.

With applying the above high tension to the discharge electrode, a kind of one-shot silent discharge was obtained. Figure 3 shows the current diagram of a discharge in a hydrogen and oxygen gas mixture which did not provoke any ignition. The fringe-like figure indicates the pulse current during the silent electric

1) B. Lewis and G. von Elbe, "Combustion, Flames and Explosion of Gases", Academic Press, Inc., New York (1951), pp. 390—425.
2) M. V. Blanc, P. G. Guest, G. von Elbe and B. Lewis, "Third Symposium on Combustion and Flame and Explosion Phenomena", Williams and Wilkins Co., Baltimore (1949), p. 363.

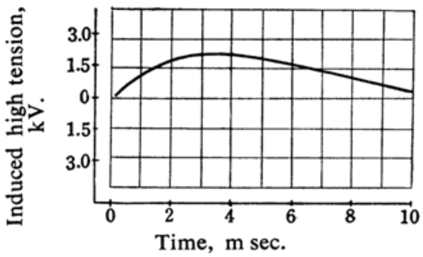

Fig. 2. Induced high tension in the secondary circuit. Dummy load 750 kΩ, primary voltage 60 V.

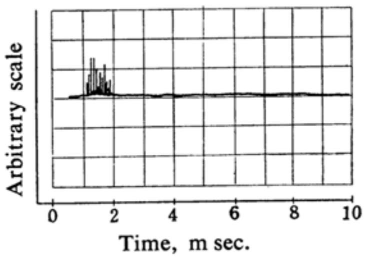

Fig. 3. Current diagram of silent electric discharge in hydrogen and oxygen gas mixture without provoking any ignition. O_2 content 33.5%; total pressure 298 mmHg; primary voltage 60V.

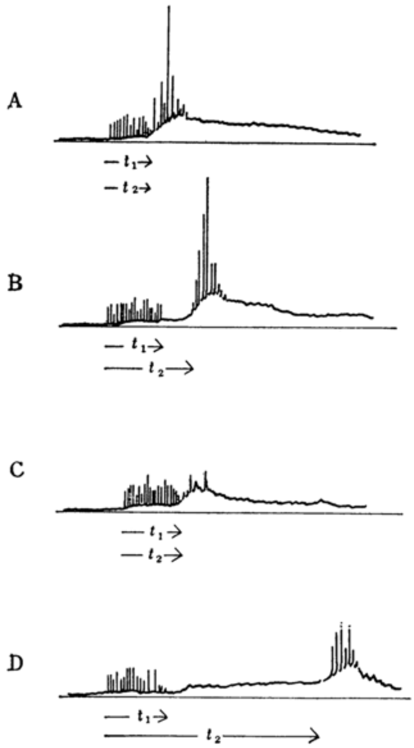

Fig. 4. Current diagram of silent electric discharge accompanied with the gas ignition.
A: O_2 content 23.5%, P=362 mmHg, t_1=1.04 m sec.
B: O_2 content 23.5%, P=226 mmHg, t_1=1.25 m sec.
C: O_2 content 15.0%, P=225 mmHg, t_1=1.33 m sec.
D: O_2 content 15.0%, P=189 mmHg, t_1=1.41 m sec.

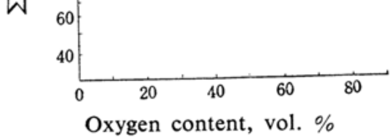

Fig. 5. Threshold value of $\sum h_i$ against oxygen content. P=200 mmHg.
○ $\sum h_i$ value obtained from ignition pattern just above the threshold condition.
◉ $\sum h_i$ value obtained from non-ignition pattern just under the threshold condition.

discharge[3-6], and the thick line shows the basic current in the secondary circuit.

In Fig. 4, some types of the oscillogram pattern accompanying the gas ignition are shown. In type A the discharge current flows for some time t_1, and then an ignition which is indicated by rather high and irregular pulse current comes in at the heel of the discharge current. In type B, there is some time delay t_2-t_1 from the quenching of the discharge current to the beginning of the ignition. Types C and D make their appearance when the condition is most contiguous to the threshold of the ignition and are very difficult to observe. The features are virtually the same as those of A and B.

In these patterns in Fig. 4, the base current or the low frequency discharge current in the gap space was appreciably elevated over the pattern of non-ignition in Fig. 3. These elevations on the current diagram could be ascribed to the ionization of the gases, which is accompanied with the inflamation or explosion of the gas[7].

3) M. Suzuki, *Proc. Japan Acad.*, **26**, 20 (1950).
4) M. Suzuki and Y. Naito, ibid., **28**, 469 (1952).
5) M. Suzuki, S. Okazaki and T. Yamamoto, *Am. Chem. Soc., Adv. Chem. Ser.*, **No. 26**, 331 (1957).
6) K. Honda and Y. Naito, *J. Phys. Soc. Japan*, **10**, 1007 (1955).
7) S. Basu and J. A. Fay, "7th Symposium on Combustion", Butterworth Sci. Publications, London (1959), p. 277.

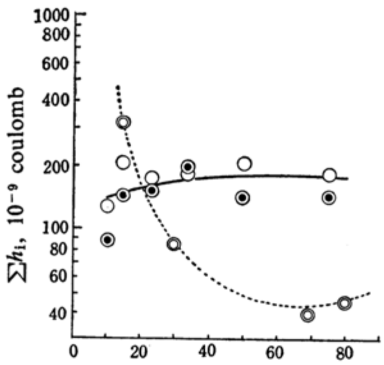

Fig. 6. Threshold value of $\sum hi$ against oxygen content. P=300 mmHg.
○ $\sum h_i$ value obtained from ignition pattern just above the threshold condition.
⦿ $\sum h_i$ value obtained from non-ignition pattern just under the threshold condition.
◎ modified result of Lewis and von Elbe in the condenser spark ignition.

In Figs. 5 and 6, the total pulse current carried through the electrode for a period of the time t_1 or $\sum h_i$, where the h_i is the height of a single pulse cuurrent appearing in an oscillogram pattern, was plotted versus the oxygen content of the detonating gas mixture. In these figures, the open circle represents the value of $\sum h_i$, obtained from the oscillographic pattern of discharge, which takes place just above the threshold primary voltage, and the dotted circle represents that of $\sum h_i$ from the pattern just under the threshold primary voltage. The real threshold condition will be in between the two plots, and a little increasing trend is observable. The double circle in Fig. 5 represents the modified result of Lewis and von Elbe in the condenser spark ignition of hydrogen and oxygen gas at 0.33 atm. The numerical value of coulomb is obtained from the C and V values cited in their data[1].

The quantities of electricity are independent of the composition of the detonating mixture, or, in other words, a fixed amount of electricity through a silent discharge is always required to initiate the ignition, no matter what the composition of the detonating gas is.

If the $\sum h_i$ is plotted against the pressure of the detonating gas mixture of a certain definite composition, then a series of straight lines is obtained (Fig. 7). The slope of the straight lines increases as the oxygen content is richer. The quantity of electricity, therefore, which is necessary to initiate a detonation in a gas mixture of a fixed pressure will be more as the oxygen content is richer.

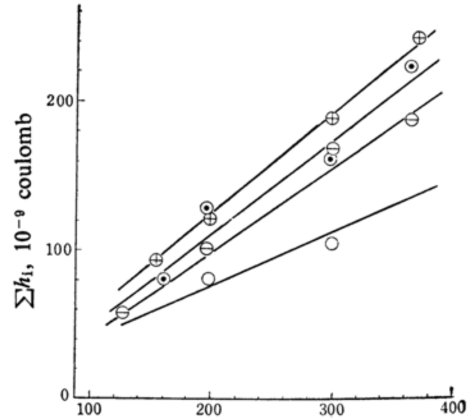

Fig. 7. The relation between $\sum h_i$ and the reactant gas pressure.
O_2 content; ○ 9.9% ⊖ 15.0% ⦿ 23.5% ⊕ 33.5%

Discussion

The fact that the quantity of electricity needed for the initiation of the ignition of a hydrogen and oxygen mixture under fixed pressure is independent of the composition of the gas mixture, implies that a certain amount of chemical entity is essential to initate the ignition. Furthermore, the amount of this chemical entity is constant for the gas composition range used in this measurement.

The chemical entity is tentatively presumed to be a OH radical, which may be concluded according to the chain branching mechanism learned from explosion limit studies[8,9];

$$H+O_2 \rightarrow OH+O \quad (1)$$

Even then, in some cases in our experiment a ignition delay was observed. The accumulation of the necessary concentration of this radical may then be achieved through any possible secondary decade which will proceed during the delay time.

The fixed amount of electricity provides, shall we say, at first a H radical of enough concentration by which reaction 1 will be initiated. The rate of secondary decades providing a OH radical sufficient for an ignition will be very rapid without an ignition delay, or otherwise, it may not be so rapid some delay time is required to attain the sufficient concentration. The alternatives will be decided by the strength of discharge current and/or by the composition of the gas mixture.

The quantity of electricity incresses linearly

8) R. R. Baldwin and A. D. Walsh, *Discussions Faraday Soc.*, **17**, 96 (1954).
9) D. R. Warren, *Proc. Roy. Soc.*, **A211**, 106 (1952).

with the pressure of the gas mixture, which indicates that the primary radical, or the H radical in this case, which is necessary to initiate the reaction 1 and then the ignition, increases in the gas mixture while keeping a linear relationship with the pressure of the gas mixture. The reaction pattern is very much like that of the ozone formation in silent electric discharge[10], where the O radical is produced by a collision process between an electron and an oxygen molecule. The same reasoning discussed there can be applied here, and the mechanism of this reaction pattern and the above relationship will then be understood without any further explanation. The study of the electric ignition of the detonative gas mixture greatly contributes to the exploration of the chain ignition mechanism, though further extensive study will be required to elucidate the actual features in more detail.

10) J. C. Devins, *J. Electrochem. Soc.*, **103**, 460 (1956).

Summary

The ignition of a hydrogen and oxygen gas mixture by a silent electric discharge was investigated.

The quantity of electricity which must be carried in the course of the discharge before a detonation will take place is almost independent of the composition of the gas mixture. Furthermore, for a gas mixture of fixed composition,the quantity of electricity increases along with the increasing pressure of detonative gas. A tentative view of the possible mechanism of the initiation of the detonation was briefly discussed.

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