The Ignition of Methane-Oxygen Mixture by Reflected Shock Wave

By Momotaro SUZUKI, Hajime MIYAMA, Shiro FUJIMOTO
and Tsuneo KASE

(Received June 26, 1961)

In a previous paper[1], measurements about the shock ignition of methane-oxygen mixture with a shock tube of 2.5 cm. internal diameter were reported. This time, measurements of the ignition of CH_4+2O_2 by reflected shock wave have been carried out with a shock tube which has a square cross section with an inside lateral of 5 cm. The tube is divided into three portions, a reservoir chamber 60 cm. in length, a buffer chamber 60 cm. in length and a test chamber 120 cm. in length. The buffer chamber was used to eliminate the effect of puncturing the membrane and was separated from a reservoir chamber by sheets of cellophane films and from a test chamber by a shutter. Details of the experimental procedure have been described elswhere[1-3]. The driver gas was air, the buffer gas a mixture of 88.8%

---

[1] M. Suzuki, H. Miyama and S. Fujimoto, This Bulletin, 31, 232 (1958).

[2] M. Suzuki, H. Miyama and S. Fujimoto, ibid., 31, 819 (1958).

[3] M. Steinberg and W. E. Kaskan, "Fifth Symposium on Combustion", The Williams and Wilkins Co., Baltimore (1953), p. 664.

methane and 11.2% nitrogen, and the test gas a mixture of CH_4+2O_2. It was confirmed, as a result of piezo-electric measurements that almost all of ignitions were caused by the reflected shock waves[2] only the case of ignitions by reflected shock wave will be considered here, however.

The minimum pressures of the reservoir chamber necessary for igniting the detonable gas of the definite initial pressure were measured. By using the results of these measurements, the temperature T_r and pressure P_r behind the reflected shock wave were calculated[4]. In this calculation, a constant value of heat capacity of detonable gas was assumed because the variation of heat capacity caused a temperature decrease of less than 4% under our experimental conditions. In Fig. 1, the explosion boundary is shown in terms of T_r and P_r. In the previous paper[1], it was shown that the shock ignition temperature is remarkably lower than the thermal ignition temperature. However, there was a mistake because the initial pressure of detonable gas was used instead of P_r. Corrected values from the previous data are shown in Fig. 1 for comparison. From this figure, it is obvious that the difference between the shock ignition and thermal temperatures[5,6] is not remarkable.

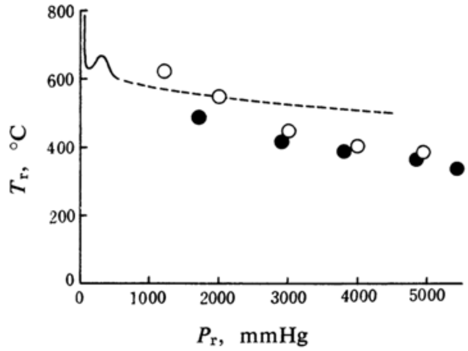

Fig. 1. Shock ignition limit expressed by T_r and P_r, where T_r and P_r are temperature and pressure behind reflected shock wave.
○ Shock ignition limit with a shock tube of 5 cm. inside lateral,
● Shock ignition limit with a shock tube of 2.5 cm. diameter[1],
—— Thermal ignition limit by Neumann and Serbinoff[5],
------ Thermal ignition limit by Sagulin[6]

Sagulin[6] found that there is the following relationship in the reaction between aliphatic hydrocarbon and oxygen:

$$\log(P/T)=A/T+B$$

in which P is pressure (cmHg), T, ignition temperature (°K), and A and B are constants. Yamazaki and Kato[7] also found that this relationship can be applied to the cases of the ignitions of a propane-oxygen mixture by incident shock waves with a shock tube 2.6 cm. in diameter. In the present case, this relationship can be also observed, as is shown in Fig. 2, where Sagulin and Yamazaki's data are shown for comparison. The slope of our line is very different from that of Sagulin's but similar to the slope of the initial part of Yamazaki's line III, although the position of our line is very far from that of line III. Although Yamazaki et al. used the initial pressure in their calculation, the pressure behind the incident shock wave should have been used. Therefore, we recalculated those values by using the pressure behind the incident shock wave and obtained line IV of Fig. 2. This corrected line is much closer to

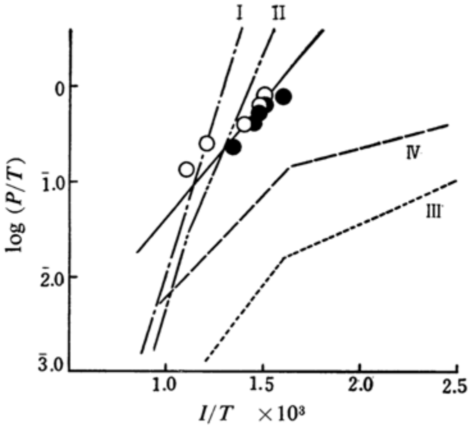

Fig. 2. Variation of log (P/T) with $1/T$ for the reaction of aliphatic hydrocarbon and oxygen.
○ Experimental values about CH_4+2O_2 with a shock tube of 5 cm. inside lateral,
● Experimental values about CH_4+2O_2 with a shock tube of 2.5 cm. diameter[1],
I Sagulin's data about CH_4+2O_2[6],
II Sagulin's data about $C_3H_8+5O_2$[6],
III Yamazaki's data about propane-oxygen[7],
IV Corrected Yamazaki's data about propane-oxygen

---

4) I. I. Glass, W. Martin and G. N. Patterson, "A Theoretical and Experimental Study of the Shock Tube", UTIA Report No. 2, Nov., 1953.

5) N. Semenoff, "Chemical Kinetics and Chain Reaction", Oxford at the Clarendon Press., London (1955), p. 308.

6) A. B. Sagulin, *Z. physik. Chem.*, **B1**, 275 (1928).

7) K. Yamazaki and Y. Kato, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 2124 (1960).

our line, and the slope of the initial part of this line is almost the same as that of our line about methane-oxygen. This result seems to confirm their conclusion that the mechanism of the breaking C–H bond is predominant at the lower pressure of a propane-oxygen mixture*.

Department of Chemistry
Defense Academy
Yokosuka

---

* Sagulin found that the above-described linear relationship for ethane, propane and pentane consists of two parts, one at the lower pressure (i. e., at the lower value of P/T) and another at the higher pressure (i. e., at the higher value of P/T). Although the slope of the line at the higher pressure is different for the different hydrocarbons, the slope at the lower pressure is the same for ethane, propane and pentane; it is also as same as the slope for methane. From this result, Sagulin (and also Yamazaki et al.) concluded that the mechanism of the breaking C-H bond is predominant at the lower pressure and that of the breaking C-C bond at the higher pressure. Details are described in Refs. 6 and 7.