*Studies on Explosion Reaction of Ethylene Mixed with Oxygen or Air. II. On the Explosion Peninsula**

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In a previous paper[1], it has been shown that the explosion boundaries of ethylene mixed with oxygen and with air was determined by the "admission method" i. e., by sudden introduction of the premixed gases into a heated and previously evacuated vessel. Also, it has been noticed that the explosion, like that of the other combustible gases[2,3], occurred in a certain region of the pressure, temperature and composition of mixed gases. In this case, there are the first (the lower), the second (the upper) and the third (the thermal) limit in the definite composition and temperature range. The explosion peninsula lies in the range bounded by the first and the second pressure limit of explosion within which pale blue ignitions occurred. On the other hand, the explosion occurred normally with a blue flame which rapidly built up into a bright flash filling the reaction vessel and accompanied by a pulse in pressure. Also, it was apparent that the induction period of the explosion, the color of flame and the propagation velocity of flame were different in the two cases described.

Now the experiment has been made between 550°C and 700°C for mainly 20% ethylene with oxygen in order to observe in detail explosion phenomena in the explosion peninsula and to compare this with normal thermal explosion. The effects of nitrogen and vessel diameter on the explosion limit were studied. They will be briefly discussed.

Experimental

Materials. — The ethylene employed in this experiment was prepared by the dehydration of absolute ethanol and purified by the method described in the previous paper. The oxygen employed was obtained from a commercial cylinder (purity: 99.4%). The oxygen and the air were employed after being purified through a train consisting of two bottles containing a concentrated aqueous solution of sodium hydroxide and concentrated sulfuric acid. Before use, the gases were dried with phosphorus pentoxide.

Apparatus and Procedure. — The apparatus used and the procedure adopted were of the types described in the previous paper. This consisted of an electrically heated reaction vessel into which a gas mixture could be admitted from a separate mixing vessel. Subsequent explosion of the mixture could be observed visually through a small window of mica in the dark room, and a blue filter of 1 mm. thickness whose transmission curve** is shown in Fig. 1 was used to eliminate the red glow of the furnace so that an ignition could be detected. Cylindrical reaction vessels of quartz 15 cm. long and 3 cm. in standard diameter, were used, but the diameter was varied to 4 cm., 2 cm. or 1 cm. as required. The apparatus was evacuated down to $10^{-4}\sim10^{-5}$ mmHg (tested by Gaisler tube) with rotary and "Hücksman's diffusion" pump.

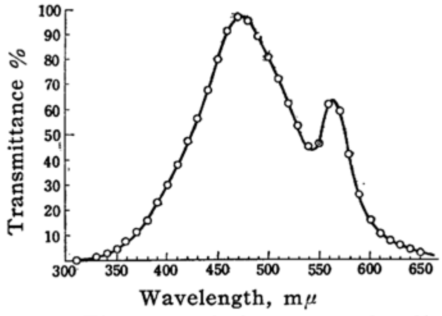

Fig. 1. The transmission curve of a filter.

Results and Consideration

The Explosion Limit.—Isochors for the explosion limits of 20% ethylene with oxygen and of 5% ethylene with air are shown respectively in Fig. 2 and Fig. 3. The evidence of an explosion was judged by observing the appearance of ignition, and usually the observation was continued for twenty minutes in the dark room.

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* A part of this investigation was reported at the Annual Meeting of the Chûgoku-Shikoku Branch of the Chemical Society of Japan in Niihama, October 19, 1956.

[1] M. Suga, This Bulletin, **31**, 515 (1958).

[2] B. Lewis and N. von Elbe, "Combustion, Flames and Explosions of Gases", Academic Press, New York (1951), p. 29.

[3] K. J. Laidler, "Chemical Kinetics", McGraw-Hill Book Co., Inc., New York (1950), p. 319.

** It was measured with a HITACHI Model EPB-U photo-electric spectrophotometer.

The results of observation were classified as follows:

(1) After the lapse of various induction periods (usually less than 10 sec.), luminous blue flames were observed.

(2) After the lapse of the relatively long induction periods (6 sec.∼20 min.), pale blue flames were observed in the dark room.

(3) No flame could be found even in the dark room.

Case 1, 2 and 3 are indicated respectively by ◎, ○ and × in Figs. 2 and 3. Also ⊕ in Fig. 2 indicates the case of the luminous flame propagating into the storage bulb owing to the shorter induction period than 0.8 sec. and the large propagation velocity of flames.

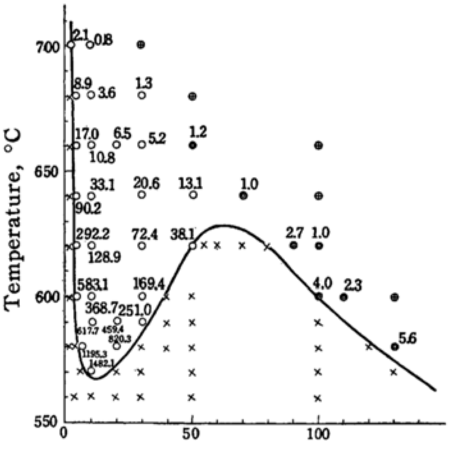

Fig. 2. Explosion limit of 20% ethylene with oxygen. (Induction periods in seconds are indicated by numbers beside observation points.)

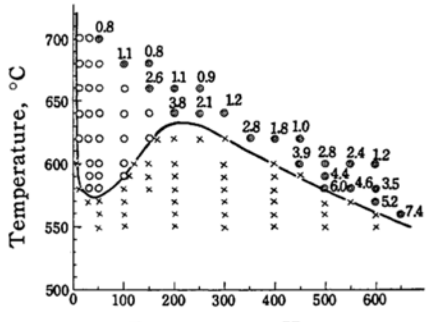

Fig. 3. Explosion limit of 5% ethylene with air. (Induction periods in seconds are indicated by numbers beside observation points and the results of longer induction period will be indicated in Fig. 6).

It is evident from the isochors that the first, the second and the third pressure limit of explosion exist in the explosion limit of ethylene-oxygen and -air mixtures. The first pressure limit of explosion does not seem to depend to a great extent on temperature, but the observation was more or less obscure because of the low admission pressure. The boundary of the first and the second pressure limit of explosion, i. e., the tip of the explosion peninsula, was determined from the results of observation for thirty minutes. The second pressure limit of explosion increases abruptly with increasing temperature, and, on the other hand, the third pressure limit of explosion decreases with increasing temperature.

Fig. 4 shows the isochors for the explosion limits of ethylene-oxygen mixtures. In this case, the explosion peninsula results in various shapes according to the composition of gas mixtures. That is to say, the composition of gas mixture affects the explosion limit considerably, and particularly it was noticed that the explosion peninsula disappears at over 25% ethylene with oxygen.

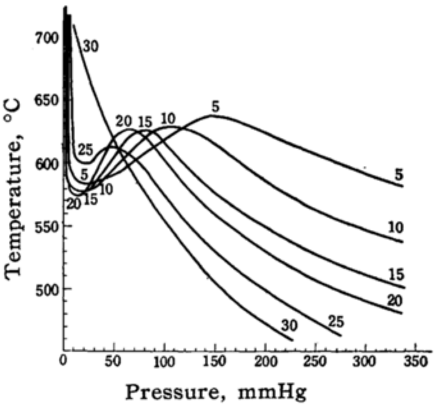

Fig. 4. Isochors for explosion limit of ethylene-oxygen mixtures. curve 5=5%, 10=10%, 15=15%, 20=20%, 30=30% ethylene.

The Effect of Nitrogen in the Air.—As shown in the previous paper, the third pressure limits of explosion for ethylene with oxygen and with air were equivalent to each other in spite of the differences of the propagation velocity of flame, the induction period, etc., so far as the partial pressure of nitrogen was neglected. Also, in order to elucidate the effect of nitrogen, an isochor for explosion limit of 20% ethylene with oxygen is shown and this is plotted with the corresponding points of the results for explosion limit of 5% ethylene with air, by calculation, subtracting the partial pressure of nitrogen.

This plot is shown by the broken line in Fig. 5. It is concluded that the first and the third pressure limit of explosion are slightly lower, and, the on other hand, the second pressure limit of explosion considerably lower, than the corresponding full line. In other words, nitrogen affects the second pressure limit of explosion, but does not affect the first and the third pressure limit of explosion.

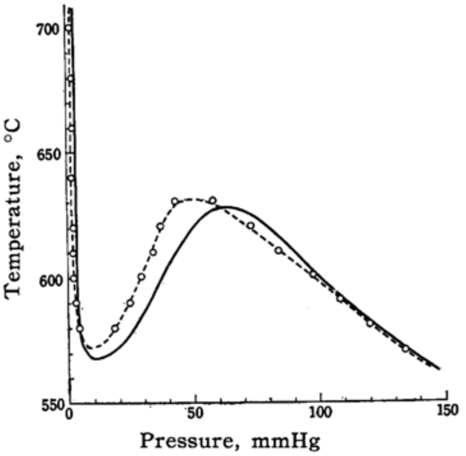

Fig. 5. Effect of nitrogen on isochor for explosion limit of 20% ethylene with oxygen. (Broken line represents the data calculated from the limit of 5% ethylene with air, Fig. 3.)

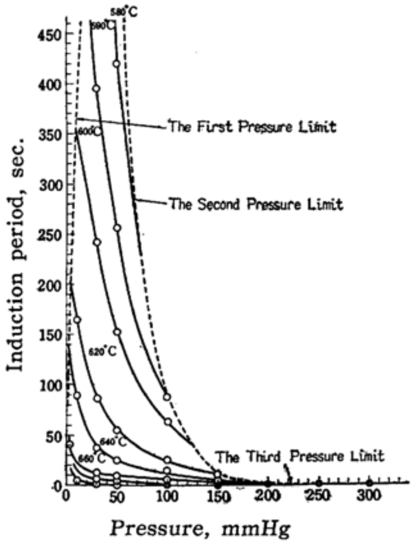

Fig. 6. Relationship between explosion limit pressure and induction period at definite temperatures for 5% ethylene with air.

The Explosion Limit and Induction Period. — The results of the experiment with regard to the induction period are shown by numbers beside the observation points in Figs. 2 and 3. The induction period was measured by a stopwatch. But in cases where the admission time required more than 0.6 sec., the induction period could not always be measured by a stopwatch with high accuracy. Fortunately, induction period is fairly long in the region

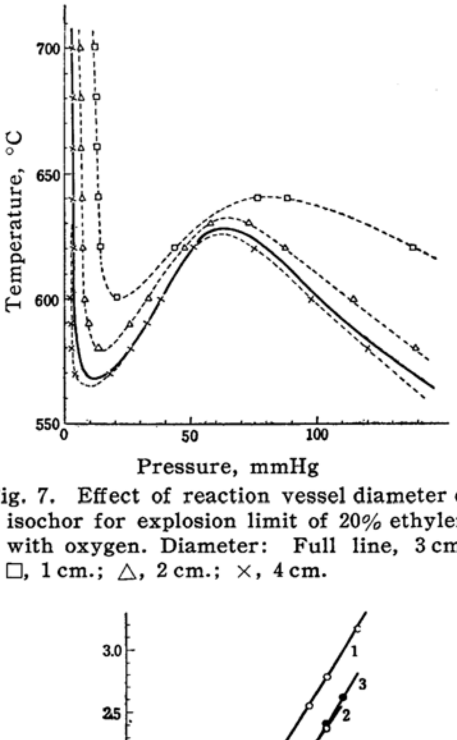

Fig. 7. Effect of reaction vessel diameter on isochor for explosion limit of 20% ethylene with oxygen. Diameter: Full line, 3 cm.; □, 1 cm.; △, 2 cm.; ×, 4 cm.

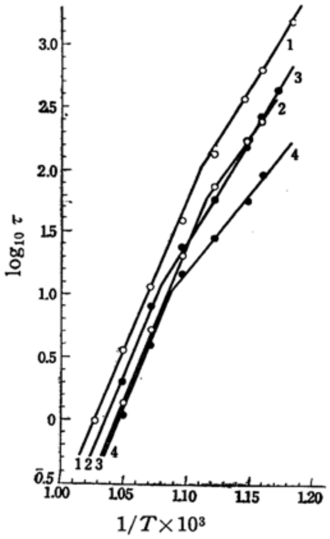

Fig. 8. $\text{Log}_{10}\,\tau$ against $1/T$ curves for the explosion of 20% ethylene with oxygen and 5% ethylene with air.
○; 20% C_2H_4 with O_2, curve 1=10, 2=30 mmHg admission pressure, ●; 5% C_2H_4 with air, curve 3=50, 4=10 mmHg admission pressure.

of the explosion peninsula and is reproducible so far as precautions are taken in accord with standard procedure[1]. Fig. 6 shows the relationship between explosion limit pressure and induction period at various different temperatures for 5% ethylene with air.

The Effect of Reaction Vessel.—For reaction vessels, quartz cylinders of 3 cm. in diameter and 15 cm. in length were usually employed. Quartz cylinders of 4, 2 and 1 cm. in diameter of the same length were also employed in order to compare the effects of the diameter of reaction vessels. The results are indicated in Fig. 7. The decrease of the vessel diameter increaed the first and the third pressure limit, and, on the other hand, lowered the second pressure limit of explosion; i. e., the decrease of the vessel diameter serves invariably to retard the explosion. It is noticed that the second pressure limit of explosion suffers the effect of the surface of the vessel only slightly, and in consequence, the explosion peninsula tends to disappear when the specific surface of the vessel is increased.

The Activation Energy of the Reaction.—In Fig. 8 is shown the relationship between the absolute temperature T and the induction period τ in relation to the results of Fig. 2 and Fig. 6. Every curve bends at the neighborhood of ca. 620°C, but is essentially linear and holds the relationship $\log_{10}\tau = A/T + B$. On the other hand, while this result has no direct relationship with the meaning of kinetics and the adaptability of the former's formula to the latter is questionable, nevertheless the gradient of these lines, A, is thought to be equal to $E/2.303\times\boldsymbol{R}$[4,5]. Thus, values for E, the apparent activation energy, may be as in Table I.

TABLE I. ACTIVATION ENERGIES ESTIMATED FROM THE INDUCTION PERIOD

Curve	A	$E=2.303\times1.987\times A$ (kcal./mol.)
1	15.03	68.77
	22.35	102.27
2	13.77	63.01
	24.30	111.97
3	15.27	69.88
	23.73	108.59
4	13.53	61.91
	23.73	108.59

Summary

In the previous paper, the explosion limit of ethylene mixed with oxygen and with air by the "admission method" was presented. It was pointed out that the explosion peninsula lies in the region between the first and the second pressure limit of explosion. The results of observation in this region differ from those in thermal explosion.

In the present experiment, the following results have been obtained.

(1) The explosion peninsulas of ethylene-oxygen and ethylene-air mixtures lie approximately in the range of the same temperature and pressure limits as that of carbon monoxide-oxygen mixture[6].

(2) If ethylene concentration exceeds ca. 25% ethylene with oxygen, the explosion peninsula disappears.

(3) The induction period of explosion in the explosion peninsula is relatively longer than those of other thermal explosions.

(4) In the explosion within the explosion peninsula, the apparent activation energy estimated in accordance with Semenoff's theory is of abnormally high value. Merely from these facts, it is difficult to determine the explosion mechanism of ethylene-oxygen mixture, but it is possible for one to assume that the explosion within the explosion peninsula has a different mechanism from other thermal explosions.

If one refers to the studies of Neumann and Serbinoff[7], Norrish and Food[8], and Lewis[2] on the explosion of methane-oxygen mixture, he will find that the explosion peninsula which is observed in the explosion limit of ethylene-oxygen or -air mixtures is not always related to the nature of ethylene itself. In other words, ethylene-oxygen mixture is decomposed into carbon monoxide first in the definite range of temperature and pressure. Furthermore, it is considered that carbon monoxide which is produced and accumulated in slow oxidation of ethylene, i. e., slow reaction, is ignited in the definite condition. Thus, if ethylene concentration is greater than the stoichiometric value crresponding to $C_2H_4+3O_2=2CO+2H_2O$, the oxygen which is required to oxidate this carbon monoxide is insufficient, and therefore the

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4) B. P. Mullins, "Spontaneous Ignition of Liquid Fuels", Butterworths Sci. Pub., London (1955).

5) N. Semenoff, *Z. Physik*, **48**, 57 (1928).

6) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, **50**. 37 (1954).

7) M. Neumann and A. Serbinoff, *Phys. Z. Sowjet*, **1**, 536 (1932).

8) R. G. W. Norrish and S. G. Food, *Proc. Roy. Soc.*, **A 157**, 503 (1936).

explosion peninsula disappears. The conclusion is a little too speculative, but it is considered that the explosion peninsula of ethylene-oxygen or -air mixtures originates in the oxidation of carbon monoxide which is accumulated in slow reaction.

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