Studies on Explosive Reaction of Ethylene Mixed with Oxygen or Air. I. Explosion Limit at Low Pressure

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The explosion and the combustion phenomenon of lower hydrocarbons have been studied extensively[1-3], but there are few investigations about ethylene. The explosion of gas has generally very complex mechanism, and various methods have been taken for the determination of the explosion limit[1,4]. The present author, considering conveniently that the spontaneous ignition was the explosion, investigated systematically on the phenomena of spontaneous ignition of ethylene-oxygen or -air mixture at lower pressures than atomospheric. The explosion limit was determinated by so-called "admission method", in which the gas mixture with a certain definite composition was admitted into the reaction vessel evacuated and heated at a definite temperature. The limit was not only decided by some parameters such as temperature, pressure or composition, but was affected considerably by the nature of the surface of the reaction vessel etc. Thus a standard procedure was adopted for convenience in order to determine the limit, and the effects were briefly discussed.

Experimental

Materials.—The ethylene employed in this experiment was prepared by the dehydration of absolute alcohol by the action of phosphoric acid and purified by the action of concentrated aqueous solution of sodium hydroxide, concentrated sulfuric acid, silica gel and phosphorus pentoxide. About 99% of the gas so treated was absorbed by fuming sulfuric acid. The oxygen employed was obtained from a commercial cylinder (purity: 99.4%). The oxygen and the air were used after being passed through a train consisting of two bottles containing a concentrated aqueous solution of sodium hydroxide, concentrated sulfuric acid and phosphorus pentoxide.

Apparatus and Procedure.—The diagram of the apparatus is shown in Fig. 1. The apparatus was partly screened with wire netting for the prevention of explosion. The inlet tube connecting the reaction vessel to the cock C_1 and the manometer M_1 was used as capillary to decrease dead space, also to prevent danger. The explosion limit was determined by the following procedures:

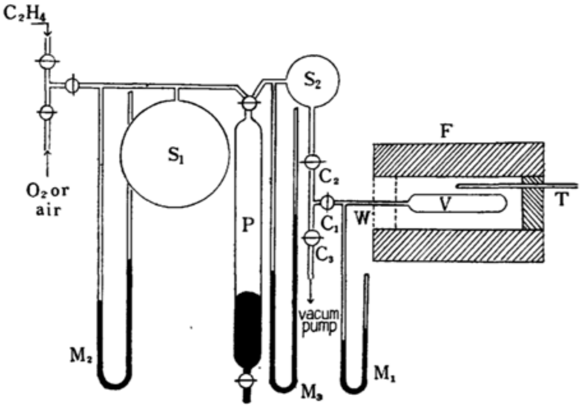

Fig. 1. The apparatus of admission method for determining the explosion limit.

S_1, S_2: Gas storages.
C_1, C_2, C_3: Stop cocks.
M_1, M_2, M_3: Mercury manometers.
P: Toepler pump.
V: Reaction vessel.
F: Electric farnace.
T: Thermocouple.
W: Window.

(1) The gas mixture of the desired composition for the test was prepared in storage S_1 (1 l.), the partial pressures of gases being measured by the manometer M_2, and stored for more than twelve hours in order to be thoroughly mixed.

(2) Then, a part of sample gas in storage S_1 was removed into storage S_2 (ca. 200 cc.) at any desired pressure by the aid of Toepler pump P.

(3) The reaction vessel V (usually 3 cm. diameter and 10 cm. length in order to examine the effect of diameter on the limit, 2 cm. or 1 cm. diameter and equal length) which consisted of a quartz cylinder was placed in a horizontal electric furnace F. The highest temperature in furnace F was measured by an alumel-chromel thermocouple T inserted into furnace F. On this occasion, the reaction vessel was maintained at a definite temperature and

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

[2] M. Prettre, "Third Symposium on Combustion, Flame and Explosion Phenomena", The Williams and Wilkins Co., Baltimore, (1949), p. 397.

[3] K. Spence and D.T.A. Townend, ibid., p. 404.

[4] F. S. Dainton, "Chain Reaction", Methuen Co., London, (1956) p. 23.

thoroughly evacuated (10^{-3} mmHg) in thirty minutes.

(4) The sample gas in storage S_2 was rapidly admitted to pre-evacuated reaction vessel V to give some previously decided initial pressure by operating cocks C_1 and C_2.

(5) The determination of the occurence of explosion or otherwise was made directly by sight through the window W made of mica on one side of the furnace and subsidiarily by the pressure change with the aid of mercury manometer M_1 for thirty minutes.

The induction period, which is the time-lag from the moment of admission of the sample gas to the occurrence of the explosion, was measured by the aid of a stopwatch. Isochors (pressure-temperature diagram) of the explosion limit were determined by the repetition of these procedures 2—5, at the temperature range between 300 and 700°C, and at the pressure range lower than atomospheric pressure for various compositions. Then, these were used to derive isotherms and isobars.

Results and Consideration

Observation.—The results of observation are classified as the following.

(1) After the lapse of various induction periods (usually less than 30 sec.) luminous flames were normally preceded by a glow which rapidly built up into a bright flash filling the vessel and accompanied by a vigorous pulse and sound.

(2) After the lapse of the relatively long induction periods, pale blue flames were observed in the dark room with a mild pressure pulse which was measured with much difficulty by mercury manometer M_1.

(3) After a considerable time interval (the so-called induction period of slow reaction), the pressure gradually rose, and the maximum pressure was maintained for an appreciable period before slowly falling off. But ignition flames were not able to be found even in the dark room.

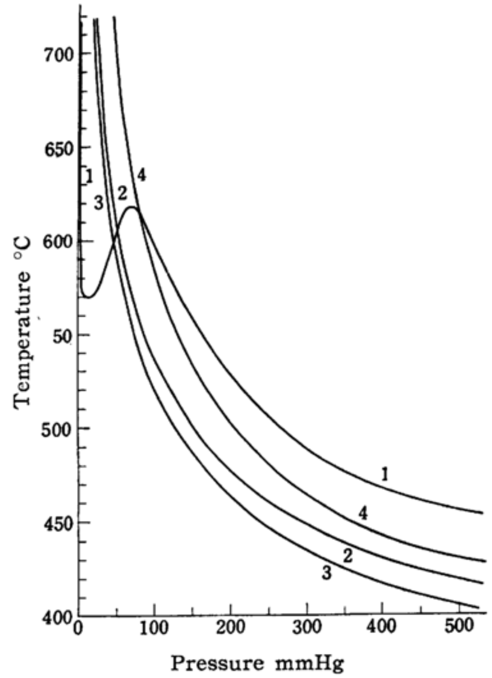

Fig. 2. Isochors for explosion limit of ethylene-oxygen mixtures. curve 1=20%, 2=40%, 3=60%, 4=80% ethylene.

(4) No change was observed.

Case 1 and 2 are considered to be the explosions.

The Explosion Limit of Ethylene-Oxygen Mixtures.—Isochors were determined for the mixture of the various compositions. Only a certain number of isochors are shown in Fig. 2. Only the

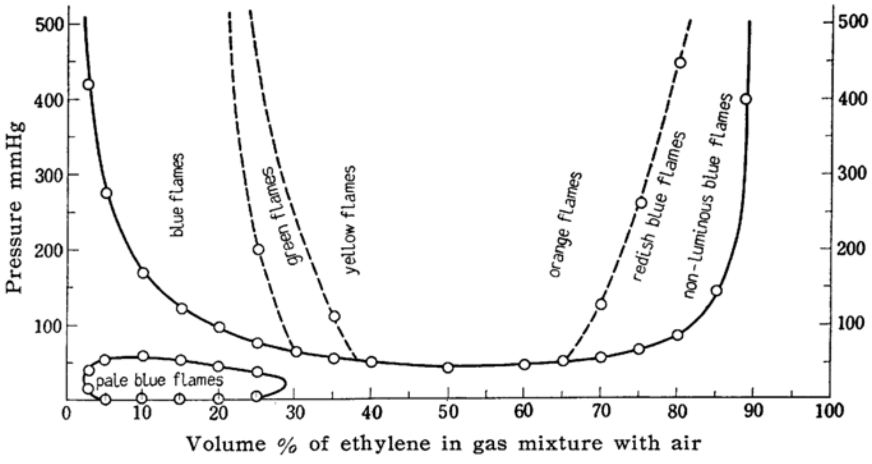

Fig. 3. Isotherm for explosion limit of ethylene-oxygen mixtures at 600°C.

600°C isotherm is shown Fig. 3. The curves shown in these figures exhibit the minima at the composition of about 50% ethylene and are situated about 2.5～90% ethylene. The explosion limit peninsula as indicated in Fig. 2 (curve 1) is found on the definite temperature and pressure condition in the mixture range 2.5～30% ethylene as indicated in the lower closed curve in Fig. 3.

a) Non-luminous blue flames are the flames observed in the ignition of the mixture of more than 70% ethylene. The pressure pulses are relatively mild in company with the flames, and no propagating flames are observed.

b) Luminous blue flames are the flames observed in the ignition of the mixture of less than 30% ethylene. Even at a lower pressure region, the pressure pulses are relatively violent with the flames and propagating flames are often observed.

c) Luminous yellow flames are the flames observed in the ignition of the mixture of 20～80% ethylene. The flames are propagated into the inlet tube of the reaction vessel, with vigorous pulses.

d) Luminous green flames are the flames observed in the ignition of the mixture of about 35% ethylene.

As a whole, the color of ignition flames, as shown in Fig. 3, changes in the order of blue, yellow, green and blue, with decrease of the percentage of ethylene.

Morever, as a remarkable phenomenon, in the mixture range 60～80% ethylene, reddish blue flames are often observed and a small quantity of deposited carbon is found on the wall of the reaction vessel V and capillary inlet tube connecting the reaction vessel V to cock C_1 and manometer M_1. The flames in the explosion peninsula are very faintly visible after the longer induction periods (10 sec.～20 min.) as described in 2). The boundary between the second and the third (thermal)

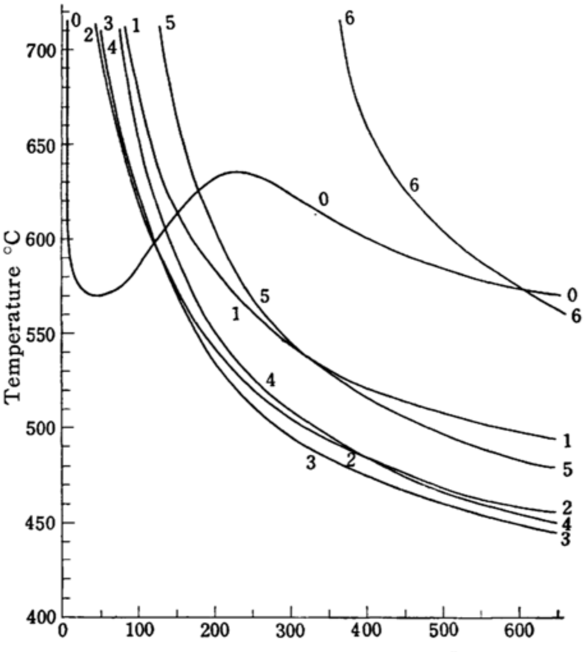

Fig. 4. Isochors for explosion limit of ethylene-air mixtures. curve 0=5%, 1=10%, 2=20%, 3=30%, 4=40%, 5=50%, 6=60% ethylene.

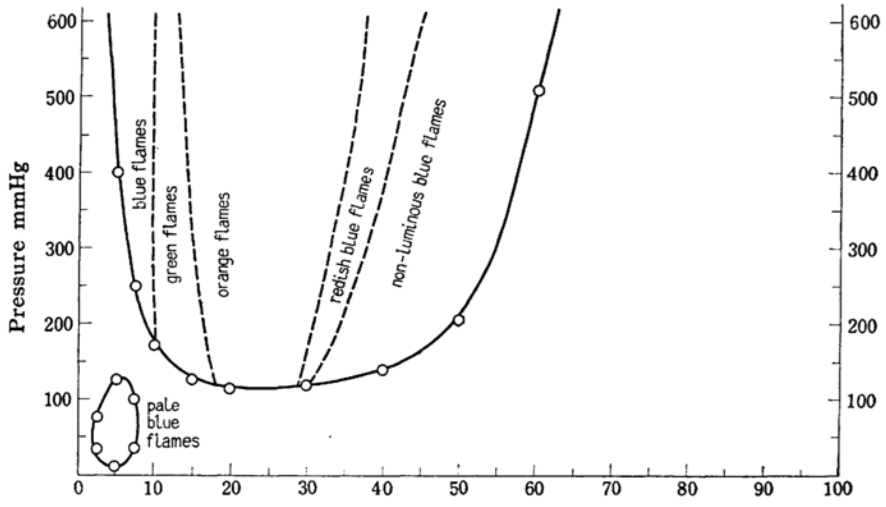

Fig. 5. Isotherm for explosion limit of ethylene-air mixtures at 600°C.

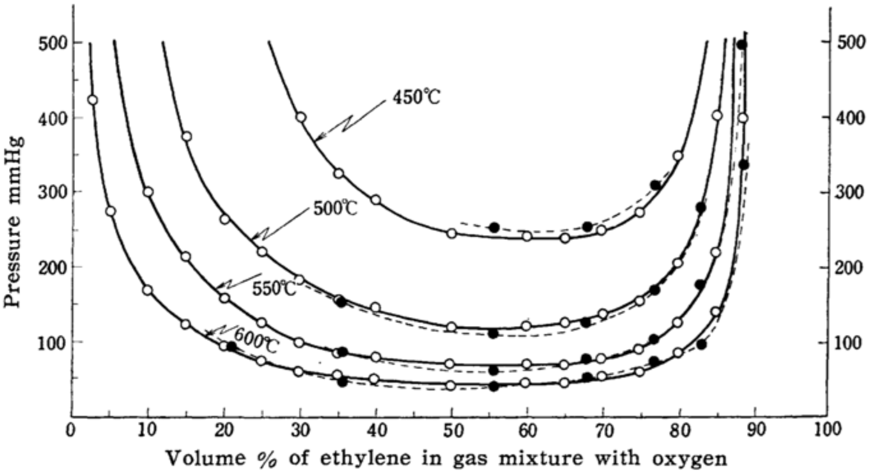

Fig. 6. Relationship between isotherms for explosion limit of ethylene-oxygen and ethylene-air. (Broken lines represent the data calculated from the limit of ethylene-air mixtures, illustrated in considerations.)

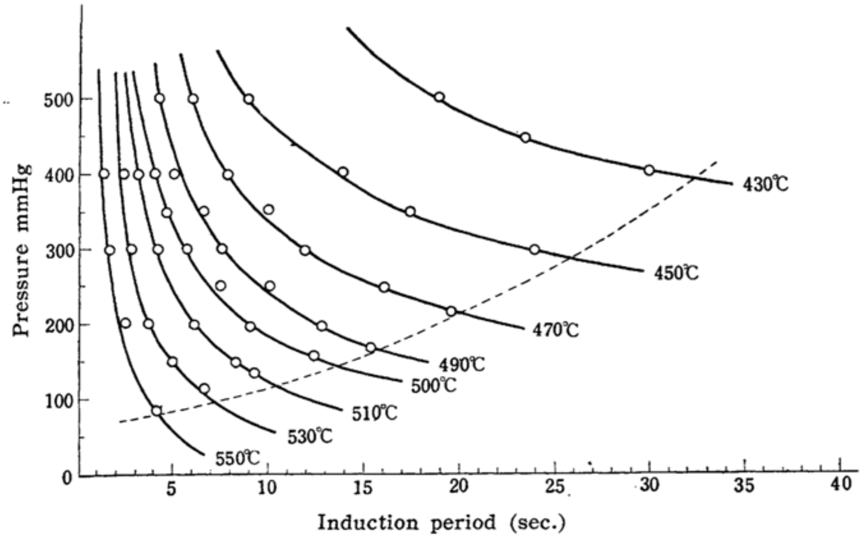

Fig. 7. Relationship between explosion limit pressure and induction period at a definite temperature.

limit was accurately determined with difficulty in the present experimental method.

The Explosion Limit of Ethylene-Air Mixtures.—Isochors of the explosion limit at the compositions of 5, 10, 20, 30, 40, 50 and 60% ethylene with air can be obtained by the same method described as with oxygen and shown in Fig. 4. Also the 600°C isotherm is shown Fig. 5.

In order to elucidate the effect of the foreign gas, N_2, the limiting pressures and composition of ethylen-air mixtures at temperatures of 600, 550, 500 and 450°C are converted in to those of ethylene-oxygen mixtures by calculation, subtracting the partial pressure of nitrogen. These calculations give the broken lines in Fig. 6 which shift little from the corresponding full lines except the second pressure limit. A further investigation of the second pressure limit is now in progress. In addition, the ignition flames are the same as ethylene with oxygen, and may lead to the conclusion that the effect of nitrogen on the first and the third pressure limit should be negligible.

The Explosion Limit and Induction Period.—The results of the experiment with regard to the induction period are shown in Fig. 7. Generally, the higher the admission pressure, the shorter the

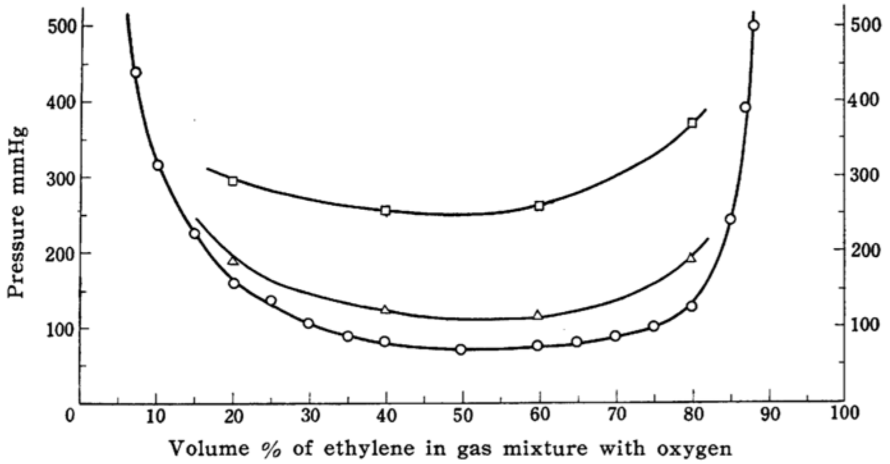

Fig. 8. (a) Effect of reaction vessels diameter for the isotherms at 550°C. Diameter: □, 1 cm; △, 2 cm; ○, 3 cm.

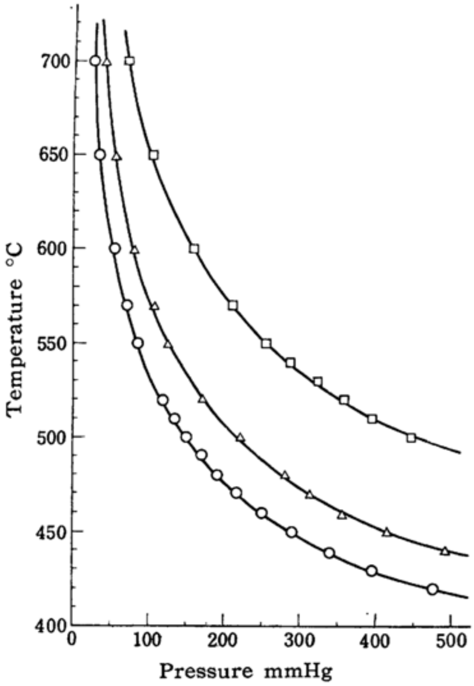

Fig. 8. (b) Effect of reaction vessel diameter for the isochors of 40% ethylene. Diameter: □, 1 cm; △, 20 cm; ○, 3 cm.

induction period. The influence of temperature is greater than that of pressure.

In consequence, the induction periods, over 650°C, became less than one second and accordingly can not be measured with a stopwatch with accuracy. Slow reactions also had the induction periods which were longer than those of explosions, but the quantitative relationship could not be described in the present experiment. Also as a remarkable phenomenon, preceding the ignition, the pressure changes which anticipated the explosion were often observed by mercury manometer M_1.

The Effect of Reaction Vessel.—The reaction vessels used were usually quartz cylinders of 3 cm. in diameter and 10 cm. in length. Quartz cylinders of 2 cm. or 1 cm. in diameter of the same length were also employed in order to examine the effect of the diameter of reaction vessels. The result is indicated in Fig. 8. The decrease of the vessel diameter serves invariably to retard the explosion. The quantitative relationship can not be discussed in detail. Furthermore it was found that the result varied with previous history of the reaction vessel (e.g. the quality and time of pumping during evacuation of the vessel between experimental runs), and that the induction period was greatly influenced. But these effects were not reproducible, so the present authors adopted the standard procedure as follows.

After the previous runs, the reaction vessel was heated to 600°C and evacuated to 10^{-3} mm Hg (tested by Gaisler tube) for thirty minutes. The virgin vessels were employed after explosive runs. It is confirmed that the experiments with these precaution are reproducible and the results are probably always reliable.

The Activation Energy of the Reaction.—In Fig. 9 is shown the relationship between $\log_{10} p/T$ and $1/T$ for the third limit of Fig. 2. Those graphs are essentially linear at a lower temperature than 600°C and adhere to the relationship $\log_{10} p/T = A/T + B$. If the ignition limit is thermal in character, the gradient of

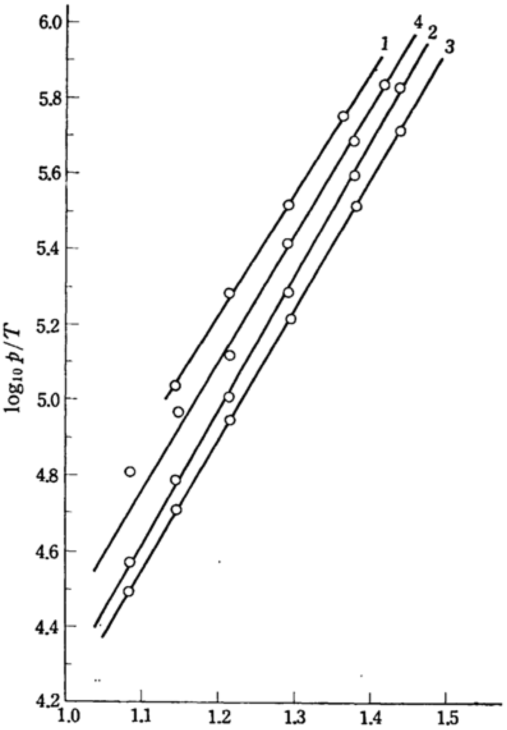

Fig. 9. $\text{Log}_{10} p/T$ against $1/T$ curves for the explosion limit of ethylene-oxygen mixtures. curve 1=20%, 2=40%, 3=60%, 4=80% ethylene.

these lines A will be equal to $E/2.303\times 2\times R$.[5,6] Thus values for E, the apparent activation energy, may be calculated as in Table I.

TABLE I
ACTIVATION ENERGIES ESTIMATED FROM SPONTANEOUS IGNITION LIMITS OF ETHYLENE-OXYGEN MIXTURES

C_2H_4%	A	$E=2.303\times2\times1.987\times A$ (kcal./mol.)
80	3.18	29.10
60	3.74	34.23
40	3.47	31.76
20	3.37	30.84

On the other hand, in Fig. 10 is shown the relationship between $\log_{10}\tau=A'/T+B'$. There will be only an in direct meaning of the kinetics, but the gradient of these lines A' is thought to be equal to $E/2.303\times R$.[7] Thus values for E', the apparent activation energy, may be as in Table II.

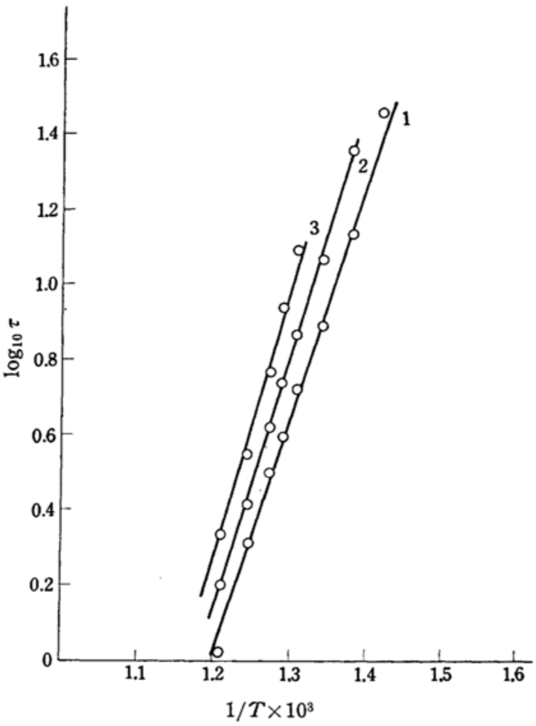

Fig. 10. $\text{Log}_{10}\tau$ against $1/T$ curves for the explosion of 40% ethylene-oxygen mixture. curve 1=400, 2=300, 3=200 mmHg.

TABLE II
ACTIVATION ENERGIES ESTIMATED FROM THE INDUCTION PERIODS

Admission pressure (mmHg)	A'	$E=2.303\times1.987\times A'$ (kcal./mol.)
400	6.05	27.69
300	6.52	29.84
200	7.12	32.58

The explosive reactions of ethylene with oxygen or air may be considered to be thermal in apparent character in the present experimental ranges.

Summary

The explosion limit of ethylene mixed with oxygen or air was determined at lower pressure than atomospheric pressure by the statical constant volume method known as the "admission method". Isochors, isotherms and isobars of the explosion limit have been shown. The colors of ignition flames change in the order of blue, yellow and blue with the decrease in the percentage of ethylene. In addition, the explosion peninsula was recognized at a definite condition in the mixture range 2.5~30% ethylene in

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[5] K. Semenoff, *Z. Physik.*, **48**, 57 (1928).
[6] K. Posthmus, *Rev. Trav. Chim.*, **49**, 309 (1930).
[7] B. P. Mullins; "Spontaneous Ignition of Liquid Fuels", Butter Worths Sci. Pub., London, (1955).

oxygen. The results of ethylene with oxygen and ethylene with air were equivalent to each other, so far as the partial pressure of nitrogen was neglected. Induction periods were also taken into consideration and the apparent activation energy was estimated to be about 30 kcal./mol.

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