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STUDIES ON THE EXPLOSIONS OF PROPYLENE AND ACROLEIN
MIXED WITH OXYGEN OR AIR

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The explosion limits of propylene mixed with oxygen or air are determined at reduced pressures and at high pressures (up to 15 kg/cm²) by the admission method. By the same method, those of acrolein mixed with oxygen or air are determined at reduced pressures. As to the propylene mixed with oxygen, the minimum explosion temperatures at any constant reduced pressures are shown by mixtures of 30~40% of propylene, but at high pressures by those of 30~70% of propylene.

On the mixtures of propylene or acrolein rich in oxygen or air, the explosion peninsulas are observed at reduced pressures. The induction periods are measured and it is found that the periods inside the explosion peninsula are much longer than those outside the peninsula.

As to the mixture of propylene (50%) mixed with oxygen, the cool flame regions are determined.

The addition of nitrogen makes the explosion much weaker and it would be considered to affect the process of the propagation.

The apparent activation energies of the reactions are estimated from the explosion limits according to Semenov's theory and from the relationship between the logarithm of the induction period and the reciprocal of the absolute temperature.

Introduction

The explosions of lower unsaturated organic compounds such as C₂H₂ and C₂F₄ have been the subject in the previous paper¹⁾. In the present case, the author continued to study the explosions of propylene and acrolein which have been recently of industrial importance, particularly as a monomer or a raw material of the polymers, by means of so-called "admission method"*.

On the explosion of propylene in parts I and II, several works have been reported in the literatures²⁻⁵⁾, but for its increasing use in industry, it is necessary for handling it safely to get more information available over sufficiently wide ranges of temperature and pressure. The author, therefore, examined in more details the explosions, particularly the explosion peninsula at reduced pressures, and also the explosions at high pressures.

As to acrolein in part III, there are few data in regard to "limit of inflammability"^{6,7)} and

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- * Gas mixtures are admitted into a reaction vessel evacuated and heated to a definite temperature.
- 1) R. Kiyama, J. Osugi and S. Kusuhara, *This Journal*, **27**, 22 (1957)
 - 2) S. Polak and V. Stern, *J. Phys. Chem. (U. S. S. R.)*, **27**, 341 (1953)
 - 3) G. P. Kane and D. T. A. Townend, *Proc. Roy. Soc. A* **160**, 174 (1937)
 - 4) B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases*, Academic Press Inc., (1951)
 - 5) G. Pannetier and A. Sicard, *5th Symposium on Combustion*, p. 620 (1955)
 - 6) J. H. Burgoyne and R. F. Neal, *Fuel*, **32**, 5 (1953)
 - 7) B. P. Mullins, *ibid.*, **32**, 481 (1953)

no study can be found on the spontaneous ignition limit, so that the author determined the limits, finding the explosion peninsula.

The detailed reaction mechanisms for the mixture of propylene-oxygen or acrolein-oxygen will be discussed in the near future.

Experimentals

Materials The propylene used was prepared by the dehydration of propyl alcohol by the action of an alumina catalyst, and purified by fractionation by means of cold traps and by the action of potassium hydroxide. The purity of the gas is found to be about 99%. The acrolein employed in this experiment is a commercial one, which is fractionated from the liquid air trap twice before experiment. The purity is about 98.5%. The oxygen employed was obtained from a commercial cylinder (purity: 99.4%).

Apparatus and procedure The apparatus used and the procedure adopted at reduced pressures are the same as described in the previous paper¹⁾. On the other hand the layout of the apparatus at high pressures is shown in Fig. 1.

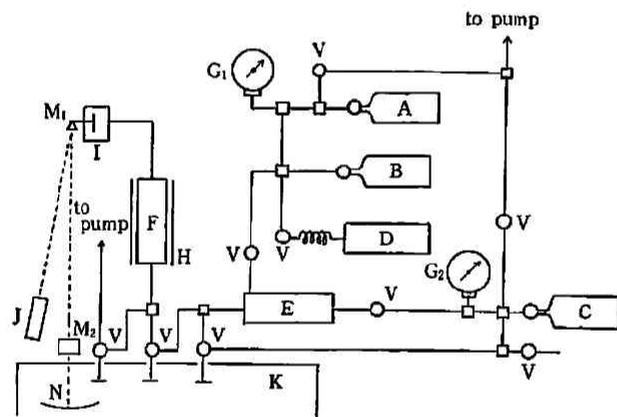


Fig. 1 Layout of the apparatus for the experiment at high pressure

- A: C_3H_6 bomb
- B: O_2 bomb
- C: air bomb
- D: steel vessel for gas mixing
- E: pressure intensifier
- G_1, G_2 : Bourdon type pressure gages
- H: electric furnace
- I: membrane pressure gage
- J: light source
- K: steel board for protection
- M_1, M_2 : mirrors
- N: scale
- V: high pressure valves

Propylene is compressed and stored in a steel reservoir A. B and C are oxygen and air bombs respectively. D is a steel vessel for gas mixing. A glass ball, the diameter of which is about two thirds of the vessel diameter, is put in the vessel and rolled to help the mixing. The vessel E is an intensifier of 250 cc in capacity by which the gas mixture is compressed to a desired pressure by means of an air driven piston. The reaction vessel F is made of mild steel having 2 cm in inner diameter and 12.5 cc in capacity. The reaction vessel is heated by an electric furnace H to a definite temperature which is measured by means of a thermocouple inserted in the hole made in the wall of the vessel. The membrane pressure gage I is constructed by a spring steel membrane (0.8~1.5 mm in thickness and 44 mm in effective diameter) and a mirror which rotates proportionally to the deflection of the membrane due to pressure. The pressure is measured from (i) the displacement of a light spot N reflected from the mirrors M_1 and M_2 ,

and (ii) the change of electric resistance of a strain gage cemented on the membrane, and recorded by an ink writing oscillograph. K is a steel board of 5 mm in thickness to protect the observer from accidents. G_1 and G_2 are Bourdon type pressure gages.

$C_3H_6-O_2$ or C_3H_6 -air mixtures of desired compositions are prepared in the vessel D. After complete mixing, the gas mixtures are made to flow into an intensifier E. Then the gas mixtures, being compressed to certain pressures (up to 15 kg/cm^2) by the compressed air of the bomb C, are admitted into the reaction vessel which has been evacuated and heated to the experimental temperature. When explosions take place, they are observed from very rapid and discontinuous displacements of the light spot and confirmed by the pressure curves recorded.

Combustibles and oxygen or air, being mixed in a reservoir at reduced pressure, were generally kept more than 12 hours for the completion of mixing.

Results and Considerations

The results are influenced by the previous history of the reaction vessel, so that in order to eliminate the effect, the author had evacuated the reaction vessel for an hour after a previous run (heating it at about 400°C when the experimental temperature was below 400°C) and gained reproducible results. When the virgin surface of a reaction vessel is used, reproducible results are obtained after the first explosion.

Pressure variation with time Typical pressure-time curves recorded by the ink writing oscillograph are indicated in Fig. 2. Curve (a) shows an abrupt rise of pressure with luminous yellowish orange or blue flames and corresponds to a normal explosion. Curve (b) shows the pressure change which appears to be a two-stage ignition and occurs under conditions near the thermal explosion limits. Curve (c) shows a feebler increase of pressure due to slower reaction, accompanied with pale-blue flames and found either in the explosion peninsula or in the cool flame region as shown later. Curve (d) shows no increase of pressure without flame, corresponding "slow reaction".

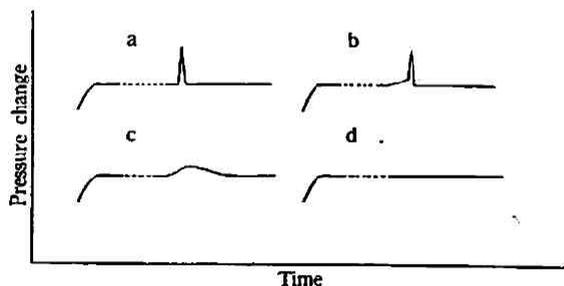


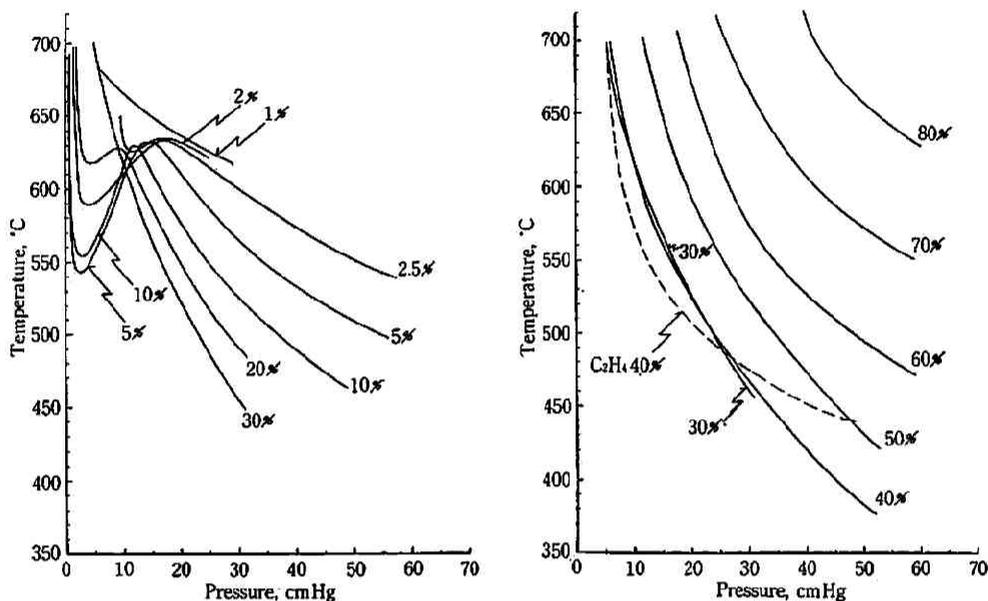
Fig. 2 Schematic pressure-time curves

I Explosive phenomena of propylene-oxygen mixture at reduced pressure

Explosion limit The changes of the pressure limits of explosion with temperature are shown in Figs. 3 and 4 at various compositions. At the composition of poorer propylene than about 21~22%, the explosion peninsula can be found, which is bounded by the first and second

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Figs. 3 and 4 Changes of pressure limit of explosion with temperature at specified compositions for the mixture of propylene and oxygen

pressure limits of the explosions. It lies on the range of 2~17% of propylene at 600°C. Isobars and isotherms for the explosion limits are shown in Figs. 5 and 6 respectively. The minimum can be found at the composition of about 30 to 40% of propylene. The minima at the composition of 5~7% of propylene in Fig. 5 and the lower closed curve at 600°C in Fig. 6 correspond to the explosion peninsula. The broken line in Fig. 6 indicates the isotherm

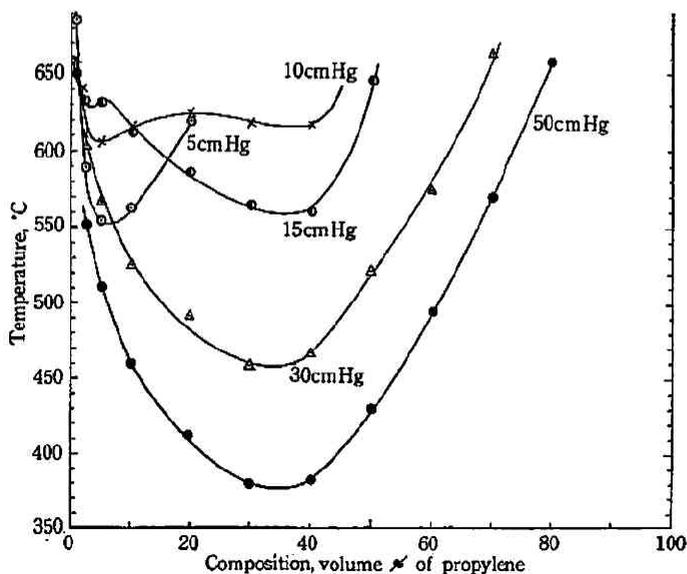


Fig. 5 Isobars for explosion limit of propylene-oxygen mixtures

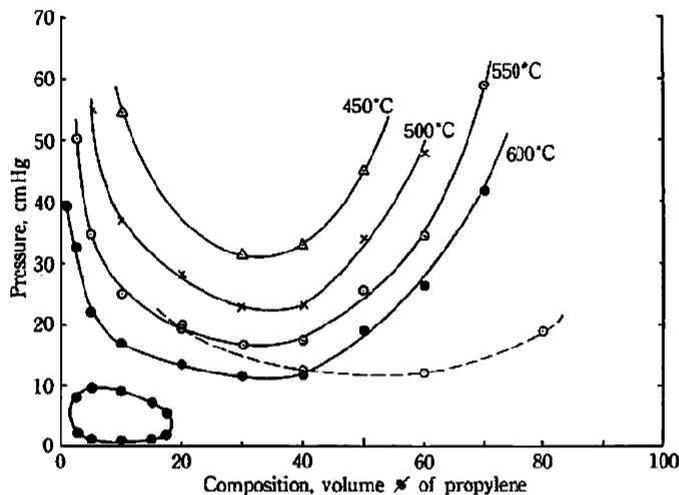


Fig. 6 Isotherms for explosion limit of propylene-oxygen mixtures

Broken line indicates the isotherm for the explosion limit of ethylene at 550°C⁸⁾.

for the explosion limit of ethylene at 550°C cited from the data of Suga⁸⁾. The curve exhibits the minimum at 40~60% of ethylene, compared with 30~40% of propylene.

The color of ignition flames changes in the order of blue, yellow and reddish blue with increase of the percentage of the propylene contained. In the mixture rich in propylene, the explosion is generally weak and a small quantity of deposited carbon is often found on the wall of the reaction vessel.

Explosion peninsula The flames in the explosion peninsula are very faint pale-blue and can be observed after the longer induction period (5~2700sec.). It is clear from Figs. 3 and 4 that the first pressure limit depends little on temperature, and the observation was somewhat obscure because of the low admission pressure. The boundary of the first and the second pressure limits of explosion i. e. the tip of the explosion peninsula was determined from the results of observation for an hour and sometimes by reducing the pressure after the gas had been kept at a definite temperature for a few tens of minutes. With the rise of temperature the second pressure limit of explosion increases abruptly, while the third pressure limit of explosion decreases. The composition of gas mixture considerably affects the first and second explosion limits and the change of the gas composition results in various shapes of the explosion peninsula, which disappears at 600°C in the case of over 17% of propylene.

Referring to the studies of Neumann and Serbinov⁹⁾, Norrish and Food¹⁰⁾ and Lewis⁴⁾ on the explosion of methane-oxygen mixture, Suga concluded that on the mixture of ethylene and oxygen, ethylene is oxidized to carbon monoxide first in the definite range of temperature and pressure and that the carbon monoxide produced and accumulated is ignited in the definite condition. He confirmed this¹¹⁾ by the disappearance of the explosion peninsula, using the

8) M. Suga, *Bull. Chem. Soc. Japan*, **31**, 515 (1958)

9) M. B. Neumann and A. Serbinov, *Phys. Z. Sowjetunion*, **1**, 536 (1932)

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

11) M. Suga, *This Journal*, **28**, 67 (1958)

reaction vessel in which certain metal wires were inserted.

The explosion peninsulas of propylene-oxygen mixtures lie approximately on the same range of temperature and pressure limits as in the case of carbon monoxide-oxygen mixture¹²⁾. It can be considered that propylene is oxidized to carbon monoxide by slow reaction, and that it is ignited in the definite condition. If the propylene concentration is, therefore, greater than the stoichiometric value corresponding to $C_3H_6 + 3O_2 = 3CO + 3H_2O$, the oxygen is insufficient for the oxidation of this carbon monoxide, and so the explosion peninsula disappears. This condition may be satisfied approximately because the explosion peninsula disappears in the case of over 21~22% of propylene as already mentioned.

Effect of reaction vessel The reaction vessels used were always quartz cylinders of 2cm in diameter and 10cm in length. Quartz cylinders of 3cm diameter of the same length were also used for the mixture of C_3H_6 (50%)– O_2 in order to examine the wall effects. At the same time the cool flame was observed and the results are shown in Fig. 7. In the cool flame region, the flames are feeble and blue, the pressure changes mild, and the induction periods very long, such as 26 minutes (340°C, 40cmHg) and 44 minutes (364°C, 24cmHg).

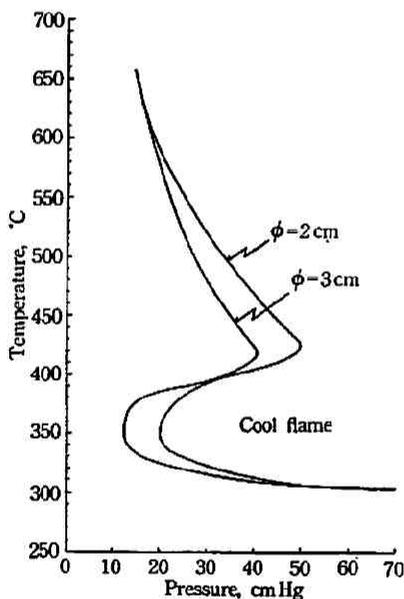


Fig. 7 Effect of reaction vessel diameter on explosion limit for the propylene (50%)–oxygen mixture

Induction period The induction period was measured by a stop-watch. Generally the higher the admission pressure and the higher the temperature, the shorter the induction period. But the influence of temperature is greater than that of pressure. In the region of the explosion peninsula, it is fairly long, while it is short at higher pressures than the third limit of explosion and its extrapolated line over the cross point with the second explosion limit as shown in Fig. 8.

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

N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Vol. 2, p. 44, Pergamon Press Ltd., London (1959)

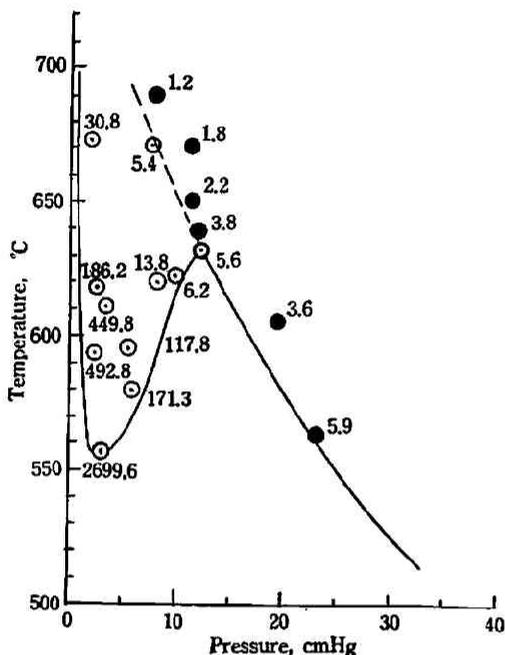


Fig. 8 Induction periods inside and near the explosion peninsula for explosion limit of propylene (10%)-oxygen mixture

They are indicated in seconds by numbers beside observation point.

As mentioned already, it is long in the cool flame region.

Activation energy of the reaction In Fig. 9 is shown the relationship between $\log P/T^2$ and $1/T^*$ for the third limit of some curves in Figs. 3 and 4. They give nearly straight lines in the temperature range between 450 and 600°C. At a lower temperature than 450°C, the relation cannot be held, because the cool flames are observed and the negative temperature coefficient appears. If the ignition is thermal in character, the gradient of these lines will be equal to $E/2.303 \times 2 \times R^{13}$. Thus the apparent activation energy E may be calculated as 31.0, 30.6 and 29.5 kcal/mole for the lines a, b and c. On the other hand, Fig. 10 shows the relationship between $\log \tau$ and $1/T^{**}$ for the various total pressures in the case of the vessel of 2 and 3 cm diameter. The linear relationship is held and the gradient of the line may give $E/2.303 R^{14}$. Thus the activation energy for lines a, b and c can be calculated to be 38.4, 33.1 and 39.8 kcal/mole which are higher values compared with those calculated above. The line d corresponding to the explosion in the explosion peninsula gives the value of 59.6 kcal/mole, which is a little higher value than those of the other thermal explosions.

Merely from these results, it is difficult to determine the explosion mechanism, but it can also be preferred that the explosion within the explosion peninsula has a different mechanism from

* P and T indicate third pressure limit of explosion and absolute temperature respectively. The relation of $\log P/T^2 = A/T + B$ was derived for bimolecular processes by Semenov¹³⁾.

** τ and T indicate induction period and absolute temperature respectively. The relation of $\log \tau = A/T + B$ was derived by Mullins¹⁴⁾.

13) N. N. Semenov, *Z. Physik*, 48, 57 (1928); *Some Problems of Chemical Kinetics and Reactivity*, Vol. 2, p. 4, Pergamon Press Ltd., London (1959)

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

the explosion outside the region.

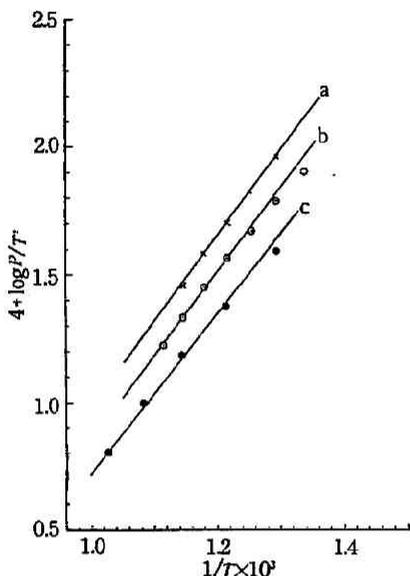


Fig. 9 Relation between $\log P/T^2$ and $1/T$ for explosion limit of propylene-oxygen mixtures

line a: 5% C_3H_6
 " b: 10% "
 " c: 40% "

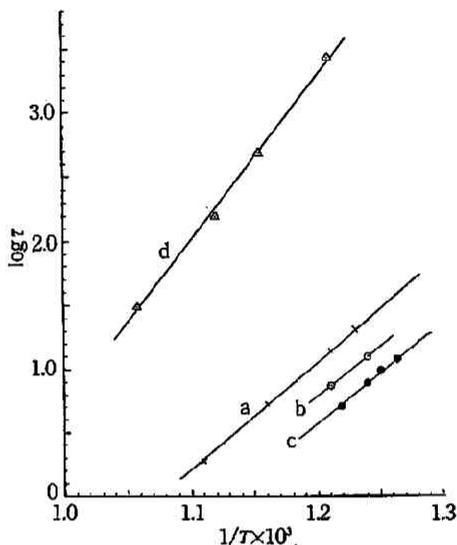


Fig. 10 Relation between $\log r$ and $1/T$ for explosion of propylene-oxygen mixtures

line a: 50% C_3H_6 , 30.2 cmHg, $\phi = 3$ cm
 " b: 60% " 40.3 " " 2 cm
 " c: 20% " 29.7 " " 2 cm
 " d: 10% " 3.0 " " 2 cm

II Explosive phenomena of propylene-oxygen or air mixture at high pressure

Explosion limit The changes of the explosion temperature with pressure at specified compositions are shown in Figs. 11 and 12 for mixtures of $C_3H_6-O_2$ and C_3H_6 -air respectively. In order to compare the results with those at reduced pressure, the broken line is plotted from the cool flame region in Fig. 7 for 50% mixture. The pressure limits of explosion determined by the high pressure apparatus are higher than that determined by the glass apparatus at the same temperature and composition. This is probably because in the latter even very feeble explosion can be recognized by light but in the former it cannot be detected owing to both the low sensitivity of steel membrane and the weakness of the explosion. Isobars of the explosion limits at 5 and 10 kg/cm² are shown in Fig. 13. The minimum ignition temperature of C_3H_6 -air mixture at 10 kg/cm² is observed in the case of the composition of about 20% C_3H_6 , while in the case of $C_3H_6-O_2$ the minima lie on the wide range of 30~70% of C_3H_6 . For the latter they are also compared with those (30~40%) at reduced pressures in Fig. 6. Both minimum temperatures for $C_3H_6-O_2$ and C_3H_6 -air under the same pressure coincide approximately with each other.

The maximum pressures attained at the explosion of $C_3H_6-O_2$ mixtures are about twofold of the initial pressures. But the higher the initial pressure, the more violent explosion and when the experimental condition is near the explosion limits, relatively weak explosions are observed.

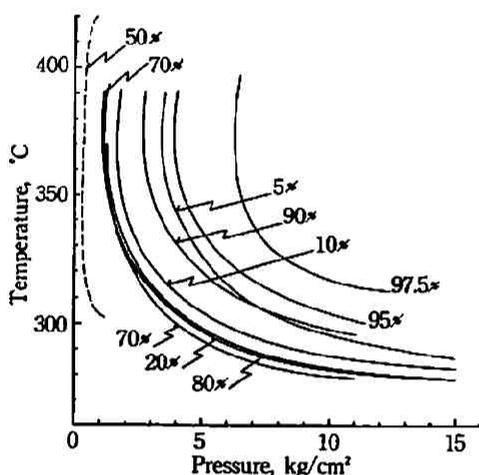


Fig. 11 Change of pressure limit of explosion with temperature at specified compositions for the mixture of compressed propylene and oxygen

Broken line is plotted from the cool flame region in Fig. 7.

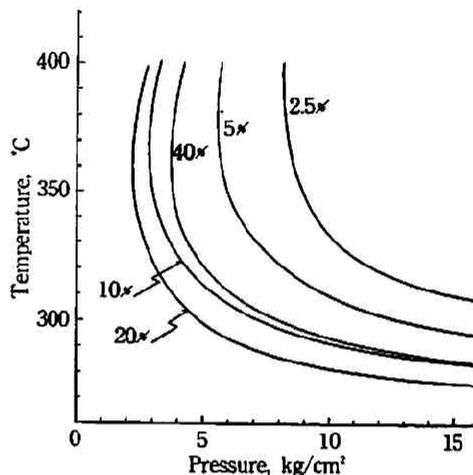


Fig. 12 Change of pressure limit of explosion with temperature at specified compositions for the mixture of compressed propylene and air

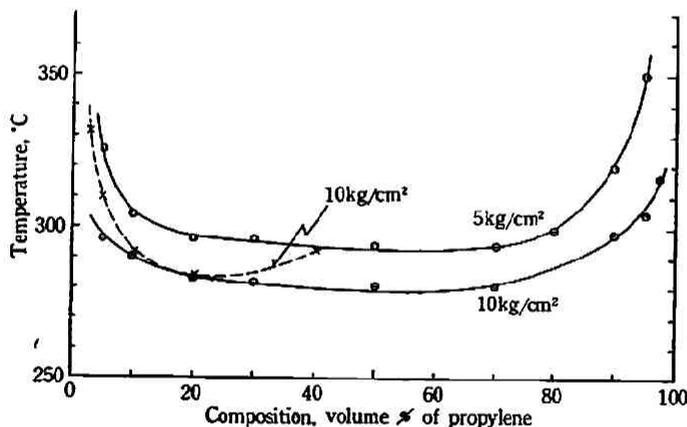


Fig. 13 Isobars for explosion limit of compressed propylene-oxygen mixtures

Broken line represents the isobar for explosion limit of propylene-air mixture.

Activation energy of the reaction The linear relationship between $\log P/T^2$ and $1/T$ for the mixtures of $C_3H_6-O_2$ or air at high pressures is not so good as in the case of reduced pressure. This is perhaps because the cool flame appears. The gradients give the values of 29 to 34 kcal/mole as the activation energy.

Effect of nitrogen The explosion of C_3H_6 -air mixtures is much weaker than that of $C_3H_6-O_2$ mixture. In particular, in the case of over 50% of propylene, the explosion is very weak and difficult to be perceived by the displacement of the spot. But as already shown, the minimum explosion temperature and composition show little difference from those of $C_3H_6-O_2$ at the same total pressure. As a whole it would be considered that the mixing of N_2 can scarcely affect

the initiation process of the explosion, but retard the propagation of the explosion.

III Explosive phenomena of acrolein-oxygen or air mixture

Explosion limit The relationships between pressure and temperature of the explosion limits are determined for the mixtures of various compositions, which are shown in Figs. 14 and 15 respectively. The experiments were carried out at lower temperatures than 500°C except 2% acrolein because of the possibility to cause the ignition of stored gas due to very short induction period. As to the richer mixtures than 70% of acrolein the experiment is not carried out because the vapor pressure of acrolein is lower and enough pressure is not obtained.

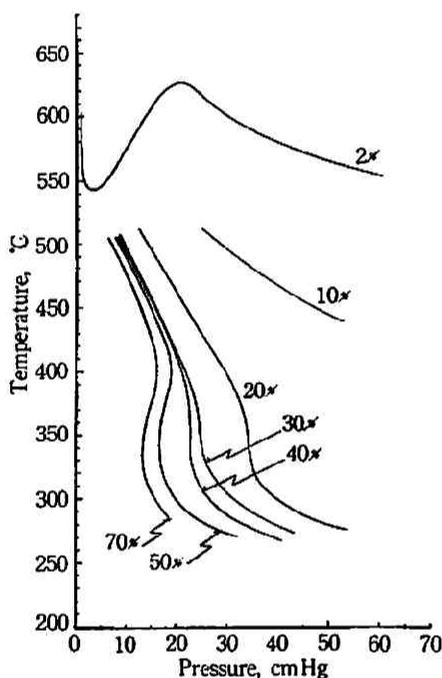


Fig. 14 Change of pressure limit of explosion with temperature at specified compositions for the mixture of acrolein and oxygen

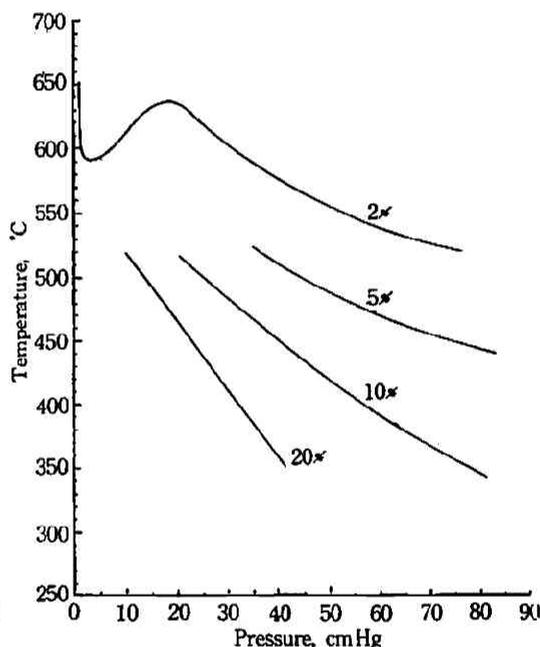


Fig. 15 Change of pressure limit of explosion with temperature at specified compositions for the mixture of acrolein and air

The color of flames changes from blue to yellowish orange with the increase of the percentage of acrolein.

The minimum temperature of the explosion is about 250°C within this experiment. In the mixture of 2% acrolein, the explosion peninsula is found, but it has not yet been determined in what range of composition it is found.

At the temperature between 250 and 380°C, the curves show shallow minima and at the lower pressure than these limits a cool flame region is expected to exist but it is not confirmed. In the larger vessel of 5 cm in diameter cool flame was observed.

Effect of nitrogen Compared the curves in Fig. 14 with those in Fig. 15, the mixing

of nitrogen little shifts the explosion limits of acrolein-oxygen, but makes the explosion much weaker and it leads to the conclusion that nitrogen would affect the propagation process rather than the initiation process of the explosion as in the case of propylene.

Activation energy of the reaction The relation of $\log P/T^2$ against $1/T$ of the third explosion limits is not certain because of the shallow minima of the limits and of the meanness of the data, but for the mixtures 2, 5 and 10% of acrolein mixed with air and 10% of acrolein mixed with oxygen the linearity is approximately held as shown in Fig. 16. These gradients give the activation energies of 35.2, 27.2, 25.7 and 26.4 kcal/mole respectively.

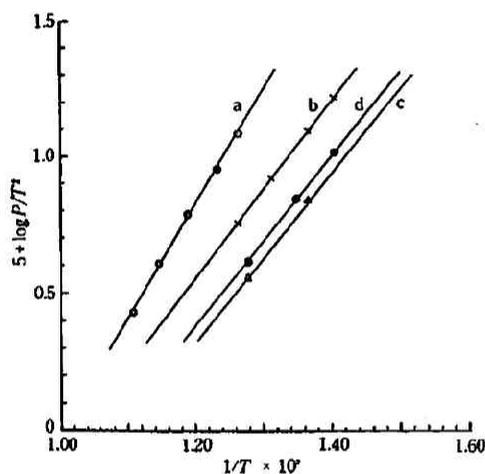


Fig. 16 Relations between $\log P/T^2$ and $1/T$ for the explosion limit of acrolein-oxygen or air mixture

line a: acrolein (2%)-air
 " b: acrolein (5%)-air
 " c: acrolein (10%)-air
 " d: acrolein (10%)-O₂

Induction period Acrolein, which can be assumed to be an intermediate compound in the oxidation process of propylene, exhibits very short induction periods, such as 0.5* and 40sec.** compared with those of propylene.

The induction periods in the explosion peninsula are also longer than those outside the peninsula.

Acknowledgement

The author has great pleasure in expressing his sincere thanks to Prof. Wasaburo Jono, Dr. Jiro Osugi and Dr. Hiroshi Teranishi for their valuable guidance and encouragement throughout this work. He is also grateful to Mr. Kenichi Yukawa for his assistance done partly in the present investigation.

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* acrolein (30%)-O₂, 410°C, 22.9 cmHg

** acrolein (30%)-O₂, 284°C, 40.1 cmHg