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STUDIES ON THE OXIDATION OF PROPYLENE
IN EXPLOSION PENINSULA*

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The oxidation of propylene has been examined in the explosion peninsula at the temperatures of 580 and 626°C for the mixtures of 8.5 and 20% propylene with oxygen respectively by gas chromatographic analysis. During the induction period, most of propylene has reacted to produce a large amount of carbon monoxide and small amounts of methane, ethylene and carbon dioxide. The decomposition of pure propylene has also been examined at 626°C, the result of which shows that only 15% of methane and ethylene produced by the oxidation reaction are formed by the decomposition reaction. In the explosion peninsula, it is demonstrated that most of propylene is oxidized to carbon monoxide by slow reaction and this plays the main role to cause ignition.

Introduction

The low-temperature oxidation of propylene and acrolein has been described in the preceding paper¹⁾. Also it has been shown that the explosion peninsula like those of other combustible gases²⁾ appeared in a certain region of pressure, temperature and composition of propylene³⁾.

On the explosion peninsula a number of investigations have been made about certain gases⁴⁾. Suga⁵⁾ investigated the explosion peninsula of ethylene and found the disappearance of the peninsula in the case of using the reaction vessel in which certain metal wires were inserted. However, no attempt has been made to analyze the intermediates and products of the oxidation reactions in the explosion peninsula of hydrocarbons. The author, therefore, studied the course of the oxidation reaction of propylene in the peninsula, using gas chromatography for gas analysis. The results show that carbon monoxide has been the main product during the induction period.

Experimentals

Materials The propylene used was prepared by the dehydration of propyl alcohol by

* This paper is part of a thesis submitted to the Graduate School of Kyoto University in partial fulfilment of the requirements for the Degree of Doctor of Science.

- 1) S. Kusuhara, *This Journal*, **31**, 34 (1961)
- 2) B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases*, Academic Press Inc., p. 29 (1951)
- 3) S. Kusuhara, *This Journal*, **30**, 34 (1960)
- 4) N. N. Semenov, *Some Problems of Chemical Kinetics and Reactivity*, Pergamon Press Ltd., vol. 2, p. 26 (1959)
- 5) M. Suga, *This Journal*, **28**, 67 (1959)

the action of an alumina catalyst, and purified by fractionation by means of cold traps. The purity of the gas was found to be about 99%. The oxygen employed was obtained from a commercial cylinder. The purity was 99.4%.

Apparatus and procedure The apparatus used and the procedure adopted were similar to those described in the preceding paper¹⁾ except the usage of the reaction vessel of quartz (3.8 cm in inner diameter and 15 cm in length). A cold trap was not used, because very small amounts of aldehydes (or acids) were produced during the reaction.

Results

The pressure-time curve was used to follow the course of the reaction. After the increase during 1~2 minutes, the pressure falls suddenly, accompanied with a blue flame, as shown in Figs. 3 and 4. Then by carrying out a series of runs and interrupting at appropriate time intervals, the gas mixture was analyzed by gas chromatography. Typical chromatograms of the mixture of 16% propylene with oxygen reacted at 626°C are shown in Figs. 1 and 2, which show

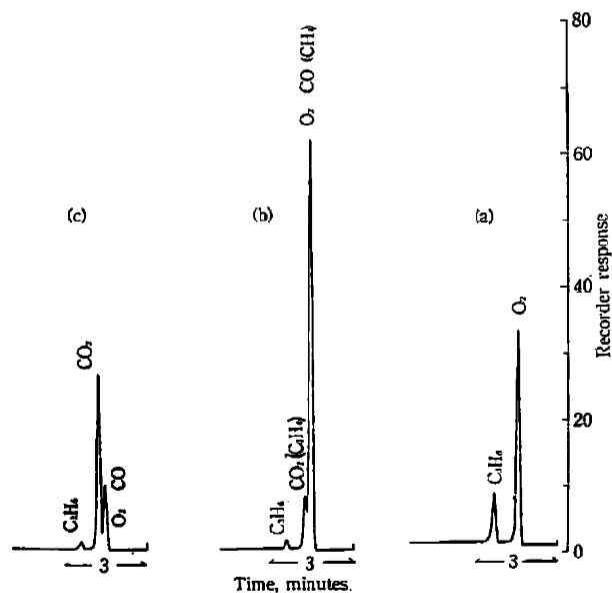


Fig. 1 Chromatograms of the mixture of 16% propylene with oxygen, using dioctyl phthalate column at 74°C (Sensitivity of the recorder: 16 mV full scale)

carrier gas: hydrogen
flow rate: 40 ml/min

- (a) the gas before reaction
(b) the gas reacted for 60 seconds at 626°C (initial pressure of the gas: 4.0 cmHg)
(c) the gas immediately after the appearance of flame at 626°C (initial pressure of the gas: 4.0 cmHg)

the results analyzed by the columns containing dioctyl phthalate and active carbon respectively. Figs. 1(a) and 2(a) show the gas before reaction. As propylene can not be analyzed by an active carbon column, only the peak of oxygen appears in Fig. 2(a). Figs. 1(b) and 2(b) show the compositions of the gases reacted until close to the end of the induction period. It is prominent that much carbon monoxide and small amounts of methane, ethylene and carbon dioxide are produced and propylene decreases to a great extent. Figs. 1(c) and 2(c) show the compositions of the gases immediately after the appearance of flame. Carbon monoxide decreases to a great extent, and methane and ethylene are not detected.

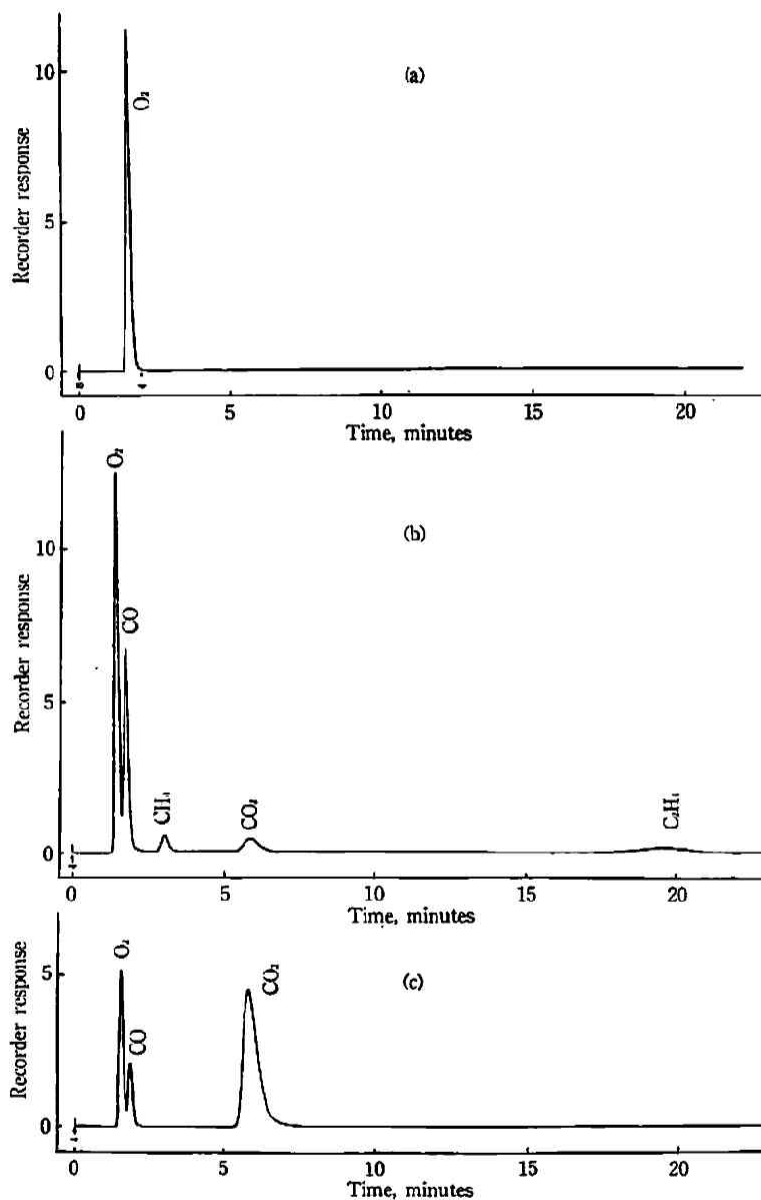


Fig. 2 Chromatograms of the mixture of 16% propylene with oxygen, using active carbon column at 100°C

carrier gas: hydrogen

flow rate: 40ml/min

(a) the gas before reaction

(b) the gas reacted for 60 seconds at 626°C

(initial pressure of the gas: 4.0 cmHg)

(c) the gas immediately after the appearance of flame at 626°C

(initial pressure of the gas: 4.0 cmHg)

All these chromatograms are compared at the same sensitivity of the recorder and at the same gas pressure. In practical analysis the sensitivity is altered appropriately in one run to make each peak area as large as possible within the width of the chart. Sensitivities are shown by numbers below arrow signs in Figs. 2 and 5, which are millivolt necessary to move the pen of the recorder to full scales. The full scales of the ordinates are 100 in Figs. 1 and 5 (a) and 18 in Figs. 2 and 5 (b).

Thus the progressive consumptions of the reagents and the formation of products at the definite time intervals are shown in Figs. 3 and 4 for the mixture of 8.5 and 20% propylene respectively.

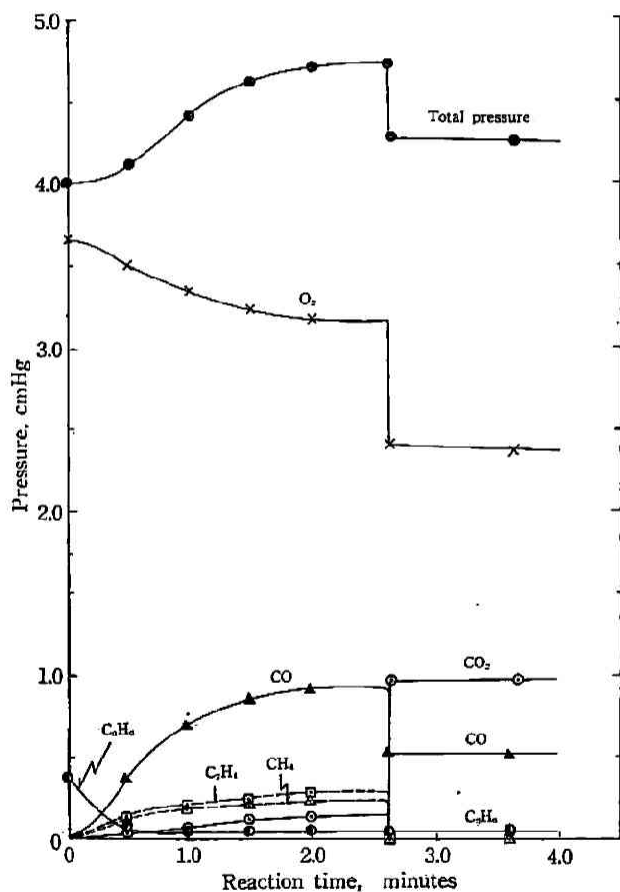


Fig. 3 Progress of reaction on the mixture of 8.5% propylene with oxygen (reacted at 580°C)

The results are expressed as cmHg partial pressure in the reaction vessel at the reaction temperature. It should be noted that the scales of the partial pressures of methane and ethylene in Fig. 3 are tripled (shown in broken lines). General aspect of the results is very similar for the two mixtures of different compositions. Rapid consumption of the reagents begins simultaneously with the pressure increase and a large amount of carbon monoxide and small amounts of methane, ethylene and carbon dioxide appear. Methane and ethylene are produced in almost

the equal amounts in both cases respectively. Aldehydes, on the other hand, do not appear in measurable concentration until close to the end of the induction period, when very small amounts of acetaldehyde and formaldehyde are observed. The sudden rises or falls of the curve at 158 and 74 seconds show the appearance of flame. Comparison of Figs. 3 and 4 shows that the amounts of carbon monoxide remaining after the appearance of flame are of almost the equal value. As to the mixture of 20% propylene with oxygen, over two thirds of carbon dioxide

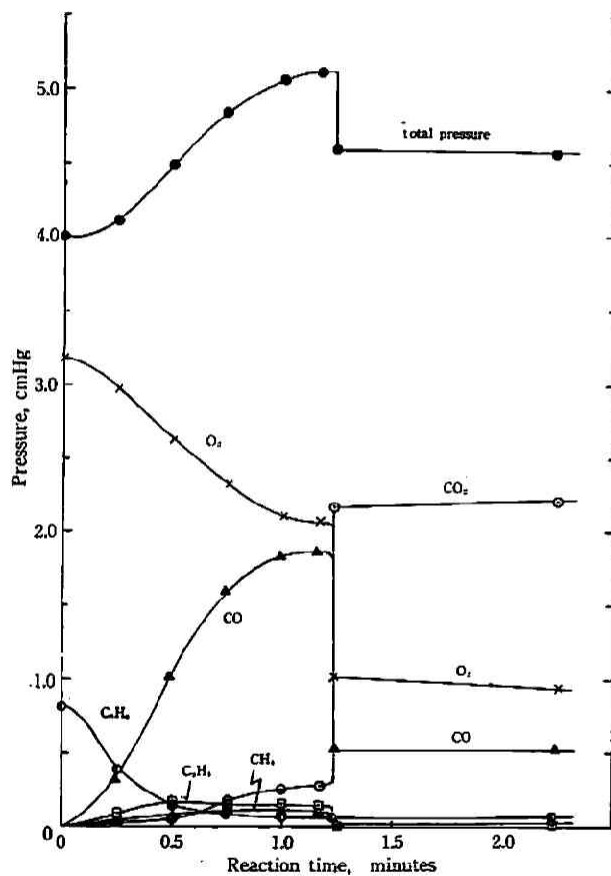


Fig. 4 Progress of reaction on the mixture of 20% propylene with oxygen (reacted at 626°C)

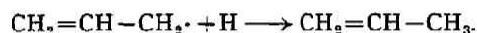
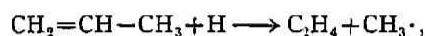
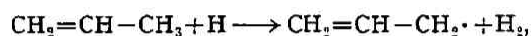
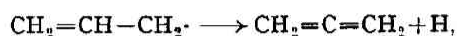
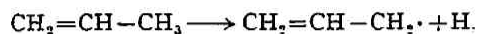
produced during the flaming period is yielded from carbon monoxide as shown in Fig. 4.

Almost all the propylene has reacted during the induction period but 0.2~0.8mmHg of propylene remained unreacted because the propylene kept in the dead space attached to the reaction system is only about 0.1 mmHg. When ignition takes place, carbon monoxide, methane and ethylene are burnt to carbon dioxide and water, but propylene is kept unburnt.

Considerations

As described above, propylene is converted into a large amount of carbon monoxide and small

amounts of methane, ethylene and carbon dioxide (of course, water is produced, but cannot be analyzed quantitatively). In addition to the production by the oxidation reaction, methane and ethylene are considered to be produced by the decomposition reaction according to the mechanism as follows⁶⁾:



Pure propylene, therefore, was reacted at the same temperature (626°C) and at the same partial pressure of propylene (8 mmHg) as those in the case of the reaction in Fig. 4 in order to examine to what extent the decomposition of propylene would take place, accompanied with the oxidation. The results are that the amount of methane and ethylene produced for 90 seconds are about 0.15 mmHg and approximately 15% of those produced in the reaction of the mixture of 20% propylene mixed with oxygen. As to the propylene remaining before the appearance of flame, it should be taken into account that propylene was kept in the dead space attached to the reacting system. But only 0.1 mmHg propylene is attributable to that in the dead space as mentioned already. Thus, it is clear that a small amount of propylene remains unreacted.

At the end of the induction period, very small amounts of acetaldehyde and formaldehyde were detected. Therefore, it can be considered that propylene reacts mainly according to the mechanism described in the preceding paper⁷⁾, but acetaldehyde and formaldehyde are oxidized immediately after the production into carbon monoxide and other products because of high reaction temperature.

Explosion peninsulas were also observed in the oxidations of H_2 , CO , PH_3 , P_4 , CS_2 , silane, etc.⁴⁾ These peninsulas exist in very wide ranges of temperature and gas composition, but those of propylene, acrolein³⁾ and ethylene⁷⁾ appear at the temperature range from 550 to 650°C and in oxygen rich mixtures. These temperature and pressure limits of the peninsulas lie approximately in the same ranges as those of carbon monoxide.

When ignition occurs, carbon monoxide, methane and ethylene burn, while the propylene which remained unreacted does not burn. Among the combustibles, the amount of carbon monoxide being very large compared with those of the others, it is considered that carbon monoxide plays the leading role in ignition.

Concerning gas composition, explosion peninsula appears only in oxygen rich compositions. In the mixtures of over 22% of propylene, oxygen is inferred to be consumed during the induction

6) M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949)

7) M. Suga, *Bull. Chem. Soc. Japan*, **32**, 425 (1959)

period and become insufficient to cause ignition. In order to examine this, the reaction of the mixture of 50% propylene was carried out at 626°C and at the initial pressure of 4cmHg for 90 seconds and it was found that large amounts of carbon monoxide, methane and ethylene were produced and oxygen was consumed to be only 3% of the total pressure as shown in Fig. 5.*

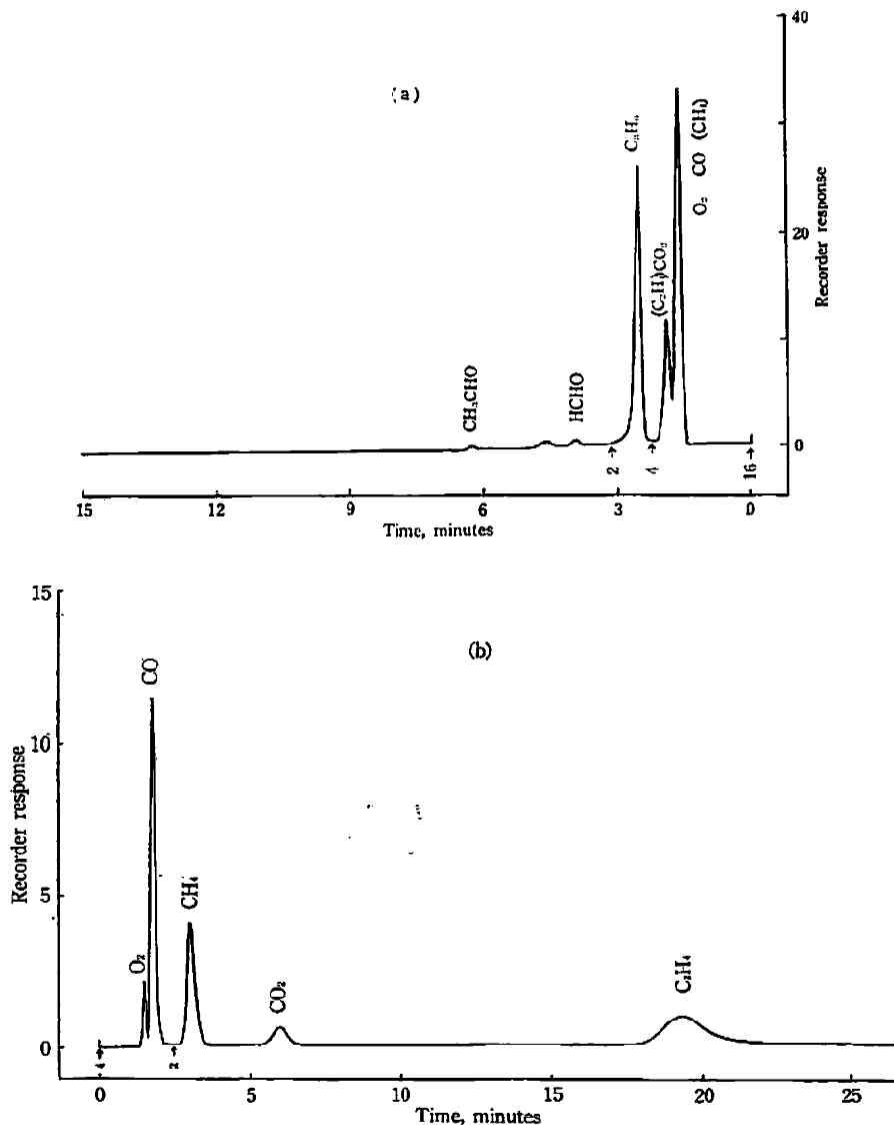


Fig. 5 Chromatograms of the mixture of 50% propylene with oxygen, reacted at 626°C (initial pressure: 4.0cmHg) carrier gas: hydrogen flow rate: 40ml/min

(a) analysis using diethyl phthalate column at 74°C

(b) analysis using active carbon column at 100°C

* A small peak in advance of CH_3CHO in Fig. 5 (a) would correspond to a higher hydrocarbon, such as butene or butadiene.

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So the disappearance of the peninsula would be ascribed to the deficiency of oxygen.

The facts described above lead to the conclusion that most of propylene is oxidized to carbon monoxide by slow reaction, and that the carbon monoxide thus produced plays the main role to cause ignition. In this way explosion peninsula would be observed at approximately the same pressure and temperature ranges as in the case of carbon monoxide.

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