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STUDIES ON GAS PHASE OXIDATION OF PROPYLENE AND ACROLEIN*

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The gas phase thermal oxidation of propylene and acrolein has been examined at temperatures of 371 and 319°C for the mixtures of 53.4% propylene with oxygen and 43.8% acrolein with oxygen respectively by gas chromatographic analysis.

By using two columns containing dioctyl phthalate and active carbon respectively, analyses have been performed to ascertain and evaluate certain intermediates and products, such as aldehydes, acid, methanol, methane, ethylene, carbon monoxide, carbon dioxide, *etc*.

Infrared absorption spectra of the reacted gases have also been used to identify the products.

The oxidation of propylene is discussed in the light of the two proposed mechanisms. The analytical results indicate a high ratio of acetaldehyde to formaldehyde. Therefore, propylene is considered to be oxidized to acrolein, which is oxidized through acetaldehyde to the final products.

Introduction

In recent years analyses during the progress of the low-temperature oxidation of many hydrocarbons have been made by a number of investigators. Peroxides and aldehydes have generally been found as the intermediates of the reaction. On the oxidation of propylene, Mulcahy and Ridge$^{1)}$, Polyak and Shtern$^{2)}$, and Mullen and Skirrow$^{3)}$ have studied the reaction. But because of the difference of the amount of acetaldehyde and formaldehyde, Mullen and Skirrow proposed another reaction mechanism in which they considered acrolein one of the intermediate compounds. However, no attempt has been made to investigate in detail the oxidation of gaseous acrolein. The author, therefore, studied the course of the oxidation reactions of both propylene and acrolein, using gas chromatography and an infrared spectrometer for the identification and estimation of the intermediates and products.

Later paper will deal with the oxidation of propylene in the explosion peninsula.

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1) M. F. R. Mulcahy and M. J. Ridge, *Trans. Faraday Soc.*, **49**, 906 (1953)

2) S. S. Polyak and V. Ya. Shtern, *Zhur. Fiz. Khim.*, **27**, 341 (1953)
S. S. Polyak and V. Ya. Shtern, *Doklady Akad. Nauk*, S. S. S. R., **95**, 1231 (1954)

3) J. D. Mullen and G. Skirrow, *Proc. Roy. Soc.*, **A244**, 312 (1958)

Experimentals

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

Apparatus and procedure A schematic diagram of the essential part of the apparatus is shown in Fig. 1. The capillary inlet tube connecting the reaction vessel to the cock C_1 and the manometer M_1 was used to decrease dead space.

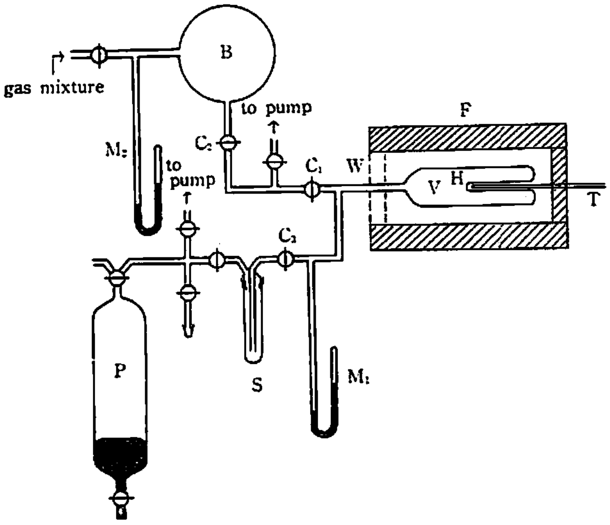

Fig. 1 Layout of the apparatus

B: gas storage
C_1, C_2, C_3: glass cocks
F: electric furnace
H: narrow tube
M_1, M_2: mercury manometers
P: Toepler pump
S: cold trap
T: thermocouple
V: reaction vessel
W: window

The gas mixture of a desired composition which had been prepared and stored in the reservoir was transferred into a storage B at a desired pressure by aid of a Toepler pump. The cylindrical vessel V made of hard glass (3.8 cm in inner diameter and 15 cm in length) was placed horizontally in an electric furnace F. The vessel V was evacuated to about 10^{-3} mmHg in 40 minutes and heated to a definite temperature which was measured by means of an alumel-chromel thermocouple T inserted in a narrow tube H. The sample gas in the storage B was rapidly admitted to the pre-evacuated vessel V to give a definite initial pressure by operating the cocks C_1 and C_2. The pressure was measured by the manometer M_1. After a suitable time interval, the products of the reaction were expanded into a large-volume Toepler pump P (about one liter in volume). Then the gas was collected into a sampling vessel for gas chromatography and analyzed.

The gas chromatography apparatus constructed by the author has a thermal conductivity cell as a detector. The gas chromatography made by Yanagimoto Co., Ltd. (Model GCG-200) was also used. A 4.8 meter column of the former was packed with 40～60 mesh fire bricks impregnated to 40 weight % with dioctyl phthalate, being used for the analysis of propylene, aldehydes, acid and alcohol. For the analysis of the rest of the gases (O_2, CO, CO_2, CH_4 and C_2H_4), a 2 meter column of the latter, packed with 30～50 mesh active carbon was employed, when aldehydes, acid and alcohol were removed by a dry ice trap S in Fig. 1. At the same experimental condition, the reaction was performed twice, one for the analysis by the dioctyl phthalate column, the other for the analysis by the active carbon column. Hydrogen could not be analyzed because it was used as the carrier gas. Also, water and peroxide could not be analyzed owing to their condensation.

The measurements of the infrared spectra were carried out with a Koken DS 301 spectrometer equipped with NaCl prism.

Results

Reproducible results were obtained after a few runs had been performed. After a run had finished the vessel had been evacuated for about 40 minutes in order to remove the effects of the previous reaction. These cares were taken to obtain good reproducibility.

The oxidation reactions of propylene and acrolein were carried out for the mixtures of 53.4% propylene with oxygen and 43.8% acrolein with oxygen at 371 and 319°C respectively. The total pressure increases after short induction periods. Toward the end of the reaction, the rate of

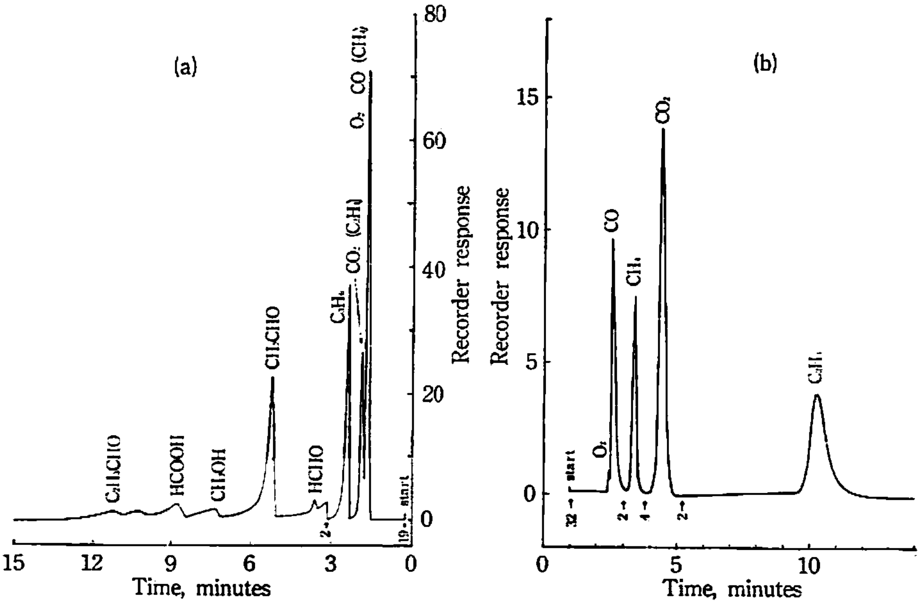

Fig. 2 Chromatograms of the mixture of 53.4% propylene with oxygen (reacted at 371°C for 3 minutes)
carrier gas: hydrogen
flow rate: 40 ml/min
(a) analysis using dioctyl phthalate column at 87°C
(b) analysis using active carbon column at 120°C

pressure increase decreased and reached the limiting values of 29.1 and 12.3 cmHg for the mixtures of propylene (initial pressure: 25.8 cmHg) and of acrolein (initial pressure: 10.4 cmHg) respectively.

By carrying out a series of runs and interrupting the reactions at appropriate time intervals, the gas mixtures were analyzed by gas chromatography. Their typical chromatograms are shown in Figs. 2 and 3 for the mixtures of propylene with oxygen and acrolein with oxygen respectively. Figs. 2(a) and 3(a) indicate the chromatograms of the gases separated by using the dioctyl phthalate column, while Figs. 2(b) and 3(b) show those separated by using the active carbon column.

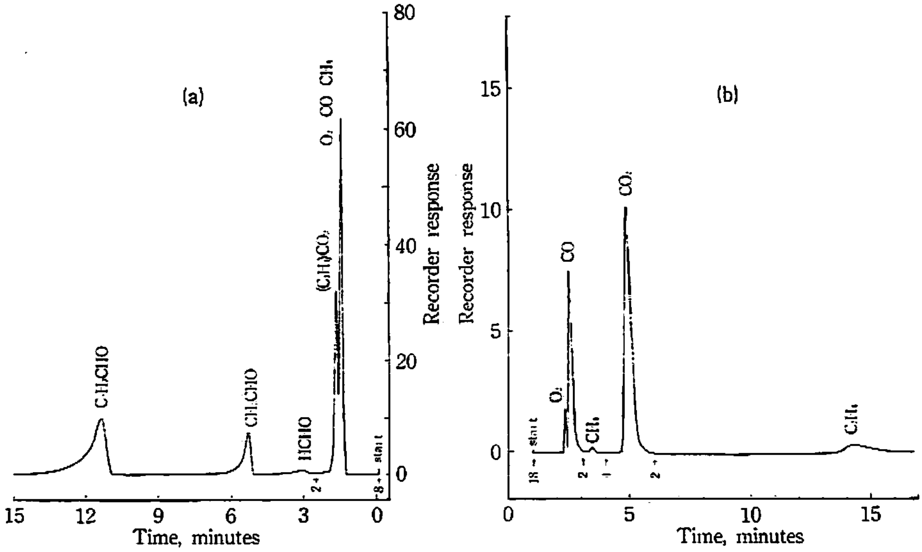

Fig. 3 Chromatograms of the mixture of 43.8% acrolein with oxygen (reacted at 319°C for 2 minutes)
carrier gas: hydrogen
flow rate: 40 ml/min
(a) analysis using dioctyl phthalate column at 87°C
(b) analysis using active carbon column at 120°C

It is shown in Fig. 2(a) that large amounts of carbon dioxide and acetaldehyde and small amounts of formaldehyde, methanol and formic acid have been produced at 371°C during 3 minutes. A small peak in advance of acrolein corresponds to propylene oxide.* Fig. 2(b) shows large amounts of carbon monoxide, carbon dioxide, methane and ethylene and a small amount of oxygen. Figs. 3(a) and 3(b) show acetaldehyde, formaldehyde, carbon monoxide, carbon dioxide, methane and ethylene.

The sensitivity of the recorder was adjusted appropriately 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 3, which are millivolt necessary to move the pen of the recorder to full scales. The full scales of the ordinates are 100 in Figs. 2(a) and 3(a) and 18 in Figs. 2(b) and 3(b).

The results of a series of experiments at 371°C with the mixture of 53.4% propylene with

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* Propylene oxide is considered to be produced by side reaction, because it appears at almost the end of the reaction.

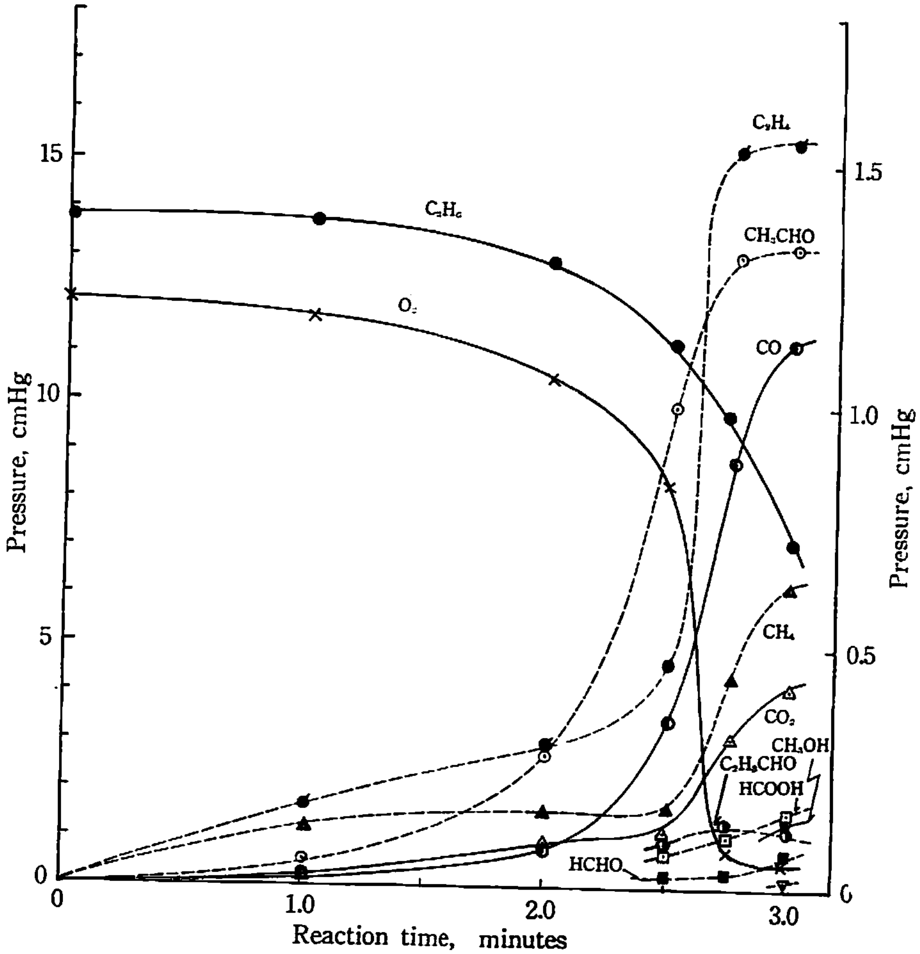

Fig. 4 Progress of reaction on the mixture of 53.4% propylene with oxygen (reacted at 371°C)

oxygen and at 319°C with the mixture of 43.8% acrolein with oxygen are summarized in Figs. 4 and 5 respectively. They are expressed as cmHg partial pressure in the reaction vessel at the reaction temperature. Differences in scale on the ordinates should be noted. Broken lines correspond to the right ordinate in which pressure unit is 10 times as large as that of the left ordinate.

The pressures of propylene and oxygen were each initially 13.7 and 12.1 cmHg. After 2.5 minutes a considerable quantity of oxygen was consumed and the pressures of products became appreciable. Carbon monoxide and carbon dioxide were produced in large amounts, but the amount of the latter is less than that of the former. Methane and ethylene were formed in somewhat smaller amounts. Aldehydes consisted of formaldehyde, acetaldehyde and acrolein, the change of the concentration of acrolein having the maximum. Among them acetaldehyde was predominant. After 3 minutes, small amounts of formic acid and methanol were found. In the oxidation of acrolein, formic acid was not detected.

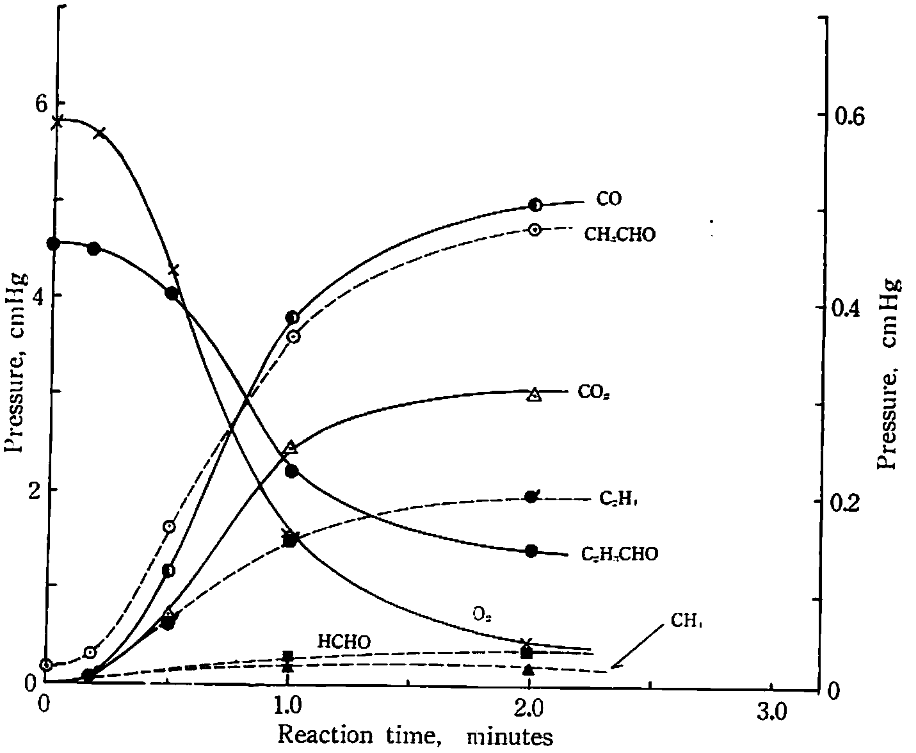

Fig. 5 Progress of reaction on the mixture of 43.8% acrolein with oxygen (reacted at 319°C)

Infrared absorption spectra of the reacted gases were also used to identify the products. For the mixture of propylene reacted, the spectrum showed the presence of carbon monoxide, carbon dioxide, aldehydes, methanol, methane, ethylene, propylene oxide, *etc.* On the other hand, infrared absorption spectrum of the mixture of acrolein reacted showed the presence of carbon monoxide, carbon dioxide, aldehydes, ethylene, methanol, *etc.* Methanol could not be detected by the gas chromatography because of small quantity.

Considerations

From many aspects of the experiments a branched chain reaction is considered to be proceeded by peroxidic mechanism. The most probable initiation reaction is the hydrogen abstraction reaction at the α(C—H) bond as follows.

$$CH_2=CH-CH_3+O_2 \longrightarrow CH_2=CH-CH_2\cdot+HO_2\cdot$$

The allyl radical thus produced may undergo peroxidation by the reactions,

$$CH_2=CH-CH_2\cdot+O_2 \longrightarrow CH_2=CH-CH_2OO\cdot.$$

This peroxide radical has been considered to have two courses (a) and (b) for the further reaction as follows:

(a) By Polyak and Shtern[2]

$$CH_2{=}CH{-}CH_2OO\cdot \longrightarrow CH_2{=}CHO\cdot + HCHO,$$

$$CH_2CHO \xrightarrow{RH} CH_3CHO.$$

(b) By Mullen and Skirrow[3]

$$CH_2{=}CH{-}CH_2OO\cdot \xrightarrow{RH} CH_2{=}CH{-}CH_2OOH,$$

$$CH_2{=}CH{-}CH_2OOH \longrightarrow CH_2{=}CH{-}CHO + H_2O.$$

By the course (a) formaldehyde and acetaldehyde should be produced in about equal amounts, while in the course (b) acrolein is produced by the decomposition of hydroperoxide. The results of this work indicate high ratio of acetaldehyde to formaldehyde not compatible with the mechanism (a). But the amount of the acrolein formed was only small, which was approximately one tenth of that of acetaldehyde. This is perhaps because of the enhanced rate of degradation of acrolein or of the enhanced rate of formation of acetaldehyde.

The oxidation products of acrolein are similar to those of propylene except the formation of formic acid. The oxidation of acrolein is considered to be initiated by hydrogen abstraction from the α(C—H) bond, *viz.*

$$CH_2{=}CH{-}CHO + O_2 \longrightarrow CH_2{=}CH{-}CO\cdot + HO_2.$$

The radical thus produced will give acetaldehyde by the following reactions.

$$CH_2{=}CH{-}CO\cdot \longrightarrow CH_2{=}CH\cdot + CO,$$

$$CH_2{=}CH\cdot + O_2 \longrightarrow CH_2{=}CH{-}OO\cdot \xrightarrow{RH} CH_2{=}CH{-}OOH,$$

$$\begin{array}{l} CH_2{=}CH{-}OOH \longrightarrow CH_2{-}CHO + OH \\ \qquad\qquad\qquad\qquad\qquad \downarrow RH \\ \qquad\qquad\qquad\qquad\quad CH_3CHO. \end{array}$$

The oxidation of acetaldehyde has been investigated in detail by Niclause[4] and a few groups of workers[5]. Radicals will be generated by the aldehyde reacting with oxygen or active radicals by the following mechanism:

$$CH_3CHO + R \text{ or } O_2 \longrightarrow CH_3CO\cdot + RH \text{ or } HO_2,$$

$$CH_3CO\cdot \longrightarrow CH_3\cdot + CO,$$

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[4] M. Niclause, *Contribution à l'etude du mechanisme de la reaction lente entre l'oxygene et une substance organique gazeuse (l'exemple de l'acetaldehyde)*, Paris (1954)

[5] A. Combe, M. Niclause and M. Letort, *Rev. Inst. franç. Pétrole*, **10**, 786 (1955)
N. J. H. Small and A. R. Ubbelohde, *J. Chem. Soc.*, 637 (1953)

$$CH_3CO\cdot + O_2 \longrightarrow CH_3CO\cdot O_2\cdot ,$$

$$CH_3CO\cdot O_2\cdot \xrightarrow{RH} CH_3CO\cdot O_2H,$$

$$\begin{tikzcd}[row sep=small] & CH_3CO_2\cdot + OH \\ CH_3CO\,O_2H \arrow[ur] \arrow[dr] & \\ & CH_3\cdot + CO_2 + OH. \end{tikzcd}$$

But the most probable reaction of the radical $CH_3CO\cdot$ is $CH_3CO\cdot \rightarrow CH_3\cdot + CO$. Then from the radical $CH_3\cdot$, CH_4 and CH_3OH will be produced as follows:

$$CH_3\cdot \xrightarrow{RH} CH_4,$$

$$\begin{tikzcd} CH_3\cdot + O_2 \arrow[r] & CH_3OO\cdot \arrow[r, "RH"] & CH_3OOH \arrow[r] & CH_3O\cdot + OH. \arrow[d, "RH"] \\ & & & CH_3OH \end{tikzcd}$$

The conclusion is that propylene is initially oxidized to acrolein and this degradates and is oxidized through acetaldehyde to the final products.

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