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STUDIES ON OXIDATION REACTION OF PROPYLENE IN THE PRESENCE OF METALLIC SILVER

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Heterogeneous oxidation reaction of propylene catalyzed by silver metal was studied in order to find the difference of mechanisms between homogeneous and heterogeneous reactions. It is proved that the reactions (2) (cf. p. 27) and (4) (cf. p. 28) are homogeneous and reactions (1) (cf. p. 27), (3) (cf. p. 28) and (5) (cf. p. 28) are heterogeneous.

Introduction

Since the beginning of this century, the slow oxidation of hydrocarbons has been studied by many investigators. From their works, it is found that the oxidation reaction proceeds via the intermediate of peroxidic substance.

The homogeneous oxidation of propylene has been extensively studied by Mulcahy and Ridge1), Polyak and Shtern2), Mullen and Skirrow3) and others4)5).

However, a few attempts have been made to investigate the heterogeneous oxidation of propylene.

The authors, therefore, have studied the heterogeneous oxidation reaction of propylene catalyzed by silver metal in order to find out the difference of the mechanisms between homogeneous and heterogeneous oxidation reaction.

Experimentals

Materials The propylene used was obtained from the dehydration of propyl alcohol catalyzed by the alumina catalyst. The purity of the gas was found by analysis to be about 99%.

The oxygen used was obtained from a commercial cylinder. The purity of the gas was 99.4%. The silver catalyst used was the silver metal wire and its purity was 99.99%. The diameter of this silver metal wire was 0.5 mm. The silver metal wire used was cut about 12 cm in length. These short wires were divided into three groups, having different numbers of these short wires. Each group had the weight of 0.975 gr. 14.014 gr and 34.507 gr, respectively. The ratio of the surface areas of these groups was 1 : 14.3 : 35.5. Before those were used as a catalyst of the reaction, they were heated to about 700°C

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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.*, A **244**, 312 (1958)
4) M. F. R. Mulcahy and M. J. Ridge, *Trans. Faraday Soc.*, **49**, 1297 (1953)
5) S. Kusuhara, *This Journal*, **31**, 34 (1961)

in vacuum for about 1 hr in order to be inactivated. After this treatment those were oxidized for about 2 hrs with oxygen at 270°C, and reduced for 5 hrs at 150°C with hydrogen.

Apparatus and procedures A schematic diagram of the main parts of the reaction apparatus is shown in Fig. 1. In the gas mixing chamber, the gas mixture of a desired composition was prepared and transferred into the storage B at a desired pressure by means of a toepler pump. In order to minimize the dead space, a capillary tube was used for connecting the reaction vessel V with the cock C and with the manometer M. The cylindorical reaction vessel V made of quartz (3.8 cm in inner diameter and 15 cm in length) was placed horizontally in the electric furnace F. The reaction vessel was evacuated to about 10^{-3} mmHg in 20 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 into the pre-evacuated reaction vessel V to give a definite initial pressure by operating the cocks C_1 and C_2.

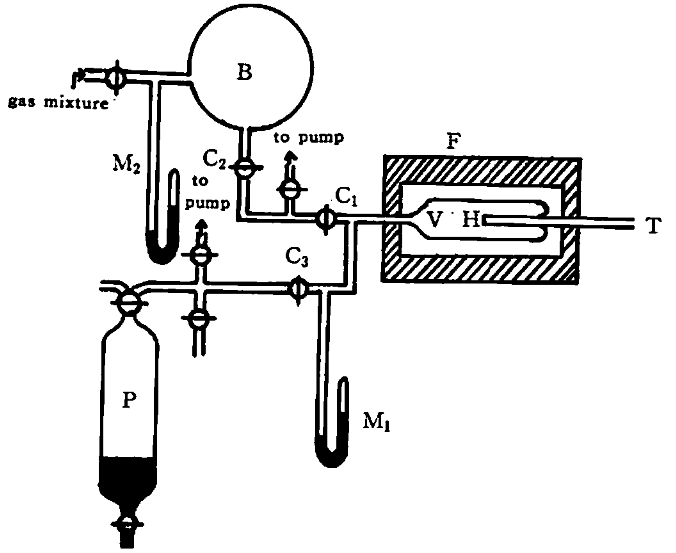


Fig. 1 Layout of the apparatus.
B: gas storage.
C_1, C_2, C_3: glass cocks.
F: electric furnace.
H: narrow tube.
M_1, M_2: mercury manometer.
P: toepler pump.
T: thermocouple.
V: reaction vessel.

The initial pressure and the pressure change were measured by the manometer M_1. After a definite time interval, the reaction products were expanded into a large-volume toepler pump P (about 1 liter in volume). Then the gas was collected into a sampling vessel for gas chromatographic analysis.

The gas chromatograph apparatus constructed in our laboratory has a thermal conductivity cell as a detector. The other gas chromatograph made by Yanagimoto Co., Ltd. (model G. C. G. 2) was also used. A 4.8 meter column in the former apparatus was packed with 40~60 mesh fire bricks permeated with 40 weight % dioctyl phthalate, being used for the analysis of propylene, aldehydes, propylene oxide, butadiene and alcohol. For the analysis of the rest of the gases e. g. O_2, CO_2, CO, CH_4 and C_2H_4, a 2 meter column of the latter apparatus packed with 30~50 mesh active carbon was employed. In the same experimental condition, the reaction was performed twice, one for the analysis in the case of the dioctyl phthalate column, the other for the analysis in the case of the active carbon column. In both cases hydrogen was used as a carrier gas.

Therefore, hydrogen could not be analyzed. Besides water and peroxide could not be analyzed owing to their low vapor pressure. After each run, the reaction vessel was evacuated for about 10 minutes in order to remove the effects of the previous reaction. After 20 runs, silver catalysts were oxidized at 270°C for about 2 hrs and reduced at 150°C for about 5 hrs with hydrogen. By taking these cares, the results gave good reproducibility.

Results

The propylene oxidation reaction was performed for the mixture of 50% propylene with oxygen at 350°C, 400°C, and 450°C, respectively. The typical pressure-time curves are shown in Fig. 2. They had the ordinary pressure change, consisting of a period of negligible pressure change (the induction period)

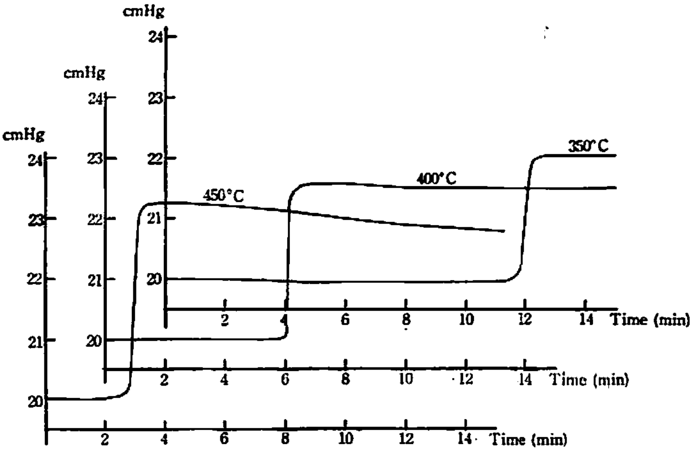


Fig. 2 Total pressure change of reaction gas mixture

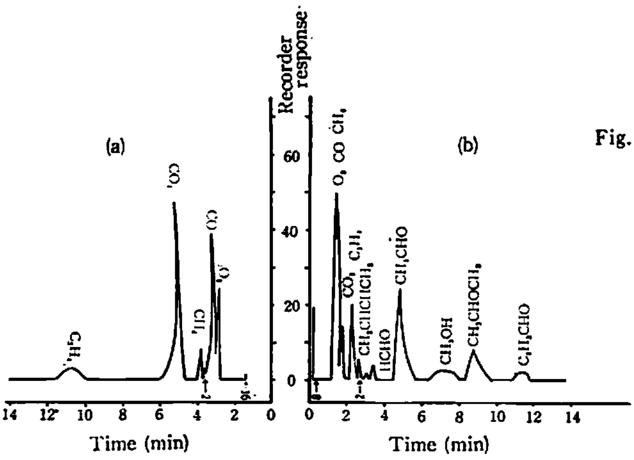


Fig. 3 Chromatograms of reaction products
carrier gas: hydrogen
flow rate: 40 m*l*/min
(a) analysis using active carbon column at 140°C
(b) analysis using dioctyl phthalate column at 80°C

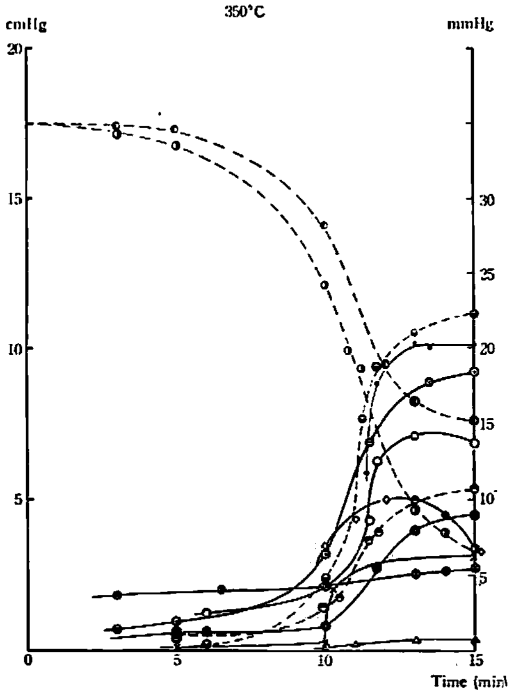


Fig. 4

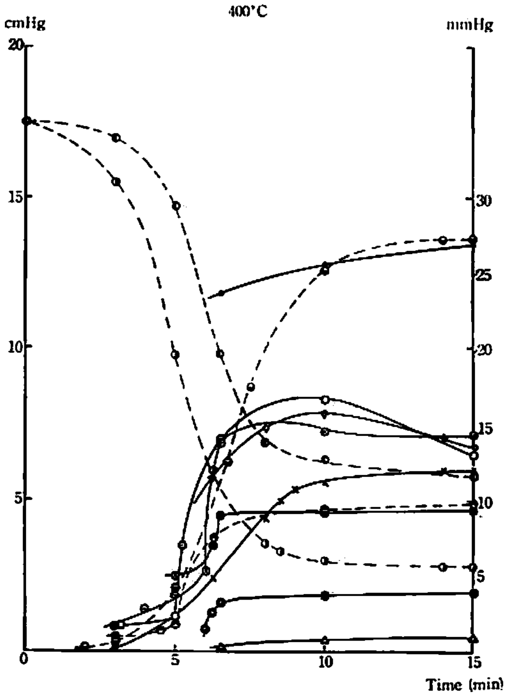


Fig. 5

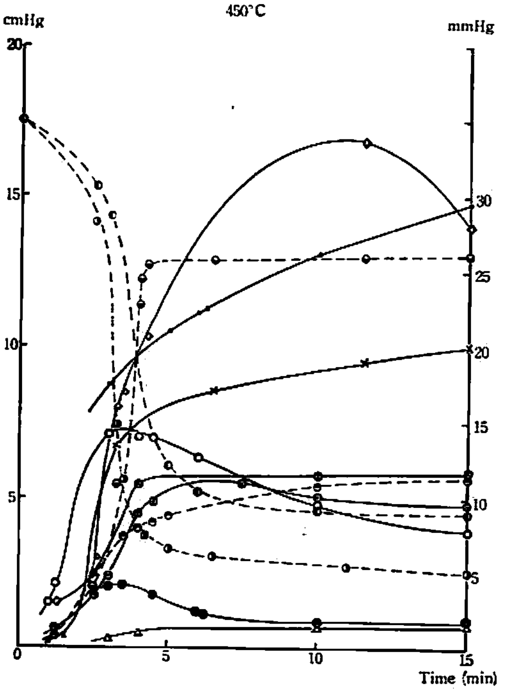


Fig. 6

Fig. 4~6 Processes of reaction
(catalyst : 0.975 g)

◐ C_3H_6
◑ O_2
◒ CO
◓ CO_2
● C_2H_3CHO
○ CH_3CHOCH_2
◎ CH_3OH
⊙ CH_3CHO
⊗ HCHO
◇ C_2H_4
△ $CH_2CHCHCH_2$
× CH_4

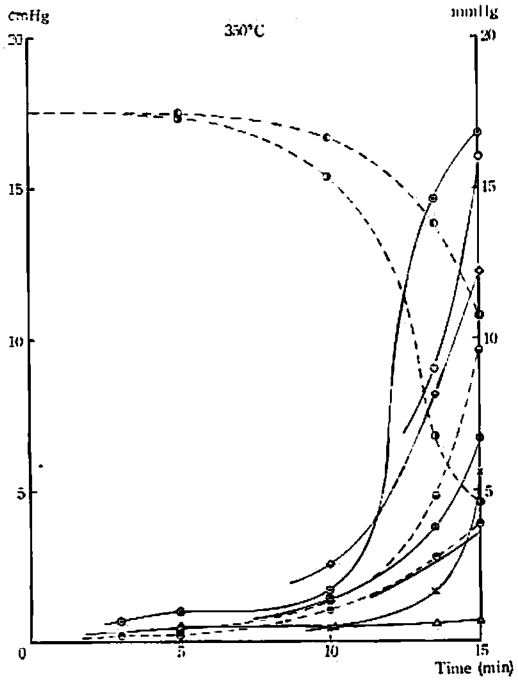


Fig. 7

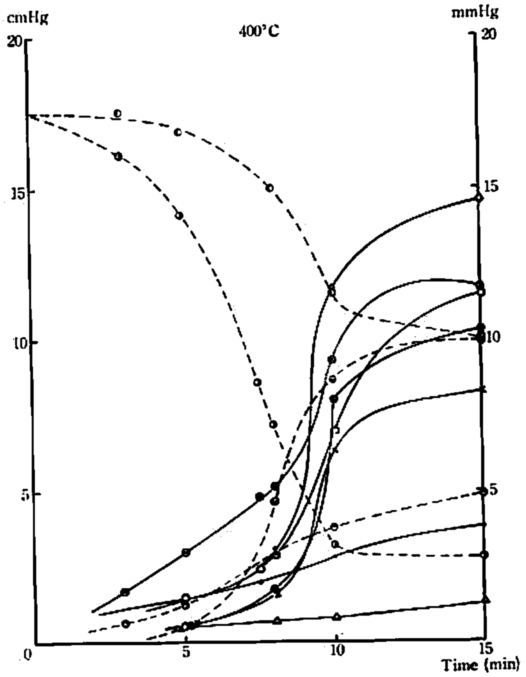


Fig. 8

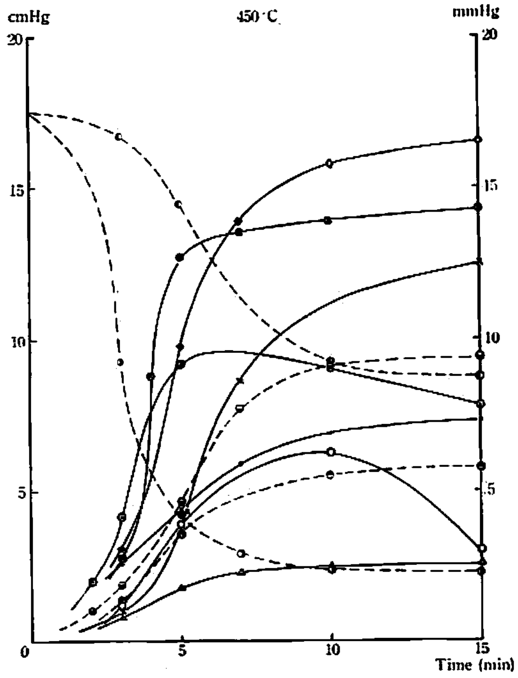


Fig. 9

Fig. 7∼9 Processes of reaction (catalyst: 14.014 g)

◐ C_3H_6
◑ O_2
◒ CO
◓ CO_2
● C_2H_3CHO
○ CH_3CHOCH_2
◎ CH_3OH
⊙ CH_3CHO
⊗ $HCHO$
◇ C_2H_4
△ $CH_2CHCHCH_2$
× CH_4

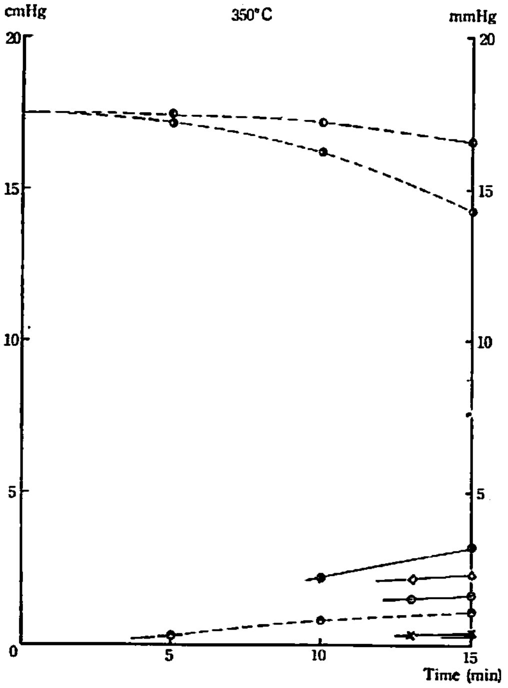


Fig. 10

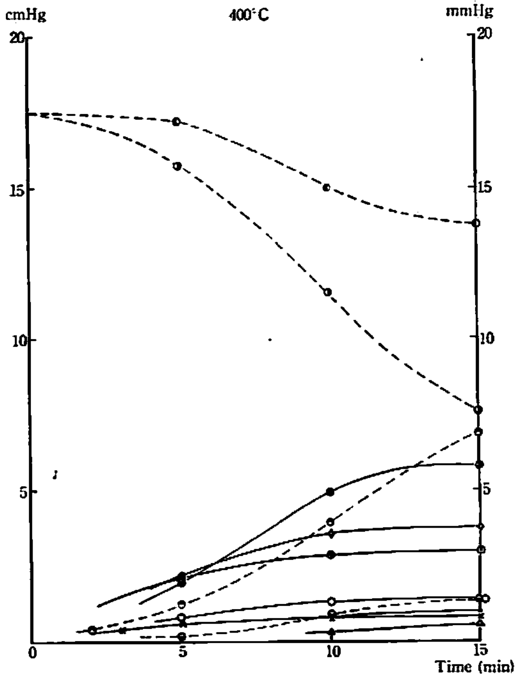


Fig. 11

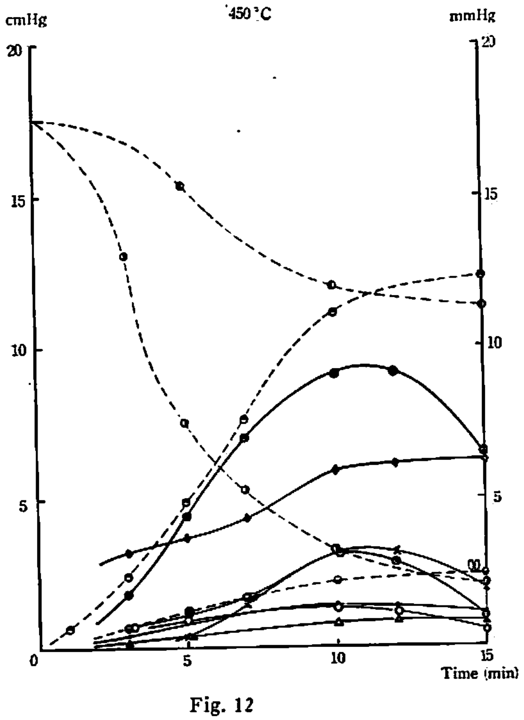


Fig. 12

Fig. 10~12 Processes of reaction
(catalyst: 34.507 g)

◐ C_3H_6
◑ O_2
◒ CO
◓ CO_2
● C_2H_3CHO
○ CH_3CHOCH_2
◎ CH_3OH
⊙ CH_3CHO
⊗ HCHO
◇ C_2H_4
△ $CH_2CHCHCH_2$
× CH_4

followed by rapid acceleration to a maximum rate. Then the rate apparently falls to zero.

The induction period reduced with the elevation of the reaction temperature. The properties and quantities of various reaction products were found by the analysis of the sample obtained by interupting the reaction at a definite time. Their typical gas chromatograms are shown in Fig. 3. While Fig. 3(a) shows the chromatograms of the gases separated by using the active carbon column, Fig. 3(b) shows those separated by using the dioctyl phthalate column. Fig. 3(a) shows large amounts of carbon monoxide, carbon dioxide, oxygen, and small amounts of methane and ethylene. Fig. 3(b) shows large amounts of carbon dioxide, acetaldehyde and small amounts of formaldehyde, methanol, propylene oxide, butadiene, and acrolein. The sensitivity of the recorder was adjusted appropriately to make each peak area as large as possible within the width of the chart paper. Sensitivity is shown by the number below the arrow signs given in Fig. 3, which shows the required mV to move the pen of the recorder to full scale. The variations of the reaction products at 350°C, 400°C, and 450°C formed from the mixture of 50% propylene with oxygen are shown in Figs. 4, 5, to Fig. 12. Figs. 4, 5, and 6 show the case of 0.975 gr catalyst and Figs. 7, 8, and 9 show the case of 14.014 gr catalyst. They also show the variations of the reaction products of 34.507 gr catalyst in Figs. 10, 11, and 12. In these figures, the ordinate shows partial pressure in mmHg on sampilng.

Differences in scale on the ordinates of both sides should be noticed. The curves expressed with full lines refer to the right ordinate in which the pressure unit is 5 times as large as that of the left ordinate in Figs. 4, 5 and 6, and 10 times as large as that of the left ordinate in Figs. 7, 8, 9, 10, 11 and 12. The initial pressures of propylene and oxygen are both 10 cmHg. An appreciable amount of each gas is consumed at the end of the induction period, but considerable quantities of propylene and oxygen remain at the end of the reaction. The system, although not at equilibrium in the thermodynamic sense, is in a state where any further reactions are negligible. The quantities of the products in oxidation processes, particularly peroxide, water and hydrogen, were not definitely produced. The carbon balances at the reaction time of 10 minutes and of 15 minutes are shown in table 1.

The results of the reaction of 0.975gr catalyst Carbon monoxide and carbon dioxide are produced in large amounts, but the amount of the latter is less than that of the former.

At each reaction temperature, acetaldehyde is formed rapidly at the end of the induction period, but it decreases slightly with reaction time. The amount of acetaldehyde decreases with the rise of reaction temperature. The amount of acetaldehyde is less than that of formaldehyde at 450°C. Formaldehyde is formed suddenly, and it increases slightly with the reaction time at each temperature. The amount of formaldehyde increases with the rise of reaction temperature. The amount of methanol decreases with rising reaction temperature. On the contrary, the amount of formaldehyde increases. The sum of the amount of methanol and formaldehyde is nearly constant at each reaction temperature. At each temperature, acrolein is formed quickly at the end of the induction period and increases with reaction time at each temperature. At each temperature, the amount of ethylene increases and then decreases with the lapse of reaction time. The amount of butadiene increases slightly as temperature increases. Methane formation occurs rapidly at the end of the induction period but the amount of methane does not increase remarkably with the lapse of the reaction time at each temperature.

Table 1 Carbon balance.

Catalyst 0.975 gr

Reaction temperature	Reaction time (min)	Total mumbers of carbon atom ($\times 10^{-17}$)		$\frac{\text{Produced}}{\text{Consumed}}$ (%)
		Consumed	Produced	
350°C	10	60	48	80
	15	168	196	115
400°C	10	190	216	113
	15	199	205	103
450°C	10	214	235	109
	15	222	235	106

Catalyst 14.014 gr

Reaction temperature	Reaction time (min)	Total numbers of carbon atom ($\times 10^{-17}$)		$\frac{\text{Produced}}{\text{Consumed}}$ (%)
		Consumed	Produced	
350°C	10	15	17	113
	15	182	153	83
400°C	10	102	118	112
	15	128	128	100
450°C	10	140	153	109
	15	148	152	103

Catalyst 34.507 gr

Reaction temperature	Reaction time (min)	Total numbers of carbon atom ($\times 10^{-17}$)		$\frac{\text{Produced}}{\text{Consumed}}$ (%)
		Consumed	Produced	
350°C	10	5.1	5.8	113
	15	15	14	93
400°C	10	43	44	102
	15	63	64	101
450°C	10	94	99	105
	15	105	100	95

The results of the reaction of 14.014gr catalyst Carbon monoxide and carbon dioxide are produced in large amounts, but the amount of the latter is less than that of the former, and the difference of the quantities between carbon monoxide and carbon dioxide are less than that in case of 0.975 gr catalyst. At each temperature, acetaldehyde is formed rapidly at the end of the induction period, and then it decreases as reaction temperature increases. As the reaction time increases, the amount of acetaldehyde increases gradually up to the maximum yield and then begins to decrease. On the contrary, the amount of formaldehyde increases with the rise of temperature. At 450°C the amount of formaldehyde becomes larger than that of acetaldehyde. Methanol formation is not found in this case. At each temperature, acrolein is formed and increased slightly with the lapse of reaction time. At each temperature of reaction, ethylene and methane are formed rapidly at the end of the induction period. The amount of ethylene is always larger than that of methane at each temperature and reaction time. The amout of butadiene increases according to the temperature rise but the quantity of butadiene is very small.

The results of the reaction of 34.507gr catalyst Carbon dioxide is produced in large amount. On the contrary, the quantity of the carbon monoxide formed is small. At each temperature, the amount of formaldehyde is greater than that of acetaldehyde. The amount of acetaldehyde increases gradually up to the maximum yield, and then begins to decrease with the lapse of reaction time. At each temperature, the amount of ethylene is greater than that of methane. Acrolein, propylene oxide and butadiene are formed very slightly at each temperature, especially propylene oxide and butadiene are too small to be measured by means of a gas chromatograph.

Discussion

Judging from the presence of the induction period, the shape of the pressure-time curve and many other aspects of the experiments, branched chain reactions are considered to proceed according to peroxidic mechanism. It is known that hydrogen abstruction reactions have low activation energies. So the most probable initiation reaction is the hydrogen abstruction reaction at the α(C–H) bond.

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

This reaction which may occur heterogeneously is most probable3). The allyl radical thus produced may undergo peroxidation by the reaction,

$$CH_2{=}CH{-}CH_2\cdot+O_2 \longrightarrow CH_2{=}CH{-}CH_2OO\cdot$$

It has been considered that there are two courses for further reaction of this peroxidic radical:

(1) by Polyak and Shtern2),

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

$$CH_2{=}CHO\cdot \xrightarrow{RH} CH_3CHO$$

(2) by Mullen and Skirrow3),

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

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

By the course (1), formaldehyde and acetaldehyde should be produced in approximately equal amounts, while by the course (2), acrolein is produced by the decomposition of hydroperoxide.

The acrolein thus formed will be attacked by oxygen or any other radical and gives acetaldehyde according to the following sequence of the reactions.

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

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

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

$$CH_2{=}CHOOH \longrightarrow \cdot CH_2{-}CHO+OH \xrightarrow{RH} CH_3CHO$$

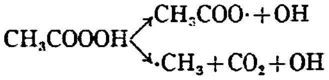
The mechanism of the oxidation reaction of acetaldehyde produced by the course (1) and the above reactions had been investigated by Niclause and others6~9). Acetaldehyde is attacked by oxygen or radicals and is decomposed to some radicals by the following mechanism,

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

The reaction of acetyl radical thus produced is considered to react through the course (3) or (4):

$$(3)\quad CH_3CO\cdot + O_2 \longrightarrow CH_3COOO\cdot$$

$$CH_3COOO\cdot \xrightarrow{RH} CH_3COOOH$$



$$CH_3COOOH \begin{cases} \nearrow CH_3COO\cdot + OH \\ \searrow \cdot CH_3 + CO_2 + OH \end{cases}$$

$$(4)\quad CH_3CO\cdot \longrightarrow CH_3\cdot + CO$$

The reaction (4) is the main source of carbon monoxide in the case of homogeneous reaction3). The present results show that when a small amount of silver catalyst is used, the higher ratio of acetaldehyde to formaldehyde is obtained. The ratio of carbon monoxide to carbon dioxide decreases as the amount of catalyst increases. So the course (2) is assumed to be predominant over the reaction in the presence of a small amount of catalyst or in the case of non-catalyst (mainly homogeneous) while the course (1) seems to be predominant over the reaction of a large amount of catalyst (mainly heterogeneous) and the route of the oxidation reaction of acetaldehyde in the case of the homogeneous reaction or a small amount of catalyst is considered to be course (4). On the other hand, according as the amount of catalyst increases, course (3) is considered to be predominant. From the methyl radical produced by the above reaction, methane and methanol are formed in the following mechanism:

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

$$CH_3\cdot + O_2 \longrightarrow CH_3OO\cdot \xrightarrow{RH} CH_3OOH$$

$$CH_3OOH \longrightarrow CH_3O\cdot + OH$$

$$CH_3O\cdot \xrightarrow{RH} CH_3OH$$

As generally known, methanol is easily oxidized in the presence of silver catalyst and produces formaldehyde.

The mechanism of the reaction is as follows:

$$(5)\quad CH_3OH + O_2 \longrightarrow \cdot CH_2OH + HO_2\cdot$$

$$\cdot CH_2OH + O_2 \longrightarrow HCHO + HO_2\cdot$$

The mechanism of the oxidation reaction of formaldehyde produced by course (1) and that of the

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

7) A. Combe, M. Niclause and M. Letort, *Rev. Inst. franç. Pétrole*, 10, 786 (1955)

8) N. J. H. Small and A. R. Ubbelohde, *J. Chem. Soc.*, 637 (1953)

9) C. A. McDowell and J. M. Thomas, *ibid.*, 2217 (1949)

above reaction have been investigated by Norrish[10], Scheer[11] and others[12~16]. Formaldehyde is attacked by oxygen or radicals and is decomposed to some radicals by the mechanisms:

$$\mathrm{HCHO+O_2\ or\ R \longrightarrow HCO\cdot + HO_2\cdot\ or\ RH}$$

$$\mathrm{HCO\cdot + O_2 \longrightarrow HO_2\cdot + CO}$$

$$\mathrm{HCO\cdot + O_2 \longrightarrow HCO_3\cdot}$$

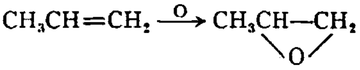
$$\mathrm{HCO_3\cdot \xrightarrow{RH} HCO_3H}$$

The mechanism of ethylene formation and butadiene is considered as follows:

$$\mathrm{CH_2{=}CH\cdot \xrightarrow{RH} CH_2{=}CH_2}$$

$$\mathrm{CH_2{=}CH\cdot + CH_2{=}CH\cdot \longrightarrow CH_2{=}CH{-}CH{=}CH_2}$$

The formation of propylene oxide is considered to be a side reaction as follows:



$$\mathrm{CH_3CH{=}CH_2 \xrightarrow{O} CH_3\underset{\diagdown\, O\, \diagup}{CH{-}CH_2}}$$

This reaction seems to be accelerated by silver catalyst.

In conclusion, by using an appropriate amount of silver catalyst, (e.g. 14.014 gr), the rate of formation of formaldehyde, ethylene, butadiene and propylene oxide is preferably accelerated. On the contrary, in the case of excess amount of silver catalyst (e.g. 34.507) used, each reaction is generally supppressed but the formation reaction of carbon dioxide becomes much faster.

With the increase of the catalyst the ratio of acetaldehyde to formaldehyde and that of methanol to formaldehyde decrease, while the ratio of formaldehyde to acrolein and that of carbon dioxide to ethylene increase.

From these ratios of the products, it is proved that reactions (2) and (4) are homogeneous reactions and reactions (1), (3), and (5) are heterogeneous reactions.

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[10] J. F. McKellar and R. G. W. Norrish, *Proc. Roy. Soc.*, A **254**, 147 (1960)

[11] M. D. Scheer, "*5th Symposium on combustion*" p. 435

[12] E. C. A. Horner, D. W. G. Style and D. Summers, *Trans. Faraday Soc.*, **50**, 1201 (1954)

[13] C. F. H. Tipper, *Quart. Rev.*, **11**, 313 (1957)

[14] Harding and R. G. W. Norrish, *Proc. Roy. Soc.*, A **212**, 291 (1952)

[15] D. W. E. Axford and R. G. W. Norrish, *ibid.*, A **192**, 518 (1948)

[16] D. W. G. Style and D. Summers, *Trans. Faraday Soc.*, **42**, 388 (1946)