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# The Gas-phase Oxidation of Propylene in an Inert Fluidized Bed Reactor under Pressure. The Effects of the Reaction Conditions on the Formation of Oxidation Products*[1]

Etsuro ECHIGOYA,*[2] Mitsuo MASAI and Kiyoshi MORIKAWA

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo*

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The oxidation of propylene is studied in an excess-propylene atmosphere under pressure, using an inert fluidized bed reactor. The effects of the temperature, the pressure, and the concentration of oxygen on the reaction were examined. The so-called "negative temperature coefficient" is clearly observed with relation to the rate of the oxidation of propylene and the rates of the formation of acetaldehyde, propylene oxide, acrolein, carbon monoxide, methane, and ethylene. Therefore, the reaction courses involving these may be regarded as radical-chain reactions. Little effect of the pressure is observed. The molar fraction of oxygen exerts a profound effect on the yields of acetaldehyde, propylene oxide, and acrolein.

Many products such as aldehydes, epoxides, alcohols, and acids, are obtained in the course of the autoxidation of hydrocarbons in the gas phase.[1] In this paper, we will attempt to determine the reaction conditions which will give the optimum yields of acetaldehyde, propylene oxide, and acrolein.

Kamiya has reported that, in narrow tubular reactors, acetaldehyde, propylene oxide, acrolein, and allyl alcohol are produced in the oxidation of propylene under pressure with a small amount of oxygen.[2-4] On the other hand, propylene oxide has not been formed in the oxidation of propylene under reduced pressure.[1a]

A fluidized bed reactor has a large heat-transfer coefficient; therefore, the temperature gradient in the bed is almost negligible, except for the gas-inlet section, and the temperature in the reactor can be easily controlled and clearly defined. The fluidized bed reactor is therefore well-suited to the study of highly exothermic reactions, such as the autoxidation of propylene in a flow system.

In the present paper, the effects of the temperature, the pressure, and the molar fraction of oxygen on the reaction results are studied using a fluidized bed reactor with inert particles such as silicon carbide. In these experiments, the negative temperature coefficient is clearly observed, on the basis of this fact,[1b] a radical-chain mechanism is suggested for the formation of all the oxidation products except carbon dioxide. It is suggested that excess propylene is an important factor in producing good yields of acetaldehyde and propylene oxide, and also that acetaldehyde plays an important role in the formation reaction of propylene oxide.

## Experimental

**Materials.** Propylene gas containing 5 mol% of propane, 1.3 mol% of ethane, and 0.2 mol% of $C_4$ hydrocarbons was supplied by the Nippon Petrochemicals Co., Ltd. The oxygen was obtained commercially. Fine particles of silicon carbide supplied by the Mitsui Mining and Smelting Co., Ltd., were washed by diluted nitric acid and water prior to the experiments.

**Procedures.** The flow sheet of the reaction apparatus is shown in Fig. 1. The propylene gas and oxygen were mixed after their flow rates had been measured and then introduced into the bottom of the reactor, R. The pressure of the product gas was reduced to a normal pressure by V, the reducing valve. The reduced gas was led to the cold traps, $T_1$ and $T_2$, and then to the wet gas meter. The linear velocity of the reactant gas was 1.5 cm/sec under the conditions of the oxidation experiments (on an empty-tube basis).

The reactor was made of stainless steel.*[3] It was 56.3 mm i.d. and 700 mm long. The reactor contained 600 cc silicon carbide (greenish color) of 100—150 mesh (Tyler) as fluidizing particles, this is considered to be inert for this kind of reaction. The minimum fluidization velocity of the particle was measured as 1.13 cm/sec (on an empty tube basis), using nitrogen at a normal

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*[2] Present address: Department of Chemical Engineering, Faculty of Engineering, Tokyo Institute of Technology.

1) V. Ya. Shtern, "The Gas-Phase Oxidation of Hydrocarbons," translated by M. F. Mullins, la) pp. 527—564, 1b) pp. 105—110, 480—492, Pergamon Press, Oxford (1964).

2) Y. Kamiya, *Sekiyu Gakkai Shi (J. Japan Petrol. Inst.)*, **5**, 18 (1962).

3) Y. Kamiya, *ibid.*, 398.

4) Y. Kamiya, *Bull, Japan Petrol. Inst.*, **5**, 13 (1963).

*[3] JIS SUS 27, AISI 304, Austenite.

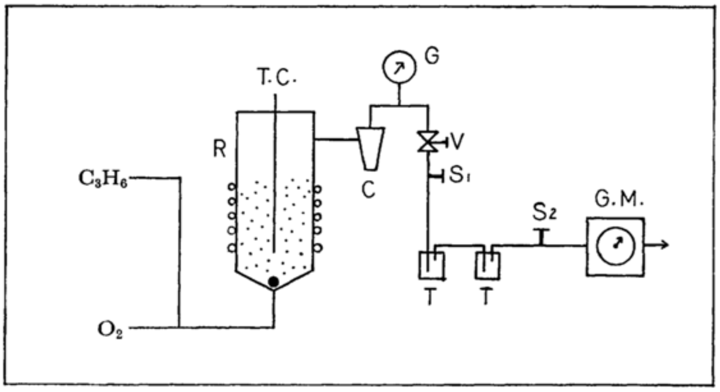

Fig. 1. Flow sheet of the reaction apparatus.
C, cyclon; G, Bourdon guage; G. M., wet gas meter; R, fluidized bed reactor; $S_1$ and $S_2$, sampling points; T, cold traps (−30—−10°C); T. C., thermocouple; V, needle valves.

temperature and pressure. The quiescent height of the fluidized bed was 320 mm. The reactor was heated electrically from outside, and controlled within ±5°C. No temperature gradient along the gas flow was observed except for the bottom gas-inlet section. The temperature was measured using chromel alumel thermocouples. The section from the outlet of the reactor to the sampling point, $S_1$, was kept at 100—120°C. The pressure of the reaction system was measured using a pressure gauge of the Bourdon type. The pressure was kept within $\pm 0.1$ kg/cm$^2$ by means of the pressure control valve, V.

**Analysis.** The product gas was analyzed in two gas chromatographs, using hydrogen as the carrier gas. Acetaldehyde, propylene oxide, and acrolein were analyzed using a 2.5 m dioctyl phthalate column (30 wt% on celite 545) at 80°C. The sample for this analysis was taken from $S_1$, using a glass syringe maintained at 40—50°C. The determinations of these three components were carried out precisely using absolute working curves calibrated every day. Oxygen, carbon monoxide, methane, and carbon dioxide were analyzed using a 2 m, activated charcoal column at 80°C. A fraction composed of oxygen plus carbon monoxide, and five fractions each composed of methane, ethane, ethylene, propane, and propylene respectively were separated using the 2.5 m column of activated alumina with 1.5 wt% squalane at 40°C. The samples for these two analysis were taken from $S_2$ by glass syringes.

## Results and Discussion

The oxidation reaction was observed above 300°C. The temperature at the point 15 cm above the fluidizing surface was always kept under 240°C so as to minimize the oxidation reaction in the gas phase over the fluidizing surface; therefore, almost all the oxidation reaction is considered to proceed in the fluidizing bed.

Small amounts of polymerized substances were observed in every experiment, but they were not examined further, for the carbon balances of the oxidation experiments were almost entirely satisfactory, as Table 1 and Table 2 show. The acids were also not analyzed, because, Kamiya's results[3)] indicate that acid formation is small.

TABLE 1. CARBON BALANCES AT 350°C

| Press. atm | Carbon balances reacted gas/reactant gas |
|---|---|
| 2.0 | 98.6 % |
| 2.5 | 102 |
| 3.0 | 102 |
| 3.5 | 97.1 |
| 4.5 | 101 |

TABLE 2. CARBON BALANCES AT 350°C

| Mol. fraction of $O_2$ | Carbon balances reacted gas/reactant gas |
|---|---|
| 0.10 | 101 % |
| 0.15 | 102 |
| 0.20 | 94 |
| 0.25 | 91 |
| 0.30 | 90 |

The effects of the surface of the fluidizing particles are considered to be small on the basis of other data, which will be discussed in a later paper.

The experimental results described below are represented using a *yield* (%) of a product determined as follows:

$$\mathit{yield} = \frac{\text{moles of a product}}{\text{moles of propylene in feed}} \times 100$$

**The Effect of the Pressure.** The reactant gas consisted of 15 vol% oxygen and 85 vol% propylene gas. The experiments were carried out at the reaction temperatures of 300, 350, and 400°C in the pressure range of 1.5—4.5 atm. Figures 2—4 show the effects of the pressure on the yields of

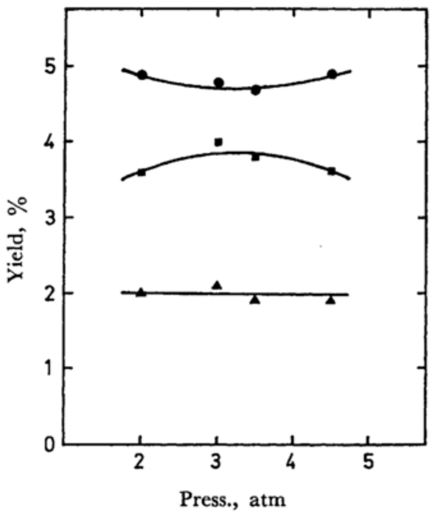

Fig. 2. Effect of press. on the yields of AA, PO and Acr at 300°C with mol fraction of $O_2$: 0.15.

● AA ■ PO ▲ Acr

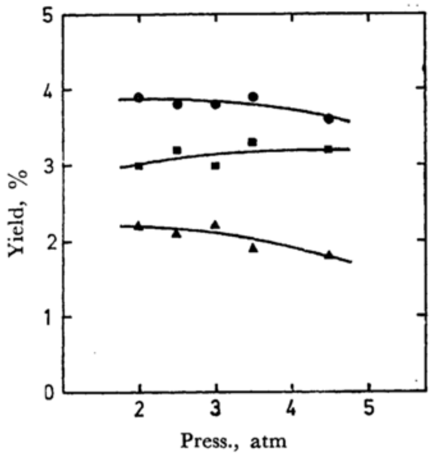

Fig. 3. Effect of press. on the yields of AA, PO and Acr at 350°C with mol fraction of $O_2$: 0.15.

● AA ■ PO ▲ Acr

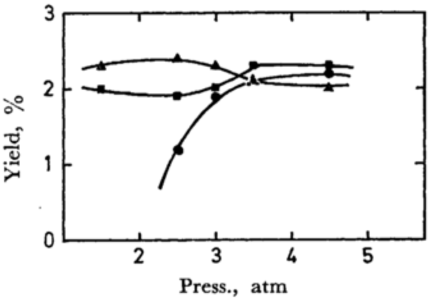

Fig. 4. Effect of press. on the yields of AA, PO and Acr at 400°C with mol fraction of $O_2$: 0.15.

● AA ■ PO ▲ Acr

acetaldehyde (AA), propylene oxide (PO), and acrolein (Acr).

At 300 and 350°C, little effect of the pressure is observed on the yields of AA, PO, and Acr, as Figs. 2 and 3 show. This observation differs markedly from that using narrow tubular reactors reported by Kamiya,[2-4] in his experiments the concentrations of AA and PO in the reacted gas showed steep maxima at 3—4 atm.[*4] The yield of AA show a rapid decrease from 3 atm with the decrease in the pressure at 400°C, as is shown in Fig. 4. The yields of AA and PO decrease with a rise in the temperature, as may be seen by comparing Figs. 2—4.

A small effect of the pressure is observed on the conversion of propylene, as is shown in Fig. 5. The conversion of propylene at 400°C is lower than those at 300 and 350°C, as Fig. 5 shows. At 350°C the formation reactions of carbon monoxide, carbon dioxide, methane, and ethylene are also indifferent to the reaction pressure in the same pressure region. These results also differed markedly from those of Kamiya, his showed that the conversion of propylene and the concentrations of carbon monoxide, carbon dioxide, methane, and ethylene in reacted gas increased as the reaction pressure increased from 2 to 4 atm, reaching constant values beyond 4 to 6 atm at 315°C (1400 $hr^{-1}$ of space velocity).[2] The rather slow rates of the oxidation reaction in the low-pressure region observed by Kamiya are very different from the present results, where the effect of reaction pressure is very small at 300 and 350°C. This difference is probably to be attributed to the effect of fluidizing particles, and/or to a difference in the surface area-to-volume ratio of the reactor, which is a measure of the wall effect of the reactor; this ratio differs by a factor of about seven. The reasons for considering the wall effect are as follows: the active species can easily reach the reactor wall rather than encounter propylene, *etc.* in Kamiya's narrow reactor (about 8 mm[2]) at a low pressure; when the pressure is sufficiently high, *i. e.*, above about 4 atm, the diffusion to the wall becomes minor.

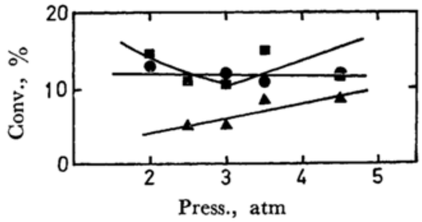

Fig. 5. Effect of press. on the conv. of $C_3H_6$ with mol fraction of $O_2$: 0.15.

● 300°C ■ 350°C ▲ 400°C

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[*4] The yield and the concentration in the reacted gas show similar trends.

Therefore, result described above is observed. At present we have no clue by which to evaluate these two effects.

Table 1 shows good carbon balances of the oxidation experiments at 350°C.

**The Effect of the Concentration of Oxygen.** The experiments were carried out at 300, 350, and 400°C under 3 atm in the range of the molar fraction of oxygen from 0.1 to 0.35. The control of the reaction temperature and pressure became difficult with the increase in the molar fraction of oxygen in the reactant gas above 0.25 at 300 and 350°C. On the contrary, the reaction proceeded quietly at 400°C over the same range of concentration.

As Figs. 6—8 show, the yields of AA and PO increase at first, reach maxima and then decrease as the concentration of oxygen increases. A comparison of these figures indicates that the maximum yield of Acr probably shifts to the side of higher oxygen concentration. The yield of Acr decreases with a rise in the temperature (Figs. 6—8). The yields of AA and PO vary similarly with the change in the oxygen concentration (Figs. 6—8).

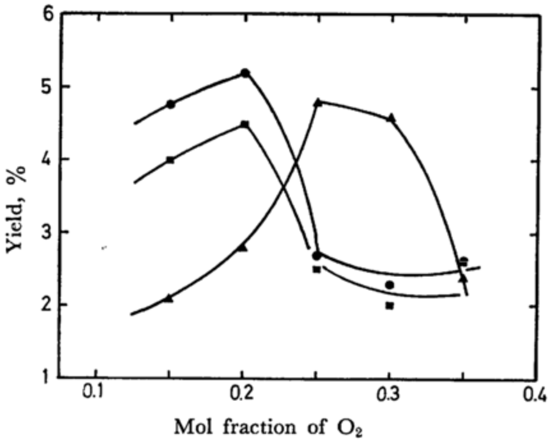

Fig. 6. Effect of $O_2$ conc. on the yields of AA, PO and Acr at 300°C under 3 atm.
● AA ■ PO ▲ Acr

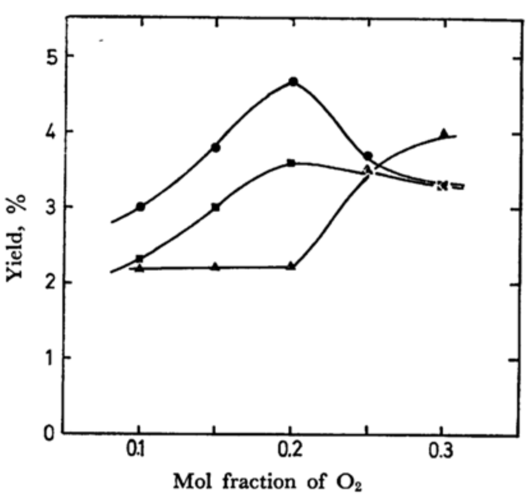

Fig. 7. Effect of $O_2$ conc. on the yields of AA, PO and Acr at 350°C under 3 atm.
● AA ■ PO ▲ Acr

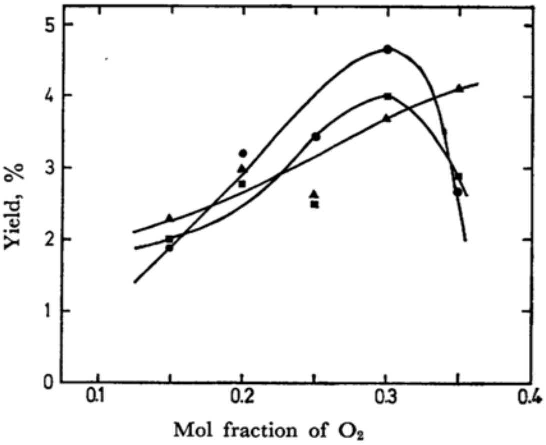

Fig. 8. Effect of $O_2$ conc. on the yields of AA, PO and Acr at 400°C under 3 atm.
● AA ■ PO ▲ Acr

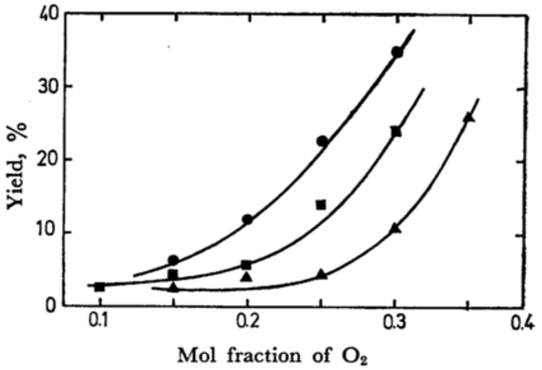

Fig. 9. Effect of $O_2$ conc. on the yield of CO under 3 atm.
● 300°C ■ 350°C ▲ 400°C

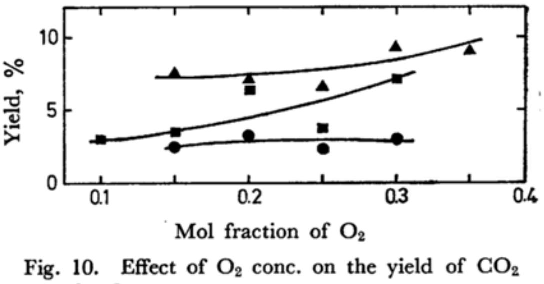

Fig. 10. Effect of $O_2$ conc. on the yield of $CO_2$ under 3 atm.
● 300°C ■ 350°C ▲ 400°C

The yield of carbon monoxide increases as the concentration of oxygen increases and decreases as the temperature rises, as shown in Fig. 9. The

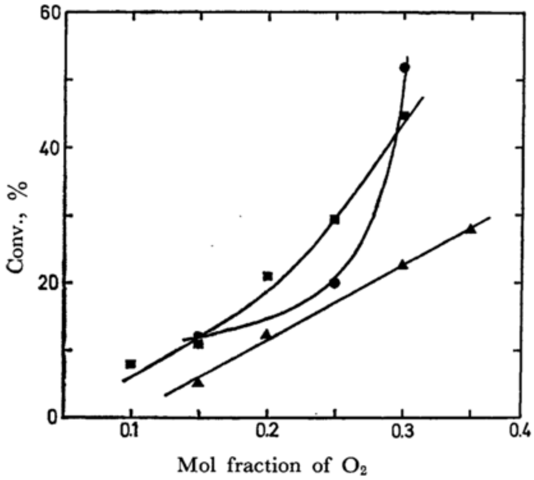

Fig. 11. Effect of $O_2$ conc. on the conv. of $C_3H_6$ under 3 atm.
● 300°C ■ 350°C ▲ 400°C

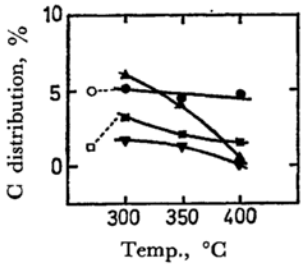

Fig. 12. Effect of temp. on the carbon distribution of hydrocarbons in products under 3 atm, with mol fraction of $O_2$: 0.20.
● $C_3H_8$ ■ $C_2H_6$ ▲ $C_2H_4$ ▼ $CH_4$
○ and □ correspond to the values in reactant gas for $C_3H_8$ and $C_2H_6$ respectively.

effect of the temperature on the yield of carbon dioxide is just the reverse, as shown in Fig. 10. The conversion of propylene increases as the concentration of oxygen increases and decreases with a rise in the temperature, as shown in Fig. 11. The formations of ethylene and methane decrease with a rise in the temperature, as Fig. 12 shows. At 350°C and 3 atm, the formations of methane and ethylene remain constant up to the molar fraction of oxygen of 0.2 and increase beyond this value. Propane retains its initial value (represented by an open circle in Fig. 12) within the limits of error. A comparison of the black square with the open square shows some formation of ethane, but it decreases as the reaction temperature rises, as shown in Fig. 12. It may be concluded, therefore, that propane and ethane, which are major impurities in propylene gas, do not play important roles in the oxidation reaction.

The trend of the effect of the oxygen concentration up to the molar fraction of oxygen, 0.2—0.25, at 300—350°C is nearly the same as that observed by Kamiya except for the yield of carbon dioxide.[3] His experiments were performed in the 7—24% range of oxygen content at 315°C between 3—6 atm, using a Pyrex reactor 12 mm in *i. d.* Kamiya's results show an increased formation of carbon dioxide with an increase in the oxygen concentration. In the present results, it is indifferent to the oxygen concentration up to a oxygen concentration of 0.25. This indicates that the existence of fluidizing particles (silicon carbide) prevents combustion reactions.

Table 2 shows the good carbon balances of the oxidation experiments at 350°C.

As has been described above, the yields of AA, PO, and Acr increase at first, reach maxima and then decrease with the oxygen concentration, as Figs. 6—8 show. In the increasing sector, the yields of AA and PO decrease as the temperature is raised. These yields *vs.* temperature relations are reversed in the decreasing sector of the said curves. The yields of carbon monoxide, methane, ethane, and ethylene decreased with a rise in the temperature (Figs. 9 and 12). It is known that propylene is a powerful inhibitor of the decomposition of a compound which contains the acetyl group,[5] and also that AA is easily decomposed by oxygen.[6] Therefore, AA is probably decomposed very easily in the range with high concentrations of oxygen. The combination of these two opposite effects may reasonably be expected to produce the maximum in the variation of the yield of AA against the concentration of oxygen. Therefore, up to an oxygen concentration which corresponds to the maximum yield of AA, species containing the acetyl group are decomposed to a lesser extent. It may be concluded from these results and discussion that the formation reaction of AA proceeds predominantly in the increasing sector of the curves, while the decomposition reaction of AA is enhanced in the decreasing sector of the curves (Figs. 6—8). In the decreasing sector of the curves for AA in Figs. 6—8, the temperature effect on the yield of AA is positive. In other words, there is a negative temperature coefficient of the decomposition of AA.

AA has been established to be a chain-branching agent in propylene oxidation at reduced pressures.[1] Imamura *et al.* obtained a relatively high selective production of PO by the direct addition of the oxidation products of AA to propylene;[7] they proposed that PO is formed by the addition of the

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[5] A. Maccoll, "Technique of Organic Chemistry," Vol. 8, 2nd Ed., Part 1, ed. by S. L. Friess, E. S. Lewis and A. Weissberger, Interscience, New York (1961), p. 472.

[6] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Vol. 1, Reinhold, New York (1954), p. 211.

[7] J. Imamura, N. Nagato, S. Sato and N. Ohta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 1863 (1966).

acetyl peroxy radical to the double bond of propylene and also by the reaction of peracetic acid with propylene.[7)] Here, it can reasonably be estimated that the further predominant reaction of AA is the oxidation to the acetyl peroxy radical in the increasing sector and decomposition into the methyl radical and carbon monoxide in the decreasing sector. This assumption accords with the steep increase in the yield of carbon monoxide at a high oxygen concentration (Fig. 9). In the increasing sector, where AA is assumed to be converted into the acetyl peroxy radical, the formation reaction of PO may be the main course of the oxidation reaction. In the decreasing sector, where AA is estimated to decompose, the formation reaction of PO may become slight. Thus, the similar variation in the curves of AA and PO can be reasonably explained. Therefore, it may be suggested that AA plays an important role in the formation of PO.

Kamiya, Sekine and Yamakawa proposed that Acr is formed by the dehydration of allyl hydroperoxide in propylene oxidation.[8)] It can be considered that the oxygen-catalyzed decomposition of AA efficiently increases the concentration of radicals (methyl and therefore, allyl) (*cf.* the discussion of Imamura *et al.*[7)]). This increase in the said radicals will enhance the formation of the allyl peroxy radical by the reaction of the allyl radical and oxygen. Thus, the formation reaction of Acr will become the main course of the oxidation reaction as a result of the increased allyl peroxide which is formed by the reaction of the allyl peroxy radical and propylene. These considerations can explain the increasing yield of Acr in the decreasing sector. The decrease in the yield of Acr at higher oxygen concentrations may be ascribed to an increased combustion.

As has been discussed above, the variation in the curves for AA, PO, and Acr (Figs. 6—8) can thus be well explained. It may be concluded from the above discussion that a small amount of oxygen, in another words, a large excess of propylene, is an essential factor in producing high yields of AA and PO. This explains well why the formation of PO was not reported in past experiments,[1a)] almost all of which were performed in an atmosphere with a relatively high partial pressure of oxygen and at a reduced reaction pressure. The reaction scheme mentioned to above will be discussed in detail in the next paper.

The so-called negative temperature coefficient is observed in the conversion of propylene and in the formations of AA, PO, Acr, carbon monoxide, methane, ethane, and ethylene. On the basis of the negative temperature coefficient,[1b)] all the reactions of propylene oxidation may be considered to proceed through the radical-chain mechanism except for the formation reaction of carbon dioxide.

The authors wish to thank the Nippon Petrochemicals Co., Ltd., for supplying the propylene gas, and the Mitsui Mining and Smelting Co., Ltd., for supplying the silicon carbide.

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[8)] Y. Kamiya, N. Sekine and Y. Yamakawa, *Sekiyu Gakkai Shi (J. Japan Petrol. Inst.)*, **8**, 951 (1965).