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Effects of the Addition of Chlorohydrocarbons on the Oxidation of Propylene[*1]; A Consideration of the Negative Temperature Coefficient

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A small amount of allyl chloride, 1,1-dichloroethane, or chloroform was added to the reactant in the oxidation of propylene in an inert fluidized-bed reactor. A negative temperature coefficient is observed in the conversion of propylene and in the formation of various products, but not propylene oxide, in the experiments with allyl chloride or 1,1-dichloroethane added. The results of the chloroform-adding experiments show a positive temperature coefficient in the conversion of propylene and in the formation of gaseous products. The results of the work described here are discussed on the basis of the probable reaction scheme. The results of the chloroform-adding experiments support the proposed catalytic effect of the chlorocarbene on the decomposition of acetaldehyde. It is concluded that the negative temperature coefficient is attributable to the apparent inactivity of acetaldehyde (the branching agent) in the high-temperature region in this reaction atmosphere.

Previous works[1,2] using an inert fluidized-bed reactor have shown that a very pronounced negative temperature coefficient is observed in the conversion of propylene and in the formation of acetaldehyde, propylene oxide, acrolein, propionaldehyde, carbon monoxide, methane, and ethylene in an excess-propylene atmosphere. The purpose of the present paper is to describe the results of oxidation experi-

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1) E. Echigoya, M. Masai and K. Morikawa, This Bulletin, **41**, 904 (1968).

2) M. Masai, E. Echigoya and K. Morikawa, *ibid.*, **41**, 910 (1968).

ments featuring the addition of allyl chloride, 1,1-dichloroethane, or chloroform to the reactant (propylene and oxygen) using an inert fluidized-bed reactor, and also to discuss the cause of the negative temperature coefficient on the basis of the reaction scheme reported previously.[2,3]

In the same reaction system, Kamiya studied the effects of the addition of chloroform or other halogenated hydrocarbons to the reactant;[4] his results showed the acceleration of the reaction by the addition of these substances. Hurst, Skirrow, and Tipper accounted for the low overall activation energy in terms of the enhanced decomposition of hydroperoxide by the hydrogen bromide added in the oxidation of butene.[5] Seakins demonstrated the strong accelerating effect of chloroform on the chain propagation in the oxidation of propane.[6]

There have been many discussions of the negative temperature coefficient.[7] Among these, Yenikolopyan discussed it in terms of the decrease in branching resulting from the decomposition of the hydroperoxy, the acetyl, and the acetyl peroxy radicals in the oxidation of propylene.[7] Shtern demonstrated that, in the oxidation of propane, the induction period was shortened by the addition of acetaldehyde to the reaction system in the low-temperature region, but no effect was observed in the high-temperature region.[8] McMillane and Calvert showed that the estimated rate constants of the oxidation of the acetyl radical were $0.7\times10^8 \cdot l\cdot \mathrm{mol}^{-1}\cdot\mathrm{sec}^{-1}$ at 290°C and 3.8×10^8 at 36°C;[9] these values were obtained on the postulation that the rate constant of the decomposition reaction of the acetyl radical increases normally with an increase in the temperature. Seakins and Hinshelwood discussed the observed maximum of the rate against the temperature on the basis of a kinetic study.[10]

In the present work, experiments featuring the addition of allyl chloride or 1,1-dichloroethane showed a temperature dependence of the reaction results, except in the formation of propylene oxide, similar to that observed in the previous works.[1,2] A different temperature dependence was, however, observed in the chloroform adding experiments. The results obtained will be discussed on the basis of a reaction scheme reported before.[2,3] It will be concluded that the negative temperature coefficient is attributable to the apparent inactivity of acetaldehyde (the branching agent) at a high temperature in this reaction atmosphere.

Experimental

Materials. The allyl chloride and the 1,1-dichloroethane, both of G. R. quality, were obtained from the Tokyo Kasei Kogyo Co., Ltd. (Tokyo). The chloroform, containing 1% of ethanol as a stabilizer, was obtained from the Wako Junyaku Kogyo Co., Ltd. (Osaka). The propylene gas, the oxygen, and the silicon carbide have been described before.[1]

Apparatus. This was as has been described for Exp. A in a previous paper.[2]

Procedures. These were as have been described for Exp. A in a previous paper.[2] The concentrations of the additives were 0.50—0.58 vol% for the allyl chloride, 0.48—0.55 vol% for the 1,1-dichloroethane, and 0.50—0.55 vol% for the chloroform, according to the reaction temperature.

Analysis. This was done as has been described for Exp. A in a previous paper.[2]

Results

The results of the oxidation experiments are shown in Figs. 1—9. In these figures, the full lines with black points are for the oxidation experiments with the additives, while the dotted lines with open points are for the oxidation experiments without the additives (standard experiment).

The additions of allyl chloride and 1,1-dichloroethane gave similar results, as is shown in Figs. 1 and 4, 2 and 5, and 3 and 6. The remarkable difference due to the additives is the increase in the yield of propylene oxide with the rise in the temperature (Figs. 1 and 4). Methane and ethylene are increased by these additives (Figs. 2 and 5). The amount of carbon monoxide and the conversion of propylene are increased by these additives (Figs. 3 and 6). Negative temperature coefficients are observed in these experiments except in the case of propylene oxide (Figs. 1—6).

Considerable differences are observed between the chloroform-adding experiments and the standard experiment as is shown in Figs. 7—9. Acetaldehyde (AA) and propylene oxide (PO) are considerably decreased at a high temperature. While acrolein (Acr) and propionaldehyde (PA) are increased slightly at a higher temperature (Fig. 7), the results for Acr and PA are nearly the same as the results shown in Figs. 1 and 4. The temperature co-

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[3] M. Masai, E. Echigoya and K. Morikawa, *ibid.*, **41**, 920 (1968).

[4] Y. Kamiya, *Sekiyu Gakkai Shi* (*J. Japan Petrol. Inst.*), **5**, 573 (1962).

[5] P. Hurst, G. Skirrow and C. F. H. Tipper, *Proc. Roy. Soc.*, **A268**, 405 (1962).

[6] M. Seakins, *ibid.*, **A274**, 413 (1963).

[7] V. Ya. Shtern, "The Gas-phase Oxidation of Hydrocarbons," English translation by M. F. Mullins, Pergamon Press, Oxford (1964), pp. 105—110, 480—492.

[8] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Japanese translation by T. Kwan and A. Matsuda, Vol. 2, Iwanami Shoten Co., Tokyo (1963), Chap. 12 § 1.

[9] G. R. McMillane and J. G. Calvert, "Oxidation and Combustion Reviews," ed. by C. F. R. Tipper, Vol. 1, Elsevier Pub. Co., Amsterdam (1965), pp. 110—111.

[10] M. Seakins and C. Hinshelwood, *Proc. Roy. Soc.*, **A276**, 324 (1963).

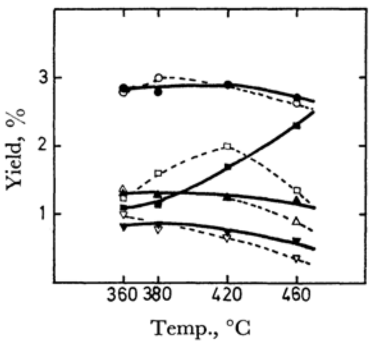


Fig. 1. Yield *vs.* temp. curves with the addition of allyl chloride; under 3.5 atm with mole fraction of O_2, 0.2.

-●-, AA; --○--, AA in standard exp.
-■-, PO; --□--, PO in standard exp.
-▲-, Acr; --△--, Acr in standard exp.
-▼-, PA; --▽--, PA in standard exp.

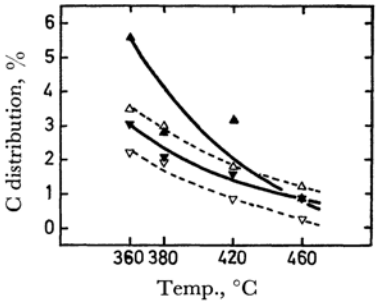


Fig. 2. Carbon distribution *vs.* temp. curves with the addition of allyl chloride; under 3.5 atm with mole fraction of O_2, 0.2.

-▲-, C_2H_4; --△--, C_2H_4 in standard exp.
-▼-, CH_4; --▽--, CH_4 in standard exp.

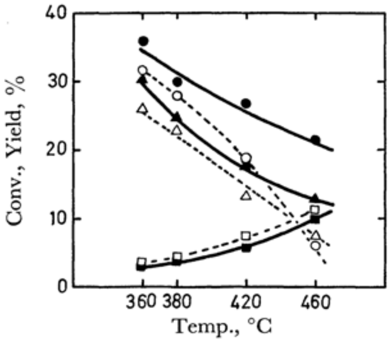


Fig. 3. Conversion and yield *vs.* temp. curves with the addition of allyl chloride; under 3.5 atm with mole fraction of O_2, 0.2.

-●-, conv. of C_3H_6
--○--, conv. of C_3H_6 in standard exp.
-▲-, yield of CO
--△--, yield of CO in standard exp.
-■-, yield of CO_2
--□--, yield of CO_2 in standard exp.

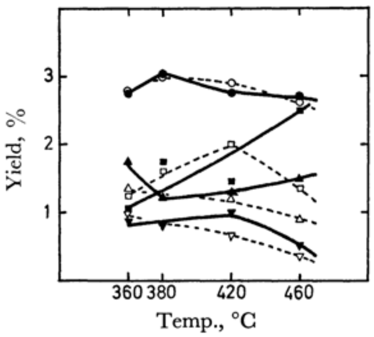


Fig. 4. Yield *vs.* temp. curves with the addition of 1,1-dichloroethane; under 3.5 atm with mole fraction of O_2, 0.2.

-●-, AA --○--, AA in standard exp.
-■-, PO --□--, PO in standard exp.
-▲-, Acr --△--, Acr in standard exp.
-▼-, PA --▽--, PA in standard exp.

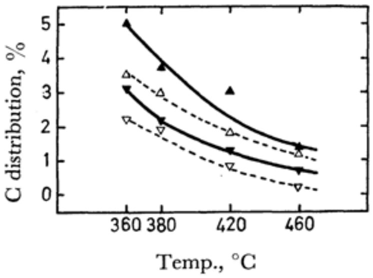


Fig. 5. Carbon distribution *vs.* temp. curves with the addition of 1,1-dichloroethane; under 3.5 atm with mole fraction of O_2, 0.2.

-▲-, C_2H_4; --△--, C_2H_4 in standard exp.
-▼-, CH_4; --▽--, CH_4 in standard exp.

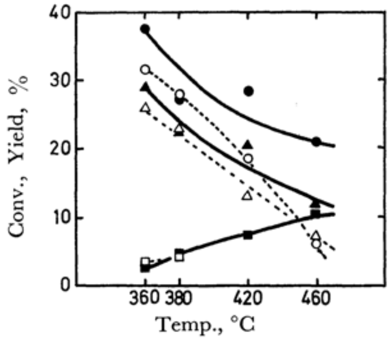


Fig. 6. Conversion and yield *vs.* temp. curves with the addition of 1,1-dichloroethane; under 3.5 atm with mole fraction of O_2, 0.2.

-●-, conv. of C_3H_6
--○--, conv. of C_3H_6 in standard exp.
-▲-, yield of CO
--△--, yield of CO in standard exp.
-■-, yield of CO_2
-□-, yield of CO_2 in standard exp.

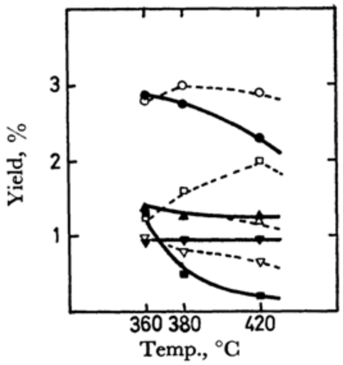


Fig. 7. Yield *vs.* temp. curves with the addition of chloroform; under 3.5 atm with mole fraction of O_2, 0.2.
-●-, AA; --○--, AA in standard exp.
-■-, PO; --□--, PO in standard exp.
-▲-, Acr; --△--, Acr in standard exp.
-▼-, PA; --▽--, PA in standard exp.

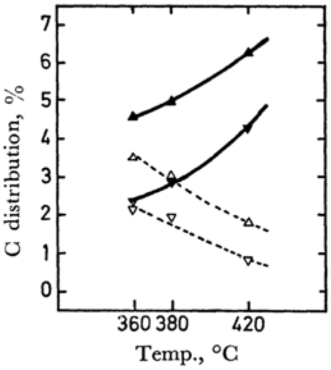


Fig. 8. Carbon distribution *vs.* temp. curves with the addition of chloroform; under 3.5 atm with mole fraction of O_2, 0.2.
-▲-, C_2H_4; --△--, C_2H_4 in standard exp.
-▼-, CH_4 ; --▼--, CH_4 in standard exp.

efficients for the formations of methane, ethylene (Fig. 8), carbon monoxide, and carbon dioxide, and for the conversion of propylene (Fig. 9) are reversed by the addition of chloroform. Ethylene is increased in all the experiments with additives (Figs. 2, 5, and 8).

Discussion

As has been described above, the lowest temperature at which the reaction occurs is not affected by the addition of allyl chloride, 1,1-dichloroethane, or chloroform. These facts indicate that these additives do not affect the initiation step. The considerable differences observed between the results of the adding experiments and the standard experiment show that these additives remarkably affect the reaction in the early steps of the chain.

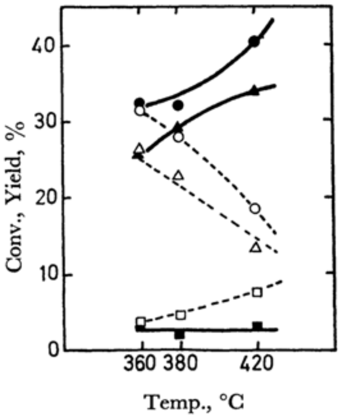


Fig. 9. Conversion and yield *vs.* temp. curves with the addition of chloroform; under 3.5 atm with mole fraction of O_2, 0.2.
-●-, conv. of C_3H_6
--○--, conv. of C_3H_6 in standard exp.
-▲-, yield of CO
--△--, yield of CO in standard exp.
-■-, yield of CO_2
--□--, yield of CO_2 in standard exp.

The results described above will be discussed below on the basis of a reaction scheme reported before.[2,3] The main part of the scheme is shown in Table 1. In this scheme, PO is mainly formed *via* AA in an excess-propylene atmosphere as has been discussed before.[2),*4]

Effects of the Addition of Allyl Chloride and 1,1-Dichloroethane. While nearly the same results are obtained by the addition of these two additives, the forms of their decompositions are different; *i. e.*, one is radical, and the other is monomolecular:[11)]

$$CH_2{=}CHCH_2Cl \rightarrow CH_2{=}CH\dot{C}H_2 + \dot{C}l$$

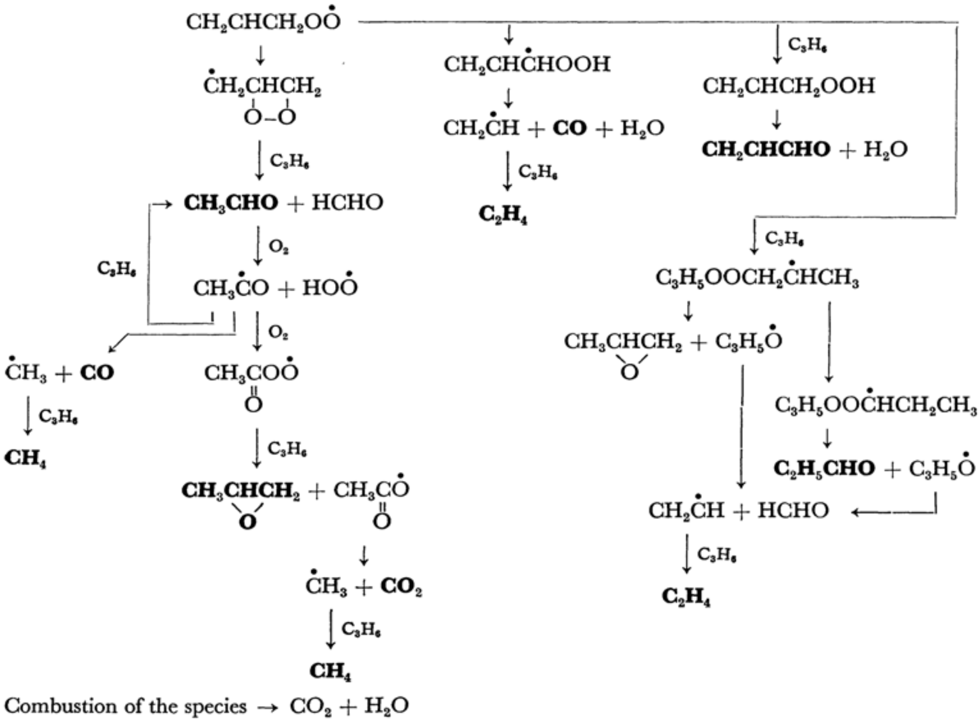
$$CH_3CHCl_2 \rightarrow CH_2{=}CHCl + HCl$$

The chlorine atom most likely reacts with propylene to form hydrogen chloride and the allyl radical, and also probably recombines into chlorine. Hydrogen chloride is produced by both these additives.

[*4] There may be some objection to this previously obtained conclusion.[2)] The objection will be that, under the conditions of Exp. B_1 of the previous paper,[2)] bromine or bromine compounds may interfere with the formation of PO. This objection cannot be sustained, however, because the interaction between bromine or bromine compounds and PO can be neglected, as has been discussed in "*4" in a previous paper,[2)] and also because the addition reaction of the bromine atom to the double bond of propylene does not interfere with the same addition reaction of the allyl peroxy radical, for an excess of propylene is present in the reaction atmosphere.[2)]

11) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Japanese translation by T. Kwan and A. Matsuda, Vol. 1, Iwanami Shoten Co., Tokyo (1963), Chap. 7 § 4, § 7.

TABLE 1. THE MAIN PART OF THE SCHEME[2)]



Quite similar results are obtained in these two adding experiments; this suggests that the hydrogen chloride is a predominantly effective species in both these experiments.*[5] The increase in the formation of methane and carbon monoxide may be attributed to the enhanced decomposition of AA, as hydrogen chloride is known to accelerate the decomposition of AA slightly.[13)] The yield of AA is little affected by the presence of these two additives or, therefore, by the presence of hydrogen chloride (Figs. 1 and 4). This suggests that the true amount of AA formed should be increased, if we consider the increased consumption of AA resulting from the enhanced decomposition. The amount of ethylene, which is mainly formed from the allyl peroxy radical (Table 1), is also increased (Figs. 2 and 5). These increase in the formation of AA and ethylene may indicate an increased formation of the allyl peroxy radical. If so, the increased conversion of propylene can be explained in terms of the increased formation of the allyl peroxy radical. The degree of the increase in the formation of ethylene is less than those of methane and carbon monoxide at 460°C in the two adding experiments. This indicates that the reaction of the allyl peroxy radical to AA becomes predominant in comparison with the reaction to ethylene at 460°C.

The most notable feature in these two adding experiments is the positive temperature coefficient observed in the formation of PO (Figs. 1 and 4). The positive temperature coefficient observed in the PO formation is mainly due to the increased formation of PO at 460°C in the two adding experiments. This increase can be ascribed to the increased formation of AA, as has been discussed above, because it has been suggested that PO is formed mainly through the addition of the acetyl peroxy radical to the double bond of propylene.[2)] The low yield of PO in the 360—420°C region in the two adding experiments (Figs. 1 and 4) indicates that the increase in the formation of the allyl peroxy radical, discussed above, contributes only a little to the formation of PO. The route to PO *via* the addition of the allyl peroxy radical to the double bond of propylene has already been established to be minor.[2)] The true amount of AA formed is certainly smaller at 360—420°C, as has been discussed above; This is the reason for the low yield of PO in this temperature region.

The Effects of Chloroform. Contrary to the case with the standard experiment, and also to the former two adding experiments, the positive temperature coefficients of the conversion of propyl-

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*[5] In the case of 1,1-dichloroethane, the presence of vinyl chloride should be considered. The accelerating effect of vinyl chloride on propane oxidation has been reported.[12)] The resemblance of the results of the two adding experiments are so remarkable that it may be reasonable to consider the hydrogen chloride formed as the predominantly effective species.

12) M. Seakins, *Proc. Roy. Soc.*, **A277**, 279 (1964).

13) H. Fromherz, *Z. physik. Chem.*, **B25**, 301 (1934).

ene and of the formation of methane, ethylene, and carbon monoxide are observed in the chloroform-adding experiments. Decrease in the formation of AA and PO are noticed in the higher-temperature region.

For the decomposition of chloroform, two kinds of reactions have been reported.[*6] Reaction (1) has been proposed in the presence of peroxide:[14a)]

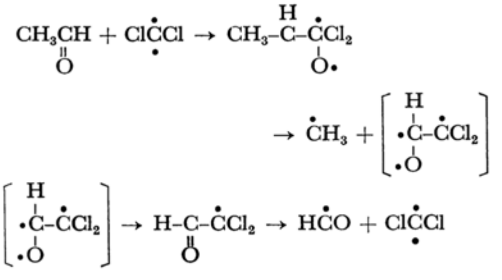
$$CHCl_3 \rightarrow \dot{C}Cl_3 + \dot{H} \qquad (1)$$

Reaction (2) has been reported to have an activation energy of 47 kcal/mol:[12)]

$$CHCl_3 \rightarrow :CCl_2 + HCl \qquad (2)$$

The bond-dissociation energy of CCl_3–H is 95.7 kcal/mol.[15)] Therefore, reaction (2) is more probably predominant.[*7] The chlorocarbene $:CCl_2$ is an electrophilic and relatively stable radical.[14b)] The chlorocarbene has been shown to add to double bonds such as C=C and C=N.[14b)]

Therefore, it is reasonable to suggest the addition of the chlorocarbene to the carbonyl group of AA. The scheme of this suggested reaction is as follows;



$$CH_3\underset{\underset{O}{\|}}{C}H + Cl\overset{\bullet}{\underset{\bullet}{C}}Cl \rightarrow CH_3\text{–}\overset{H}{\underset{O\bullet}{C}}\text{–}\dot{C}Cl_2 \rightarrow \dot{C}H_3 + \left[\bullet\overset{H}{\underset{\bullet O}{C}}\text{–}\dot{C}Cl_2\right]$$

$$\left[\bullet\overset{H}{\underset{\bullet O}{C}}\text{–}\dot{C}Cl_2\right] \rightarrow H\text{–}\underset{\underset{O}{\|}}{C}\text{–}\dot{C}Cl_2 \rightarrow H\dot{C}O + Cl\overset{\bullet}{\underset{\bullet}{C}}Cl$$

Thus, the chlorocarbene is regenerated. This hypothetical catalytic action of the chlorocarbene on the decomposition of AA is supported by the results of the chloroform-adding experiments and also by a reaction scheme reported earlier[2)] (Table 1). Here, the effect of hydrogen chloride is considered to be small in view of the results of the allyl chloride and 1,1-dichloroethane-adding experiments.

Table 2 shows that the addition of chloroform increased the formation of methane considerably in comparison with ethylene and carbon monoxide. In the case of the addition of allyl chloride or 1,1-dichloroethane, the increase in methane is not very obvious in comparison with ethylene and carbon monoxide. As a result of the reaction of the chlorocarbene and AA, only the formation of methane is increased. The decreases in AA and PO also support the catalytic effect of the chlorocarbene.

TABLE 2. COMPARISON OF THE EFFECTS OF THE ADDITIVES ON THE FORMATION OF METHANE, ETHYLENE AND CARBON MONOXIDE AT 420°C (THE VALUES FOR THE STANDARD EXPERIMENTS ARE TAKEN AS UNITY)

Product	Additive		
	$CHCl_3$	C_3H_5Cl	CH_3CHCl_2
CH_4	5.8	1.7	2.0
C_2H_4	3.3	1.6	1.7
CO	2.5	1.3	1.5

As has been discussed in the case of the former two additives, hydrogen chloride accelerates the oxidation reaction considerably at 360°C. In the chloroform-adding experiments at 360°C, only the value of ethylene varies from those of the standard experiment. Therefore, the decomposition of chloroform into the chlorocarbene and hydrogen chloride is not as sufficient at 360°C as at 420°C.

As has been shown in the discussions of the former two additives, the negative temperature coefficient of the oxidation reaction is observed in spite of the acceleration by hydrogen chloride. Because of the catalytic effect of the chlorocarbene on AA, which is the degenerate branching agent,[2,3)] the main path of the oxidation reaction changed from I to II as below:

$$\text{I} \quad C_3H_5O\dot{O} \rightarrow AA \rightarrow PO$$

$$\text{II} \quad C_3H_5O\dot{O} \rightarrow AA \xrightarrow{:CCl_2} CH_4$$

Therefore, the change in the temperature coefficient from negative to positive is quite reasonable because of the increase in the concentration of the chlorocarbene with the rise in the reaction temperature.

Thus, the catalytic action of the chlorocarbene—though hypothetical—on the decomposition of AA changes these temperature correlations. The hypothetical reaction is the branching reaction, for number of radicals increases in the course of the reaction of AA with the chlorocarbene. This probably shows that the negative temperature coefficient is caused by the retarded reactivity of AA in the high-temperature region in this reaction atmosphere. This accords with Shtern's conclusion[8)] described above, that AA does not behave as a branching agent in the temperature region where the negative temperature coefficient is observed. The cause of this inactivity of AA has not yet been elucidated.[8)]

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

[*6] The route to $\dot{C}HCl_2$ is not considered here, because $\dot{C}HCl_2$ is not as stable as $\dot{C}HBr_2$[14a)] and also because no precise and accurate value of D($CHCl_2$–Cl) can be found.

14) J. I. G. Cadogon and M. J. Perkins "The Chemistry of Alkene," ed. by S. Patai, Interscience Pub., London (1964), a) p. 589; b) pp. 640—642.

15) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[*7] The reverse reaction of reaction (1) is a radical recombination reaction: The activation energy for this reverse reaction is negligible. Therefore, the activation energy of reaction (1) is 95.7 kcal/mol.