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Kyoto University

Synthesis of Methylacetylene by Pyrolysis of Propylene. (III)[*]

Effect of Catalysts on Product Yields

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Propylene has been pyrolyzed in a flow system with several catalysts under a wide range of conditions (temperature, 950-1300 °C; contact time, 1.5×10^{-3}–11.0×10^{-3} sec.) to find suitable conditions for producing methylacetylene (and allene). Generally, the radical sources which have a lower dissociation energy than that of α(C-H) of propylene (79 Kcal./mol.) and abstract hydrogen atom from propylene were found to be suitable as catalysts. Among them, chlorine, bromine, and hydrogen bromide were most effective. Good results were obtained in shorter contact time and lower temperature in comparison with the case of no catalyst. The catalytic effect was most remarkable in the low conversion. When allyl chloride was added, hydrogen and carbon balance was considerably worse than those of no catalyst. Although the contact time was most shortened with diazomethane, the catalytic effect was poorer than those of chlorine, bromine and hydrogen bromide.

INTRODUCTION

In our previous papers[1,2] and several patents[3], which were published in the course of our study, the suitable conditions for the production of methylacetylene and allene by the pyrolysis of propylene were reported and the reaction mechanism was proposed by one of us. On the basis of our reaction mechanism which indicates that high temperature dehydrogenation of propylene proceeds by a radical chain reaction, the following prediction is supposed: various compounds which form radicals readily, that is, redical sources would catalyze this dehydrogenation process to initiate the reaction at lower temperatures than those of our previous experiments. As a result, addition of the radical sources would be expected to bring about better results. Some reports were recently made in patents of addition of radical sources such as diazomethane[4] and hydrogen bromide[5]. In the present investigation, oxygen, chlorine, allyl chloride, diazomethane, hydrogen bromide, and bromine were selected as the potential radical sources, and an effort was made to find suitable conditions for the preparation of methylacetylene and allene by the pyrolysis of propylene in the presence of these radical sources as the catalyst.

EXPERIMENTAL

Materials

Propylene was supplied by Maruzen Sekiyu Kagaku Co. Gas chromatographic analysis showed that its purity was 94.0 mol. % and that its principal impurity was

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5.7 mol. % of propane. Cylinder nitrogen of 99.9 mol. % purity was used as a diluent, a known amount (about six times of the propylene volume) being added to propylene. Oxygen and chlorine also were obtained in commercial cylinders. E.p.grade allyl chloride was distilled before use. Diazomethane was prepared by a slight modification of Urry's method[6]; To a magnetically stirred aqueous potassium hydroxide solution was added a solution of p-tolylsulfonylmethylnitrosamide in methanol. Hydrogen bromide was prepared by adding bromine to a mixture of tetrahydronaphthalene and iron metal powder with stirring at room temperature[7]. E.p.grade bromine was used without further purification.

Apparatus and Procedure

A conventional flow system was used. The apparatus and the technique were essentially the same as used previously for the pyrolytical study of propylene under reduced pressure[1]. The reactant gas, consisting of about 13 vol. % propylene diluted by nitrogen, was introduced into a silica reaction tube from a gas holder, and pyrolyzed under the specified conditions at atmospheric pressure. The tube was heated with a furnace, being constructed from a spiral "Siliconit" heating element. To 100 mol. of propylene were added 1–22 mol. of catalysts. Catalysts were mixed with the reactant gas in a mixing bottle before the furnace. Oxygen and chlorine were respectively introduced at a constant flow velocity using regulating valves and flow meters. Allyl chloride was added at a constnat rate using an automatic injector. Diazomethane and hydrogen bromide were swept by a measured flow of nitrogen into the reactant gas. Bromine was added at a constant rate through a capillary. The pyrolysis was performed under conditions varying over the following wide range: temperature, 950-1300 °C; contact time, 1.5×10^{-3}–11.0×10^{-3} sec.

Analysis

Gaseous products, consisting of hydrogen and hydrocarbons (mainly from methane up to C_4's,) were analyzed by a gaschromatograph (g.l.c.) using the following three different columns: (1) a molecular sieve 5-A column (2.5 m.) for hydrogen at 60 °C with 25 ml./min. of nitrogen as a carrier gas and for methane at 60 °C with 25 ml./min. of hydrogen as a carrier gas, (2) an 8.0-wt. % β, β'-oxydipropionitril on silica gel column (2.5 m.) for C_2- and C_3- hydrocarbons at 60 °C with 25 ml./min. of hydrogen as a carrier gas, and (3) a 30-wt. % dioctyl phthalate column (5.0 m.) for C_3- and C_4- hydrocarbons at room temperatures with 25 ml./min. of hydrogen as a carrier gas. Allyl chloride also was analyzed by the gas chromatograph using a 30-wt. % dioctyl phtalate column (2.5 m.) at 60 °C with 25 ml./min. of hydrogen as a carrier gas. The quantity of chlorine and hydrogen bromide was determined by ordinary titrations. The amount of diazomethane in the reactant gas was determined by passing it into a solution of benzoic acid in ether and by titrating the unreacted benzoic acid with a standard sodium hydroxide solution[8].

Table 1. Pyrolysis of propylene with various catalysts.

Catalyst	None	None	None	O_2	O_2	C_3H_5Cl	C_3H_5Cl	C_3H_5Cl	Cl_2	Cl_2	CH_2N_2	CH_2N_2	HBr	HBr	Br_2	Br_2
Temp., °C	1200	1200	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150
Contact time, 10^{-3} sec.	2.44	3.66	4.99	2.20	3.51	3.98	2.63	3.61	2.46	2.98	1.71	1.64	2.52	2.84	2.96	3.52
Composition of reactant gas, vol %																
Nitrogen	84.4	85.2	85.8	85.0	85.5	84.6	85.2	93.0	88.5	87.5	85.0	85.2	85.0	85.2	85.7	86.0
Propylene	12.5	12.1	13.6	13.0	12.2	12.4	12.8	(8.0)[a]	12.2	12.1	11.5	11.6	11.8	12.2	12.1	12.2
Propane	0.8	0.8	0.8	0.8	0.8	0.8	0.8		0.8	0.7	0.7	0.7	0.7	0.7	0.8	0.8
Catalyst				1.2	1.6	0.7	1.0		0.6	0.8	0.4	0.4	2.4	2.7	0.8	0.9
Composition of pyrolyzed gas, vol %																
Nitrogen	81.4	83.4	84.9	83.6	84.3	84.0	83.3	88.5	87.5	85.6	83.9	82.6	84.1	83.1	83.7	83.3
Hydrogen	1.2	1.8	1.2	0.6	0.8	1.2	1.0	0.8	0.6	1.1	0.9	0.8	0.6	1.3	1.1	1.5
Methane	2.2	3.1	2.3	1.3	1.5	2.0	1.4	0.3	0.8	1.4	1.5	1.3	1.0	1.7	1.7	2.3
Acetylene	0.5	0.9	0.5	0.3	0.3	0.6	0.6	0.3	0.2	0.4	0.3	0.3	0.2	0.3	0.3	0.4
Ethylene	2.3	3.0	2.6	1.5	1.8	2.2	1.7	0.4	1.2	1.8	1.7	1.6	0.8	1.2	1.5	1.8
Ethane	0.1	0.2	0.1	0.1	0.1	0.1	0.1		0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Propylene	7.9	5.6	7.9	10.3	8.8	7.8	8.9	0.7	9.8	8.2	8.1	8.4	10.1	9.0	8.5	7.8
Propane	0.3	0.1	0.2	0.4	0.3	0.3	0.4	(1.7)[a]	0.4	0.3	0.3	0.3	0.4	0.2	0.3	0.2
Allene	0.6	0.6	0.6	0.4	0.4	0.6	0.6	0.3	0.5	0.6	0.5	0.5	0.4	0.4	0.5	0.6
Methylacetylene	0.6	0.8	0.7	0.4	0.5	0.7	0.6	0.2	0.4	0.6	0.5	0.4	0.3	0.6	0.6	0.7
1-Butene (+Isobutene)	0.1	0.1	0.1	0.2	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Butadiene (+2-Butene)	0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1
Rate of expansion	1.038	1.021	1.010	1.015	1.014	1.009	1.021	1.050	1.010	1.020	1.012	1.030	1.010	1.024	1.022	1.031
Conversion, %	38.2	54.6	43.6	21.7	28.5	41.2	33.9	77.0	20.3	32.6	30.4	26.9	15.7	26.9	29.8	36.6
Yield, mol./100 mol. of propylene pyrolyzed																
Hydrogen	25.0	25.8	19.5	19.4	24.5	21.0	21.2	13.7	22.3	25.8	23.7	24.8	29.0	38.2	29.3	32.2
Methane	42.4	44.6	36.8	42.4	41.4	34.5	29.1	5.6	30.4	33.6	39.6	40.8	51.0	49.2	46.8	49.1
Acetylene	11.0	12.7	8.3	8.5	9.0	10.5	12.2	5.7	8.4	9.7	8.3	8.5	7.7	8.7	8.8	9.4
Ethylene	46.7	44.0	41.0	50.2	48.0	39.4	35.6	7.2	45.6	44.2	47.0	50.1	41.2	35.6	40.0	39.3
Ethane	2.5	2.3	2.1	2.9	2.6	1.4	1.4	(11.4)[b]	2.1	1.7	2.6	2.6	1.5	1.2	1.1	0.8
Allene	11.6	9.1	9.4	14.2	12.0	11.4	13.1	4.9	17.4	14.3	13.6	15.1	18.0	12.9	13.8	12.6
Methylacetylene	12.8	12.2	10.9	11.9	12.4	11.7	12.9	3.7	14.4	14.8	12.8	13.4	16.4	18.4	15.3	16.1
1-Butene	2.3	1.0	2.2	5.2	3.3	3.3	5.3	0.9	5.5	3.4	3.7	4.3	1.3	0.3	1.2	0.6
Butadiene	3.0	2.9	3.0	3.4	3.7	3.0	3.7	3.4	3.5	3.2	2.3	2.9	2.8	1.4	1.6	3.0
Total yield of methylacetylene and allene	24.4	21.3	20.3	26.1	24.4	23.1	26.0	8.6	31.8	29.1	26.4	28.5	34.4	31.3	29.1	28.7
Percentage of hydrogen and carbon accounted for in gaseous products through C_4 hydrocarbons																
Hydrogen	96.5	92.5	82.6	99.5	97.6	84.0	83.7	44.6	95.0	92.5	94.3	100	101	94.4	92.9	95.0
Carbon	85.7	80.6	76.4	93.5	89.7	69.5	80.5	36.5	91.4	86.4	86.5	93	90.5	80.2	81.8	83.0

a) The values shown in parentheses are the amount of allyl chloride.

b) The value shown in parenthesis is moles of propylene per 100 mol. of allyl chloride pyrolyzed.

RESULTS

A part of the experimental results is shown in Table 1. The yield of each product was given by moles per 100 mol. of propylene pyrolyzed. Since methylacetylene and allene are equilibrated rapidly over isomerization catalysts[9], the total yield of them was shown to evaluate conditions for the synthesis of methylacetylene. In order to examine the hydrogen and carbon balance, the percentage of hydrogen and carbon accounted for in gaseous products (H_2 and C_1-C_4 hydrocarbons) was calculated from their yields.

No Catalyst

For the purpose of comparison, propylene alone was pyrolyzed. The effect of temperature on methylacetylene and allene yields is shown in Fig. 1. The yields
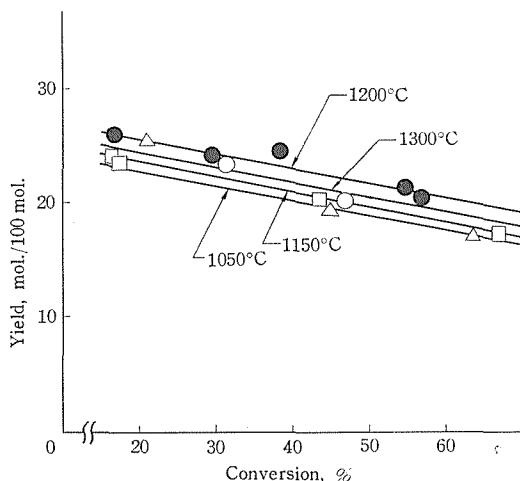
Fig. 1. No catalyst.

increased with increasing temperature in the range of 800 to 1200 °C. This trend agrees with the observation described in the previous papers[1,2]. Thus, the temperature near 1200 °C was recognized as the optimum temperature for the synthesis, where a 24 mol. yield was obtained at 38% conversion (Table 1).

Effect of Oxygen

The effect of oxygen is shown in Fig. 2. The maximum yields obtained near 1100 °C were not better than those of no catalyst. The catalytic effect was scarcely recognized even in the low conversion. Consequently, oxygen is not effective as the catalyst. A 24 mol. yield was obtained at 29% conversion (Table 1). The imput oxygen reacted ca. 40% at 60% conversion, and ca. 40-80% of oxygen consumed was used in the formation of carbon monoxide over the conversion range of 20 to 80%. Considering hydrogen, carbon, and oxygen balance, the large part of oxygen was found to be consumed in the formation of carbon monoxide.
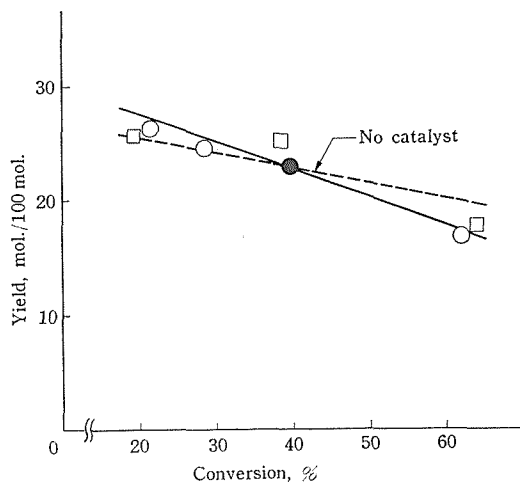
Fig. 2. Effect of oxygen.
● 1200 °C, ○ 1150 °C, □ 1050 °C.

Effect of Allyl Chloride

The effect of allyl chloride is shown in Fig. 3. The catalytic effect was considerably recognized in the low conversion. The temperature near 1150 °C was found to be the optimum temperature, where a 26 mol. yield was obtained at 34% conversion (Table 1). Moreover, a considerable amount of undecomposed allyl chloride was detected even at 35% conversion. The relation between the amounts of allyl chloride and the yields is shown in Fig. 4. The amount of allyl chloride was sufficient in only 1–2 mol. Because allyl chloride as well as propylene produce methylacetylene and allene, allyl chloride also was considered as a starting material in the calculation of the yield, and it is further considered that the better results by
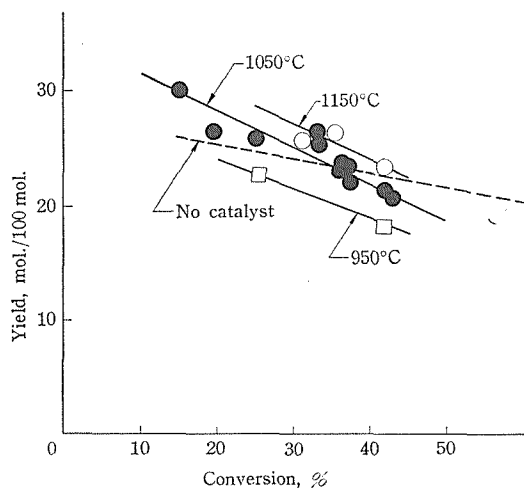
Fig. 3. Effect of allyl chloride.
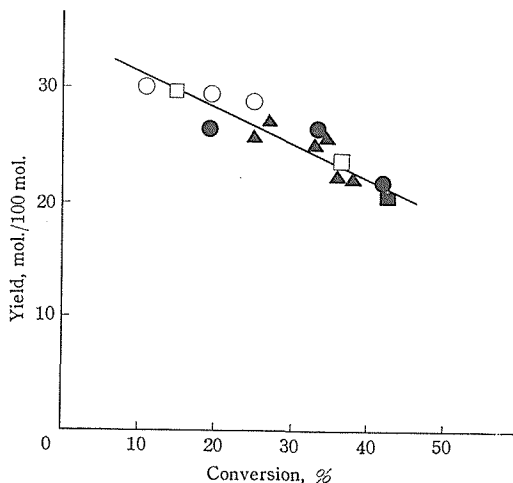
Fig. 4. Relation between the amounts of allyl chloride
and the yields. Temp., 1050°C.
■ 15 mol., □ 13 mol., ▲ 10 mol.,
● 4 mol., ○ 1∼2 mol.

the addition of allyl chloride may be due to the good conversion of allyl chloride itself to methylacetylene and allene. Thus, the pyrolysis of allyl chloride alone was attempted (Table 1). The decomposition was very violent. Hydrogen and carbon balance and also the yields were very low. In addition, it was found that the amount of propylene produced from allyl chloride was much more than the total amount of methylacetylene and allene. Furthermore, the yields of methylacetylene and allene scarcely changed even when the amounts of added allyl chloride were reduced to 1—2 mol., as mentioned above. On the other hand, Hughes and Yates[10], who investigated the pyrolysis of allyl chloride at lower temperatures (720-765 °C), reported that 41.6% propylene and 58.0% benzene were obtained at 99.5% conversion. The formation of benzene was explained on the basis of the combination of two allyl radicals, an allyl and a chloroallyl, and two chloroallyls. In our experiments, we did not try to identify benzene; however, considering the low carbon and hydrogen balance and the formation of a substantial amount of propylene, a considerable amount of benzene must be produced also in our experimental conditions. In view of the above facts on the pyrolysis of allyl chloride alone, it seems most reasonable to conclude that the catalytic effect is not due to the good conversion of allyl chloride to methylacetylene and allene, but due largely to the hydrogen atom abstraction from propylene by the chlorine atom produced from allyl chloride.

Effect of Chlorine

The effect of chlorine is shown in Fig. 5. The yields were considerably better even in the high conversion, and the optimum temperature was near 1150°C,
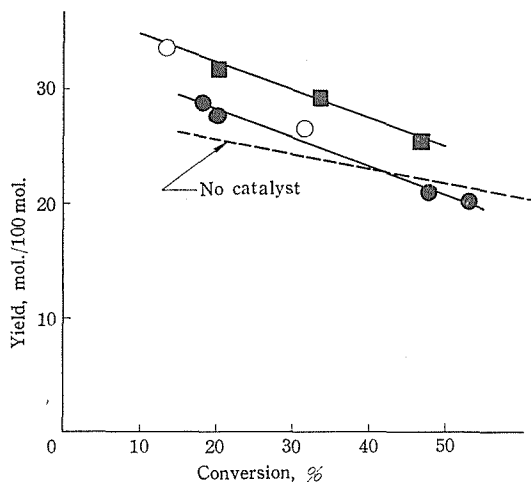
Fig. 5. Effect of chlorine.
○ 1200 °C, ■ 1150 °C, ● 1050 °C.

where a 29 mol. yield was obtained at 33 % conversion (Table 1). It is probable that this good catalytic effect results from the hydrogen atom abstraction by the chlorine atom.

Effect of Diazomethane

The effect of diazomethane is shown in Fig. 6. Diazomethane was as effective as allyl chloride. A 29 mol. yield was obtained at 27 % conversion.
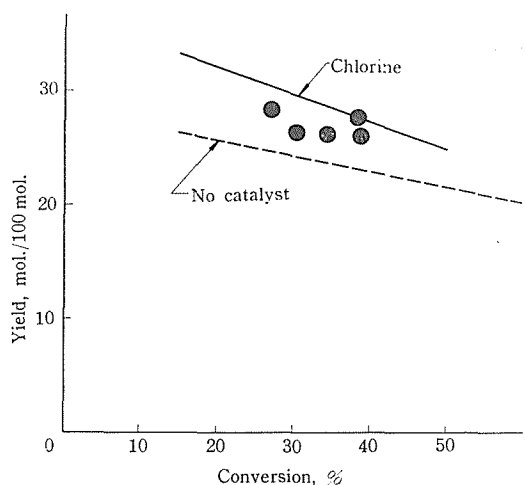
Fig. 6. Effect of diazomethane. Temp., 1150 °C.
● Diazomethane

Effect of Hydrogen Bromide and Bromine

Recently, it has been reported by a patent[5] that the additon of hydrogen

bromide is effective for the preparation of methylacetylene and allene from propylene. Hereupon, the effects of hydrogen bromide and bromine were examined under our conditions. The results are shown in Fig. 7. These catalytic effects were much the same as that of chlorine. With hydrogen bromide a 31 mol. yield was obtained
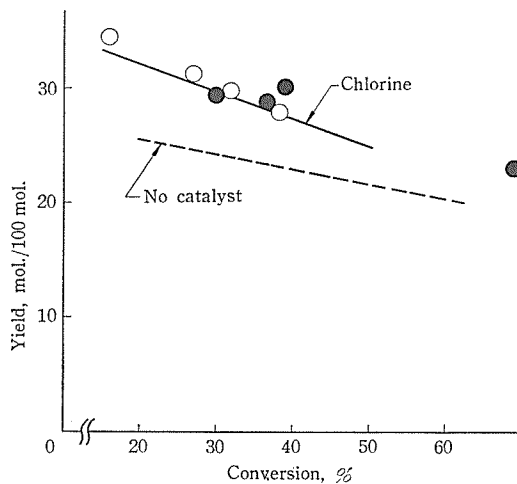

Fig. 7. Effect of hydrogen bromide and bromine.
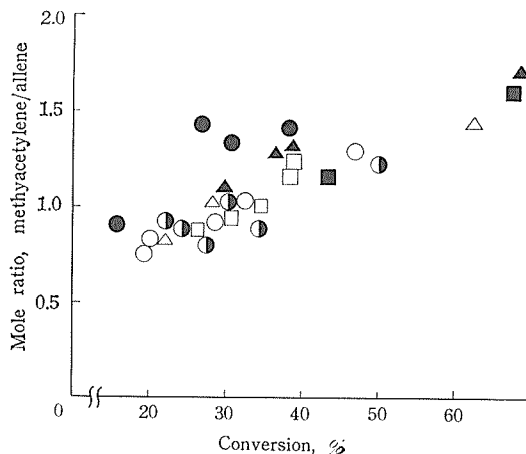Temp., 1150°C.
○ Hydrogen bromide, ● Bromine.

Fig. 8. Mole ratio of methylacetylene to allene in gaseous products. Temp., 1150°C.

catalyst	amount
● Hydrogen bromide	2.4~4.7%
▲ Bromine	0.8~1.3%
○ Chlorine	0.6~0.9%
□ Diazomethane	0.4~0.5%
△ Oxygen	1.1~1.6%
◐ Allyl chloride	0.7~2.1%
▨ No catalyst	

at 27% conversion, while with bromine a 29 mol. yield was obtained at 30% conversion (Table 1). The catalytic effects of chlorine and bromine must result from the abstraction of hydrogen by their radicals, being formed easily by the dissociation of chlorine and bromine. On the other hand, in spite of the fact that hydrogen bromide has a higher dissociation energy, 86.5 Kcal./mol.[11] than that of α (C-H) of propylene, it showed the catalytic effect at the same level as chlorine and bromine. Furthermore, it is worthy of note that the addition of hydrogen bromide gave high ratio of methylacetylene to allene in the gaseous products, compared with other cases (Fig. 8).

Comparison of the Catalytic Effect

The comparison of various catalysts on their catalytic effects is shown in Fig. 9. Among them, chlorine, hydrogen bromide, and bromine showed the best catalytic
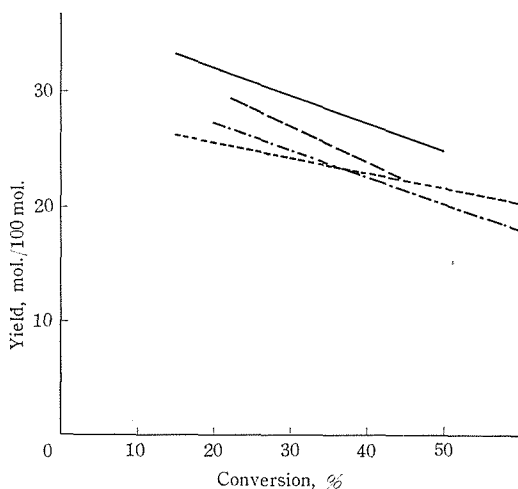

Fig. 9. Comparison of the catalytic effect.
————— Chlorine, hydrogen bromide, and bromine (1150 °C)
————— Allyl chloride and diazomethane (1150 °C)
– – – Oxygen (1150 °C)
– – – – No catalyst (1200 °C)

effect, and their effects were most remarkable at the low conversion. The catalytic effect of allyl chloride was poorer than those of chlorine, hydrogen bromide, or bromine. The poor effect may be explained by assuming that the formation of chloroallyl radical from allyl chloride would take place considerably even in the low conversion. The effect of oxygen was poorest and the yield in high conversion was lower than that in no catalyst. Generally, as the catalyst concentration and the conversion were increased, the hydrogen and carbon balance was appreciably worse than that in no catalyst, especially in the case of allyl chloride. This must be explained by the formation of higher halogenated hydrocarbons, and hydrogen halide, etc,

Relation between Contact Time and Conversion

The relation between contact time and conversion under identiacl conditions is shown in Fig. 10. It was found that there was a linear relationship between contact time and conversion as illustrated. In comparison with the case of no
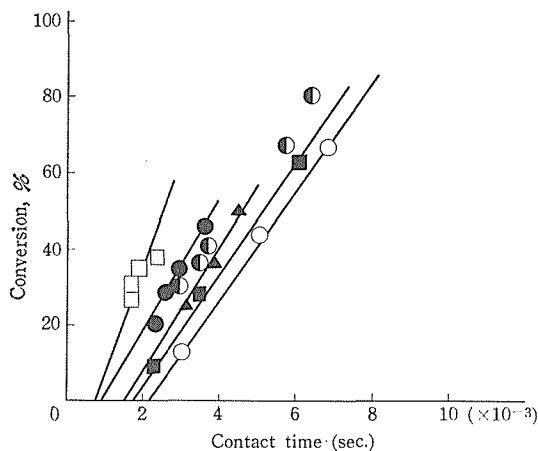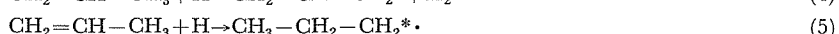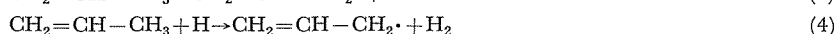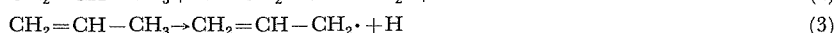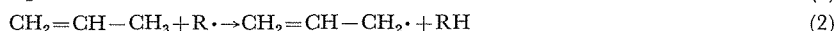

Fig. 10. Relation between contact time and conversion
with various catalysts. Temp., 1150 °C.
☐ Diazomethane, ● Chlorine, ◖ Bromine,
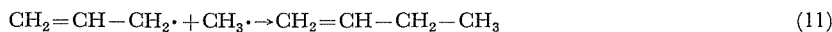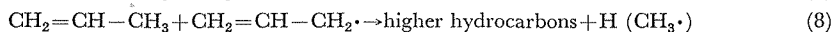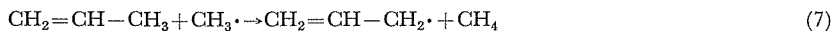▲ Allyl chloride, ▧ Oxygen, ○ No catalyst.

catalyst, the contact time was considerably shortened when chlorine, allyl chloride and bromine were added. Among the catalysts used in this investigation, the contact time was most shortened with diazomethane. It was further noticed that the contact time was reduced to a considerable extent upon increasing catalyst concentration. In connection with the effect of catalyst, it may be thought to be an important matter that such shortening of contact time by catalysts reduces the loss of methylacetylene and allene by the secondary reactions to give better yields. Diazomethane, however, did not show a significant effect in spite of giving a shortest contact time. Thus, as expected, the yield would be related also to type of reaction of propylene with catalysts.

DISCUSSION

On referring to the mechanism for the pyrolysis of propylene described in our previous paper[2], the following free-radical chain mechanism was proposed to explain the primary reactions under the present conditions.

$$R_2 \rightarrow 2R \cdot \tag{1}$$
$$CH_2=CH-CH_3 + R \cdot \rightarrow CH_2=CH-CH_2 \cdot + RH \tag{2}$$
$$CH_2=CH-CH_3 \rightarrow CH_2=CH-CH_2 \cdot + H \tag{3}$$
$$CH_2=CH-CH_3 + H \rightarrow CH_2=CH-CH_2 \cdot + H_2 \tag{4}$$
$$CH_2=CH-CH_3 + H \rightarrow CH_3-CH_2-CH_2^* \cdot \tag{5}$$
$$CH_3-CH_2-CH_2^* \cdot \rightarrow C_2H_4 + CH_3 \cdot \tag{6}$$

$$CH_2=CH-CH_3+CH_3\cdot \rightarrow CH_2=CH-CH_2\cdot +CH_4 \tag{7}$$
$$CH_2=CH-CH_3+CH_2=CH-CH_2\cdot \rightarrow \text{higher hydrocarbons}+H\ (CH_3\cdot) \tag{8}$$
$$CH_2=CH-CH_2\cdot \rightarrow CH_2=C=CH_2+H \tag{9}$$
$$CH_2=CH-CH_2\cdot +H \rightarrow CH_2=CH-CH_3 \tag{10}$$
$$CH_2=CH-CH_2\cdot +CH_3\cdot \rightarrow CH_2=CH-CH_2-CH_3 \tag{11}$$

(The asterisks indicate a hot radical. R_2 shows a radical source which decomposes easily into $R\cdot$ radical.) Generally, the initiation reaction in the thermal decomposition of propylene is considered to be the splitting of the α(C-H) bond leading to the formation of a hydrogen atom and an allyl radical. This requires a high activation energy, E_3 (79 Kcal./mol.). Therefore, if certain radical source, R_2, whose dissociation energy is smaller than E_3, is present, reaction (1) instead of reaction (3) would predominate in the early stage of the pyrolysis, and the chain would be initiated. According to reaction (2), the $R\cdot$ radical formed would abstract a hydrogen atom from propylene to form an allyl radical, which should in turn either be converted to allene according to reaction (9) or be polymerized to higher hydrocarbon according to reaction (8). Thus, the chain would be propagated through many cycle similar to those of no catalyst. So far as the radical source, R_2 is present, the chain would be always started by its decomposition. The $R\cdot$ radical formed is successively supplied into the chain. As compared with no catalyst, this leads to the drop of over-all activation energy, followed by the approach of the relative stability of reactant and product, methylacetylene and allene. As a result, good results would be expected at a considerably low temperature and short contact time. The experimental data seem to confirm this (Table 1). When the pyrolysis proceeds to a certain extent and the concentration of the catalyst decreases, reaction (3) as the initiation reaction would prevail, and the pyrolysis would shift to that of propylene alone. Consequently, the pyrolysis would approach gradually to that of no catalyst. Therefore, the catalytic effect was found to decrease in the high conversion. In some special cases, the yields were lower rather than those of no catalyst, especially in the high conversion.

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