

## The Synthesis of Methylacetylene by the Pyrolysis of Propylene. (V)

### The Pyrolysis of Allyl Halides

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Three allyl halides,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$ ; ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ), have been pyrolyzed in a flow system over a wide range of conditions (temperature, 800-1000°C; contact time,  $0.777 \times 10^{-3}$  -  $42.6 \times 10^{-3}$  sec.; pressure, atmospheric pressure) to find which of allyl halides is most effective for the production of methylacetylene. Diallyl was also pyrolyzed at 1000°C for reference. The effect of added propylene in the pyrolysis system was further studied. The main products of the decomposition were found to be hydrogen, methane, acetylene, ethylene, ethane, propylene, allene, methylacetylene, 1-butene, butadiene, diallyl, 1,3-cyclohexadiene, and benzene. Based on the pyrolysis products, a free-radical mechanism is proposed for the main reactions in the pyrolysis. Among these allyl halides, allyl iodide showed the highest yield of methylacetylene and allyl bromide the lowest, both in the presence and in the absence of added propylene. For example, a maximum total yield of allene and methylacetylene was 13 mol. per 100 mol. of allyl iodide pyrolyzed under suitable conditions. From the characteristic nature of the iodine and the effect of added propylene on allene-methylacetylene yields, it was suggested that iodine or iodine atom have a catalytic effect for converting allyl radical into allene-methylacetylene.

#### INTRODUCTION

In previous papers the authors reported the synthesis of methylacetylene by the pyrolysis of propylene<sup>1)</sup> and allyl chloride.<sup>2)</sup> This report describes the pyrolysis of three allyl halides,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$ ;  $\text{X}=\text{Cl}, \text{Br}, \text{I}$ , at high temperatures in connection with the above subject. Since the C-X bond dissociation energy of allyl halides<sup>3)</sup> (35-58 kcal./mol.) is considerably lower than that of  $\alpha$  (C-H) of propylene<sup>4)</sup> (85 kcal./mol.), the pyrolysis of allyl halides would be expected to bring about good results under moderate conditions and to give available information about the behavior of allyl radical at high temperatures. Although many papers have been published on the pyrolysis of allyl halides;  $\text{X}=\text{Cl}$ ,<sup>2,5-8)</sup>  $\text{Br}$ ,<sup>9-13)</sup>  $\text{I}$ ,<sup>3,14-16)</sup>, there is no information on the production of methylacetylene except for our previous study.<sup>2)</sup>

The purpose of this report is to investigate the effects of substituents X ( $\text{X}=\text{Cl}, \text{Br}, \text{I}$ ) and of added propylene on the yields of methylacetylene and allene, and to obtain data on the distribution of the pyrolysis products. Based on the experimental results, an effort was made to clarify the reaction mechanism for the pyrolysis of allyl halides at high temperatures (800-1000°C). Diallyl was

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also pyrolyzed at 1000°C for reference, and a pyrolysis mechanism was discussed in comparison with that for allyl halides. Emphasis was placed on clarifying the way of the formation of allene and methylacetylene and the reason for the differences of product distribution.

## EXPERIMENTAL

### 1) Materials

Allyl chloride was prepared from allyl alcohol;<sup>17)</sup> b. p. 44–45°C,  $n_D^{22}$  1.4135. Allyl bromide was prepared similarly from allyl alcohol;<sup>18)</sup> b. p. 70–71°C,  $n_D^{20}$  1.4689. Allyl iodide was readily prepared from allyl chloride;<sup>19)</sup> b. p. 101–102°C,  $n_D^{22}$  1.5540. Diallyl was conveniently prepared from allyl chloride;<sup>20)</sup> b. p. 60°C,  $n_D^{20}$  1.4034. Propylene (99.5 mol. % pure) was purchased from the Takachiho Chemical Co. Cylinder nitrogen of 99.9 mol. % purity was used as a diluent and carrier gas.

### 2) Apparatus and Procedure

The apparatus and the technique were essentially the same as used previously for a pyrolytical study of allyl chloride.<sup>2)</sup> In the pyrolysis of allyl iodide, in order to prevent the reactions of unsaturated hydrocarbon products (especially, allene and methylacetylene) with hydrogen iodide or residual iodine after emergence from the reaction tube, the gaseous effluent, after passage through a water trap, was bubbled through two washing bottles containing 150 ml. of *aq.* 1 N NaOH solution. This alkaline solution was extracted twice with 50 ml. ether, and then a portion of the ether solution was taken up as described previously.<sup>2)</sup> Propylene was introduced into the reaction system at a constant flow velocity using a regulating valve and a flow meter.

### 3) Analysis

The analytical method for the pyrolysis products was essentially the same as that previously described.<sup>2)</sup>

## RESULTS AND DISCUSSION

A part of the experimental results is shown in Table 1. Though we tried to identify C<sub>5</sub> components (for example, cyclopentadiene, *etc.*), they were not found in the reaction products except for the case of diallyl.

### Pyrolysis of Allyl Chloride

Studies on the pyrolysis of allyl chloride have been carried out in the temperature range from 370 to 1200°C. The reaction products reported by previous investigators are summarized in Table 2.

The pyrolysis of allyl chloride at low temperatures was concluded by Goodall and Howlett<sup>5)</sup> to be complex processes which yielded, initially, allene and hydrogen chloride. On the other hand, Shilov,<sup>6)</sup> Porter and Rust,<sup>7)</sup> and Hughes and Yates<sup>8)</sup> proposed a free-radical mechanism which involved an initial dissociation of allyl chloride into chlorine atom and allyl radical, based on activation energy

Table 1. Pyrolysis of Allyl Halides.

Run No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Allyl halide	C <sub>3</sub> H <sub>5</sub> Cl	C <sub>3</sub> H <sub>5</sub> Cl	C <sub>3</sub> H <sub>5</sub> Cl	C <sub>3</sub> H <sub>5</sub> Br	C <sub>3</sub> H <sub>5</sub> Br	C <sub>3</sub> H <sub>5</sub> Br	C <sub>3</sub> H <sub>5</sub> I	C <sub>3</sub> H <sub>5</sub> I	C <sub>3</sub> H <sub>5</sub> I	C <sub>3</sub> H <sub>5</sub> I	C <sub>6</sub> H <sub>10</sub> <sup>a)</sup>	C <sub>3</sub> H <sub>5</sub> Cl	C <sub>3</sub> H <sub>5</sub> Br	C <sub>3</sub> H <sub>5</sub> I
Temp., °C	800	900	1000	800	900	1000	800	900	1000	1000	1000	1000	1000	1000
Contact time, 10 <sup>-3</sup> sec.	42.6	20.0	12.5	3.72	2.58	1.50	1.96	0.989	0.985	0.777	2.96	12.8	1.64	1.09
Composition of reactant gas, mol. %														
Nitrogen	87.2	88.4	92.1	95.0	93.4	95.8	97.5	97.6	97.1	94.7	94.1	90.1	93.9	95.5
Allyl halide	12.8	11.6	7.9	5.0	6.6	4.2	2.5	2.4	2.9	5.3	5.9	8.1	4.5	2.8
Propylene												1.9	1.9	1.8
Rate of expansion	1.00	0.963	0.957	0.995	0.980	0.987	0.996	0.990	0.980	0.980	1.00	1.03	1.00	0.966
Conversion	41.2	47.4	48.4	47.7	48.8	48.0	57.5	44.6	69.8	57.0	48.6	54.3	49.8	68.7
Yield, <sup>b)</sup> mol./100 mol. of allyl halide pyrolyzed														
Hydrogen	4.1	8.1	15.7	5.4	8.1	9.8					2.6	25.2	13.8	
Methane	trace	trace	trace	trace	trace	trace					trace	10.1	3.4	
Acetylene	1.5	2.5	4.8	trace	0.3	0.8					0.8	7.0	1.1	
Ethylene	3.8	5.8	7.3	2.1	3.0	3.4					6.1	13.1	7.2	
Ethane				0.8	0.7	0.4							trace	
Propylene	13.8	12.7	9.7	23.4	21.6	18.1	37.0	39.4	36.5	37.8	23.1	(0.7) <sup>c)</sup>	(13.9) <sup>c)</sup>	(35.4) <sup>c)</sup>
Allene	4.4	4.2	3.7	1.6	1.5	2.0	4.4	6.7	7.0	5.9	5.1	5.1	2.8	9.2
Methylacetylene	1.2	1.7	2.8	0.8	1.2	1.8		trace	2.9	1.9	1.6	4.7	2.3	3.6
1-Butene	1.0	1.1	0.7								4.8	1.4		
Butadiene	2.2	3.0	2.0	0.7	1.0	1.3					3.7	3.6	2.5	
Cyclopentadiene											2.4			
Methylcyclopentadiene											1.3			
Diallyl	1.5	1.1	trace	trace	trace	trace	3.2	2.5	0.5	3.7		1.1		0.5
1,3-Cyclohexadiene	4.3	1.9	trace								0.8	trace		
Benzene	19.1	19.0	16.1	19.0	22.1	21.4	8.2	7.6	7.8	8.8	2.7	16.9	22.1	7.4
Total yield of methylacetylene and allene	5.6	5.9	6.5	2.4	2.7	3.8	4.4	6.7	9.9	7.8	6.7	9.8	5.1	12.8
Percentage of hydrogen and carbon accounted for in products (H <sub>2</sub> , C <sub>1</sub> -C <sub>6</sub> hydrocarbons)														
Hydrogen	63.4	61.5	53.6	58.5	62.9	59.5	64.1	66.2	63.1	69.5	60.9	69.0	64.6	62.4
Carbon	76.5	68.9	60.0	66.9	72.7	69.5	64.1	66.2	63.1	70.5	59.4	73.0	73.1	63.9

a) The result of diallyl is shown for the purpose of reference.

b) In the case of diallyl, the yield of each product is given by moles per 50 mol. of diallyl pyrolyzed for the purpose of comparison with those of allyl halides.

c) The values shown in parentheses are the amount of propylene increased in comparison with that in the reactant gas.

Table 2. Summary of Previous Investigations.

reference	temperature range (°C)	products
5) Goodall and Howlett	370 to 475	allene, allene polymers, acetylene, <i>etc.</i>
6) Shilov*	594 to 709	allene, propylene, diallyl, dibenzyl, 4-phenyl-1-butene, <i>etc.</i>
7) Porter and Rust	550	propylene, benzene, C <sub>8</sub> H <sub>4</sub> , 1, 3-cyclohexadiene, hydrogen, methane, ethylene, diallyl, <i>etc.</i>
8) Hughes and Yates	540 to 765	propylene, diallyl, benzene, 1, 3-cyclohexadiene, <i>etc.</i>
Kunichika, 2) Sakakibara and Taniuchi	800 to 1200	hydrogen, methane, acetylene, ethylene, propylene, allene, methylacetylene, 1-butene, butadiene, diallyl, benzene, 1, 3-cyclohexadiene, <i>etc.</i>

\* toluene-carrier technique

data for the pyrolysis and on the identification of the products.

Although many workers<sup>5-8)</sup> reported that only small amounts of methylacetylene and allene were detected in the products, both compounds were obtained in moderate amounts, as would be expected, under our reaction conditions. The major products were propylene and benzene, as reported by previous workers.<sup>7,8)</sup> A methylacetylene-allene yield of 7 mol. per 100 mol. of allyl chloride pyrolyzed was realized at 1000°C and 48.4% conversion. In addition to the above main products through C<sub>6</sub> hydrocarbons (methylacetylene, allene, propylene, benzene, and hydrogen), methane, acetylene, ethylene, 1-butene, butadiene, diallyl, and 1, 3-cyclohexadiene (Table 1, Run No. 1-3) were found as previously mentioned.<sup>2)</sup>

The total yield of methylacetylene and allene increased slightly with increasing temperature, *i. e.*, it ranged from 6 mol. at 800°C up to 7 mol. at 1000°C. In this connection, the yield of allene fell gradually as the temperature was increased, while that of methylacetylene increased little by little. Propylene, on the other hand, decreased with an increase in the temperature from 14 mol. to 10 mol. The yields of hydrogen, acetylene and ethylene increased gradually with increasing temperature, while those of 1-butene and butadiene were much the same over the temperature range studied. Besides, as the temperature was increased, the yield of benzene decreased from 19 mol. at 800°C to 16 mol. at 1000°C. The yield of 1, 3-cyclohexadiene decreased rapidly, but that of diallyl fell slowly.

### Pyrolysis of Allyl Bromide

Studies on the pyrolysis of allyl bromide have been carried out in the temperature range from 320 to 592°C. The reaction products reported by previous investigators are summarized in Table 3.

Earlier studies on the pyrolysis of allyl bromide have been concerned with the kinetics of the pyrolysis and the identification of the decomposition products. From the activation energy for the pyrolysis and the reaction products, Maccoll<sup>9,10)</sup> and Szwarc *et al.*<sup>11)</sup> proposed a free-radical mechanism involving an initial dissociation of allyl bromide into bromine atom and allyl radical.

## Pyrolysis of Allyl Halides

Table 3. Summary of Previous Investigations.

reference	temperature range (°C)	products
10) Maccoll	320 to 380	benzene, 1-bromopropene, isopropyl bromide, <i>etc.</i>
11) Szwarc, Ghosh* and Sehon	459 to 592	hydrogen, methane, dibenzyl, propylene, allene, <i>etc.</i>
12) Brown and Throssell*	473 to 575	hydrogen, methane, propylene, ethylene, allene, cyclopropane, benzene, diallyl, dibenzyl, <i>etc.</i>

\* toluene-carrier technique

In the previous studies<sup>9-13)</sup> only small amounts of allene were identified,<sup>11,12)</sup> but methylacetylene was not obtained. Allene and methylacetylene, however, were obtained as the minor products and the major products were propylene and benzene under our reaction conditions. A methylacetylene-allene yield of 4 mol. per 100 mol. of allyl bromide pyrolyzed was realized at 1000°C and 48.0 % conversion. In addition to the above main products through C<sub>6</sub> hydrocarbons (methylacetylene, allene, propylene, benzene, and hydrogen), methane, acetylene, ethylene, ethane, butadiene, and diallyl (Table 1, Run No. 4-6) were found.

In the pyrolysis, allyl bromide showed essentially the same tendency as allyl chloride did. Each yield of methylacetylene and allene increased with increasing temperature, *i. e.*, the total yield of them ranged from 2 mol. at 800°C up to 4 mol. at 1000°C. Propylene, on the other hand, decreased with increasing temperature from 23 mol. to 18 mol. The yields of hydrogen, acetylene and ethylene increased gradually with increasing temperature, while those of butadiene, diallyl and benzene was much the same over the temperature range studied. The yield of benzene was almost constant at about 20 mol.

As compared with the case of allyl chloride, larger amounts of propylene and benzene were obtained, but smaller amounts of acetylene, ethylene, allene, methylacetylene, butadiene, and diallyl were found. It was further noted that small amounts of ethane were formed and that 1-butene and 1, 3-cyclohexadiene were not detected.

### Pyrolysis of Allyl Iodide

Studies on the pyrolysis of allyl iodide have been carried out at low temperatures except for the study of Lossing, Ingold and Henderson.<sup>15)</sup> The reaction products reported by previous investigators are summarized in Table 4.

Earlier works on the pyrolysis of allyl iodide have been generally concerned with the strength of the C-I bond. From the kinetics of the pyrolysis of allyl iodide, Szwarc<sup>3)</sup> and Benson<sup>16)</sup> proposed a radical mechanism involving an initial dissociation of allyl iodide into iodine atom and allyl radical. Besides, Lossing *et al.*<sup>15)</sup> found that the formation of allyl radical appeared to be almost quantitative in the pyrolysis of allyl iodide, the only other hydrocarbon product of any importance being the dimerization product, diallyl.

In the previous studies<sup>3,14-16)</sup> product analyses have been limited and little is known about the decomposition products. Recently, the dehydrogenation process

Table 4. Summary of Previous Investigations.

reference	temperature range (°C)	products
3) Szwarc	<i>a)</i>	diallyl
15) Lossing, Ingold and Henderson	750 to 915	diallyl
16) Benson	<i>a)</i>	C <sub>6</sub> H <sub>10</sub> <sup>b)</sup>

a) No accurate information was designated about the temperature range of the pyrolysis.

b) Benson suggests that the C<sub>6</sub>H<sub>10</sub> is undoubtedly cyclohexene or methylcyclopentene.<sup>16)</sup>

of paraffins with iodine<sup>21,22)</sup> is highly developed and is being watched with keen interest. In this connection, the present authors carried out the pyrolysis of allyl iodide in order to obtain a clue to elucidation of the mechanism of the iodine-catalyzed dehydrogenation of paraffins. According to the results of previous investigations, diallyl alone was positively identified in the pyrolysis products and there was no information about the other pyrolysis products. However, methylacetylene and allene were obtained as minor products under our reaction conditions. The major product was propylene. A methylacetylene-allene yield of 10 mol. per 100 mol. of allyl iodide pyrolyzed was realized at 1000°C and 69.8 % conversion. In addition to the above main products through C<sub>6</sub> hydrocarbons (allene, methylacetylene and propylene), diallyl and benzene (Table 1, Run No. 7-10) were found.

While definite differences in product distribution are found, the behavior of allyl iodide in the pyrolysis is quite similar to that of allyl chloride and bromide. In fact, the yields of both methylacetylene and allene increased with increasing temperature, *i. e.*, the total yield of methylacetylene and allene ranged from 4 mol. at 800°C up to 10 mol. at 1000°C. The yield of propylene, on the other hand, was almost constant at 37 mol. As the temperature was increased, the yield of diallyl decreased, but that of benzene was almost constant at about 8 mol. over the temperature range investigated.

As compared with the cases of allyl chloride and bromide, larger amounts of allene, propylene and diallyl were obtained, but smaller amount of benzene was found. In addition to propylene, allene, methylacetylene, diallyl, and benzene, no other products were detected in considerable amounts. Besides, the total yield of C<sub>6</sub> components (diallyl and benzene) was fairly low and considerable amounts of diallyl were observed even in the high conversion.

### Pyrolysis of diallyl

Studies on the pyrolysis of diallyl have been carried out in the temperature range from 425 to 890°C. The reaction products reported by previous investigators<sup>15,23-26)</sup> are summarized in Table 5.

Earlier works on the pyrolysis of diallyl have been concerned with the kinetics of the pyrolysis and identification of the decomposition products. As the result, it was confirmed that the pyrolysis of diallyl should involve the formation of two allyl radicals through the dissociation of the C-C bond in diallyl in the

Pyrolysis of Allyl Halides

Table 5. Summary of Previous Investigations.

reference	temperature range (°C)	products
23) Hurd and Bollman	425 to 650	acetylene, propylene, ethylene, hydrogen, <i>etc.</i>
24) Ruzicka and Bryce	460 to 520	propylene, methane, ethylene, 1-butene, cyclopentene, cyclopentadiene, benzene, <i>etc.</i>
26) Akers and Throssell*	577 to 677	hydrogen, methane, ethylene, propylene, 1-butene, allene, butadiene, acetylene, <i>etc.</i>
15) Lossing, Ingold and Henderson	690 to 890	hydrogen

\* toluene-carrier technique

primary step.

It has been generally considered that the bond dissociation energy of diallyl is comparable to that of allyl iodide<sup>3)</sup> and the high temperature pyrolysis of diallyl may produce allyl radical easily.<sup>15)</sup> The present authors carried out the pyrolysis of diallyl as a reference experiment to examine the behavior of allyl radical itself at high temperatures in the absence of halogen atoms and to compare thoroughly with the pyrolysis of allyl halides. In the case of diallyl, the yield of each product was given by moles per 50 mol. of diallyl pyrolyzed for convenience of comparison with the pyrolysis data of allyl halides. In the previous studies<sup>15,23-26)</sup> only small amounts of allene<sup>26)</sup> were obtained and methylacetylene was not identified. However, methylacetylene and allene were obtained as the minor products under our reaction conditions (Table 1, Run No. 11). The major product was propylene, as reported by previous workers.<sup>23,24,26)</sup> A methylacetylene-allene yield of 7 mol. per 50 mol. of diallyl pyrolyzed was realized at 1000°C and 48.6% conversion. In addition to the above main products through C<sub>6</sub> hydrocarbons (methylacetylene, allene, propylene, and hydrogen), methane, acetylene, ethylene, 1-butene, butadiene, cyclopentadiene, methylcyclopentadiene, 1,3-cyclohexadiene, and benzene were found. The yield of propylene was much the same as the case of allyl bromide, and the total yield of methylacetylene and allene was almost the same as that in the pyrolysis of allyl chloride.

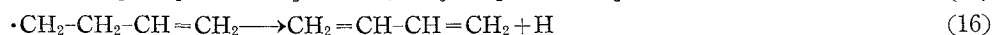
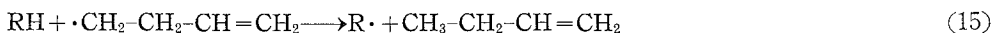
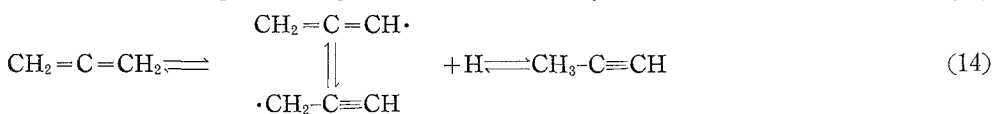
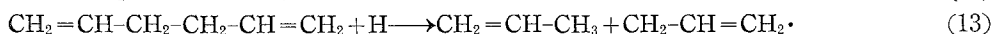
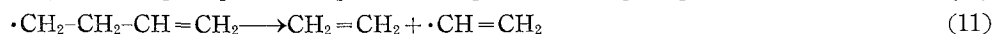
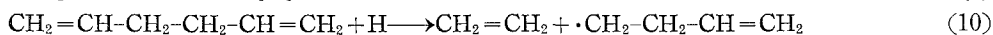
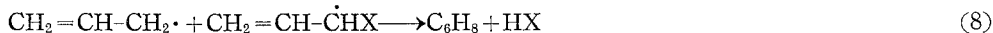
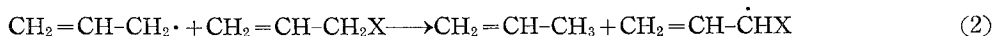
As compared with allyl halides mentioned above, larger amounts of 1-butene and butadiene and smaller amount of benzene were obtained. It was further found that cyclopentadiene and methylcyclopentadiene were produced in our reaction conditions.

### Mechanism

On the basis of the products obtained from the pyrolysis of three allyl halides and diallyl, the following free-radical mechanism is proposed, where the characteristic formation of allene and methylacetylene being taken into account. The scheme is not intended to be comprehensive but only to indicate how the main products are probably formed.

### Pyrolysis of Allyl Chloride and Bromide

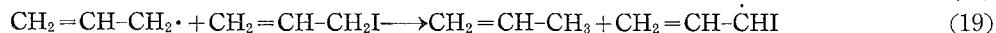




(X indicates chlorine or bromine atom, and RH shows hydrogen donors.)

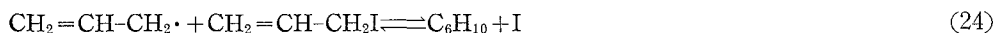
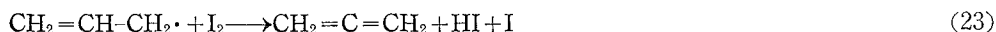
Reaction 1 is the initiation step. All the main products, propylene, allene, hydrogen, diallyl, 1, 3-cyclohexadiene, benzene, ethylene, acetylene, methylacetylene, 1-butene, and butadiene are formed largely by subsequent reactions 2 and 4-16. Reaction 4, being the step of the formation of allene from allyl radical<sup>1b, 27, 28)</sup> appears to play an important role under the conditions studied. Reactions 2, 4, 6, 7 and 8 involving allyl radical proceed competitively with each other. Of these reactions, reaction 4 appears to become predominant at higher temperature, as supported by the experimental results that the total yield of allene and methylacetylene increases with the increase of temperature. This may be plausible judging from the theoretical foundation that reaction 4 is an unimolecular reaction which requires a high activation energy of about 62 kcal./mol.<sup>28a, 29)</sup> Reactions 8 and 9 are complicated reactions which include combination of allyl and chloro- or bromo-allyl radicals followed by cyclization.<sup>7, 10)</sup> Concerning thermal isomerization of allene to methylacetylene, it has been reported by the present authors that allene isomerizes to methylacetylene in fairly good yield at high temperatures.<sup>1b)</sup> As the conversion increases, the participation of hydrogen abstraction by chlorine or bromine atom from the reaction products would play an important role under our experimental conditions, though it is not shown in the reaction mechanism.

### Pyrolysis of Allyl Iodide



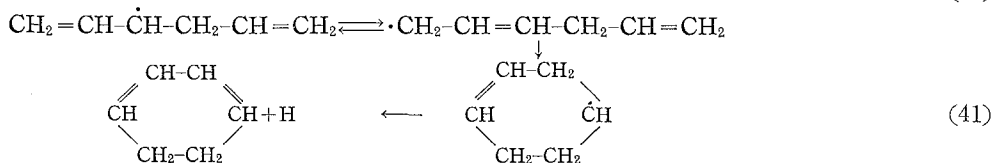
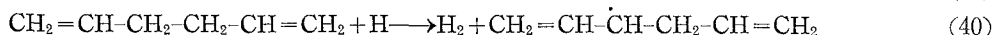
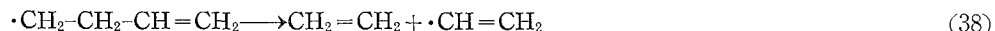
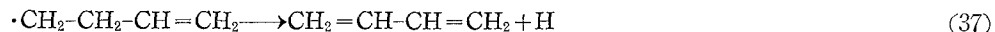
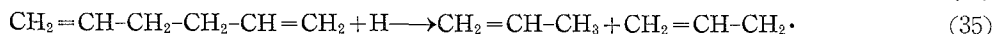
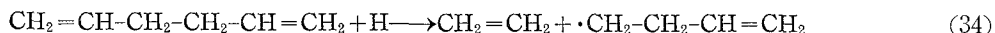
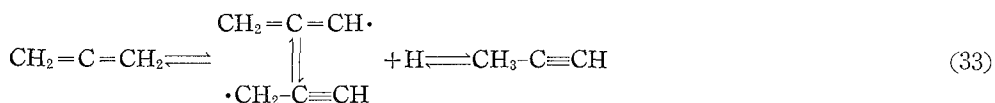
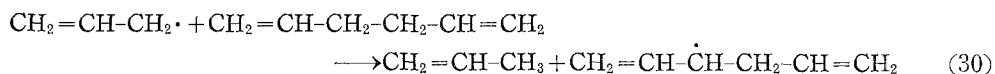


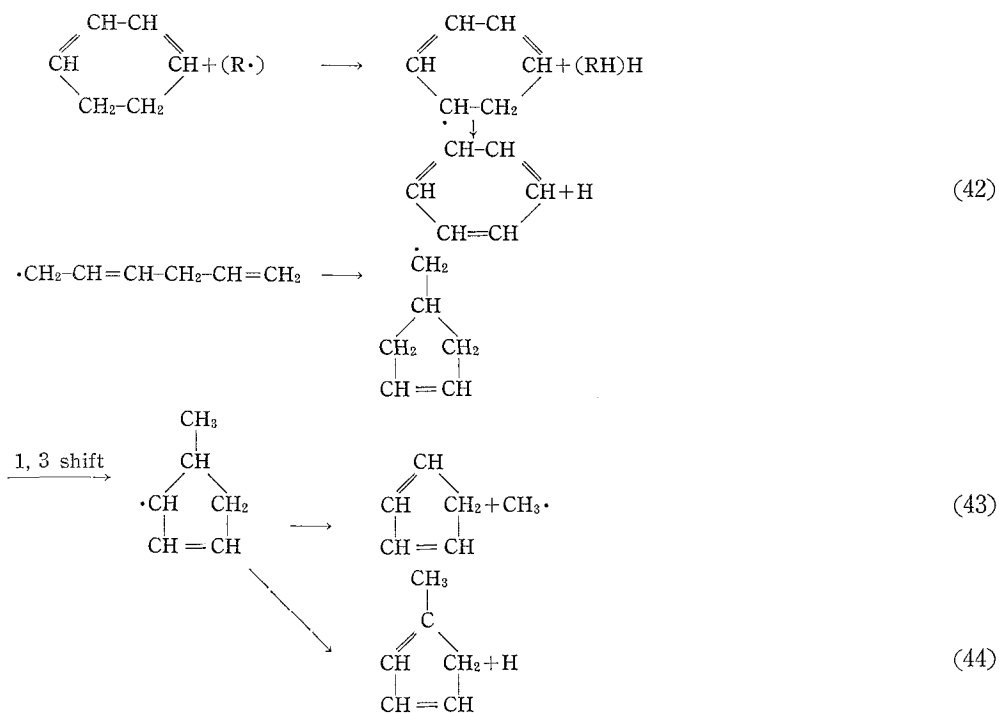
Pyrolysis of Allyl Halides



Reaction 17 is the initiation step. All the main products, propylene, allene, diallyl, benzene, and methylacetylene are formed largely by subsequent reactions 19, 21-26, and 28. As the formation step of allene, two reactions 22 and 23 are present in our mind. Although reaction 22 should have a high specific rate from an energetic point of view, reaction 23 should also be important in view of the known rapidity of the reaction between alkyl radicals and iodine and the high ratio of molecular to atomic iodine.<sup>21)</sup> Although it is considered that reactions 19 and 24 of allyl radical with allyl iodide proceed competitively with each other and that reaction 24 has advantages over reaction 19 energetically, the reaction 19 should not be neglected because the reverse of reaction 24 is very rapid. Reactions 18 and 20 of iodine atom with allyl iodide are competitive reactions with each other. The hydrogen abstraction from allylic position would result in iodoallyl radical. Benzene would arise from the combination of two iodoallyl radicals as in the cases of the other allyl halides (Reaction 26). The isomerization of allene to methylacetylene would proceed through the same mechanism as the iodine-catalyzed isomerization of butene.<sup>30)</sup>

Pyrolysis of Diallyl





Reaction 30 is the initiation step. All the main products, propylene, allene, methylacetylene, ethylene, 1-butene, butadiene, acetylene, hydrogen, 1, 3-cyclohexadiene, benzene, cyclopentadiene, and methylcyclopentadiene are formed largely by subsequent reactions 30-44.

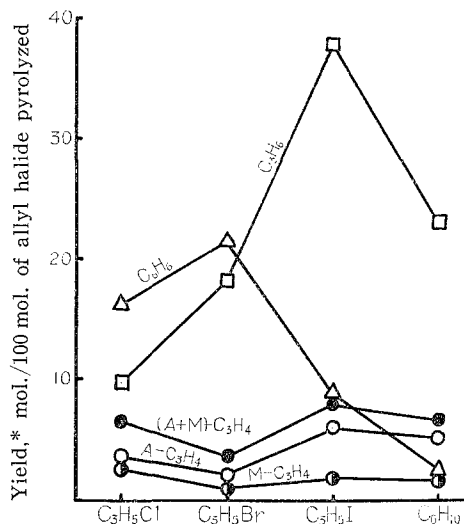


Fig. 1. Comparison of three allyl halides. Temp., 1000°C

\* In the case of diallyl, the yield of each product is given by moles per 50 mol. of diallyl pyrolyzed.

## Comparison of Three Allyl Halides in Pyrolysis

Comparison of the pyrolysis products derived from three allyl halides is made in Fig. 1 and Table 1. As shown in the figure, it may be concluded that allyl iodide is best; allyl chloride second; allyl bromide last for the production of methylacetylene and allene. The yield of allene decreased in the order; iodide > chloride > bromide, while that of methylacetylene fell in the order; chloride > iodide > bromide.

In addition, the decrease in the yield of propylene was found in the order; iodide > bromide > chloride and in the yield of benzene; bromide > chloride > iodide. The kinds of the decomposition products increased in this order; iodide < bromide < chloride.

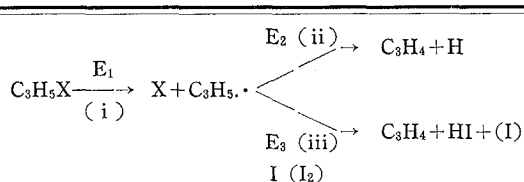
As would be expected from the C-X bond dissociation energy (Table 6), the pyrolysis of allyl iodide is almost kept within primary reactions because allyl iodide itself is rather reactive in comparison with the products produced. But, as a starting material varies from allyl bromide to allyl chloride, the further

Table 6. Bond Dissociation Energy of Allylic Compounds kcal./mol.

	X=H <sup>(4)</sup> ,	Cl <sup>(3)</sup> ,	Br <sup>(3)</sup> ,	I <sup>(3)</sup> ,	CH <sub>2</sub> =CH-CH <sub>2</sub> <sup>(26)</sup>
CH <sub>2</sub> =CH-CH <sub>2</sub> X	85	58	48	35-37	56

decompositions of the decomposition products such as propylene, diallyl *etc.*, would increase because the difference in stability between the starting material and the products becomes more and more small. In fact, comparison of the amounts of propylene for three cases (Run No. 12, 13 and 14 or No. 3, 6, and 10) indicated that, with allyl chloride and allyl bromide, the secondary decomposition of propylene proceeds considerably, while with allyl iodide its decomposition hardly proceeds, regardless of the presence of added propylene in the reaction system. It is worthy of special mention that, in the case of allyl iodide, all the decomposition products possess C<sub>3</sub> and C<sub>6</sub> skelton derived from allyl and iodoallyl radicals; hydrogen, and C<sub>1</sub>, C<sub>2</sub> and C<sub>4</sub> hydrocarbons were detected in only small amounts, though the highest yield of propylene was observed. As allyl halide varies from allyl bromide to allyl chloride, the kinds of the decomposition products become abundant and the yield of propylene decreases.

Table 7. Formation Process of Allene from Allyl Radical.



E<sub>1</sub>: bond dissociation energy of allyl halides.

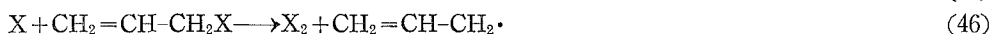
E<sub>2</sub>: activation energy of formation of allene from allyl radical.

E<sub>3</sub>: activation energy for hydrogen abstraction from allyl radical by I-atom, or for reaction between allyl radical and I<sub>2</sub>.

(X denotes Cl, Br, and I)

Concerning the total yield of allene and methylacetylene, allyl iodide was best; allyl chloride second; allyl bromide last. This seems to be explained by considering the relationship as described in Table 7. Based on the C-X bond dissociation energy (Table 6) and the fact that  $E_2$  is about 62 kcal./mol.<sup>28a,29)</sup>, the difference between  $E_1$  and  $E_2$  is 4 kcal./mol. in chloride, 14 kcal./mol. in bromide and 25-27 kcal./mol. in iodide, respectively. It can therefore be presumed that the total yield of allene and methylacetylene would become worst with allyl iodide. However, this is not the case, *i. e.*, the best yield of allene and methylacetylene was obtained with allyl iodide. This value is higher than that of diallyl. This may be explained principally by the fact that, in the case of allyl iodide, reaction (iii) instead of reaction (ii) would predominate in the presence of iodine or iodine atom, since  $E_3$  is considered to be comparatively lower than  $E_2$ .<sup>21)</sup> Namely, iodine or iodine atom appears to have the catalytic effect for the production of allene and methylacetylene through allyl radical.

The yield of benzene from allyl iodide is roughly one half of those of allyl chloride and bromide. This seems to be explained by the following schema.



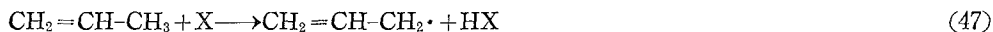
(X shows halogen atom)

While reaction 45 is more favorable than reaction 46 with allyl chloride and bromide, the reverse is the case with allyl iodide.<sup>31)</sup> Thus, the formation of haloallyl radical should become easier in the former two cases. Hence, the yield of benzene is higher with allyl chloride and bromide, as compared with allyl iodide. It is not clear why 1, 3-cyclohexadiene is not formed with allyl bromide and iodide. Further work is being carried out on the pyrolysis of allyl halides, which may promise a more complete description of the reaction mechanism.

### Effect of Added Propylene

Because considerably large amounts of propylene were found in the pyrolysis products of allyl halides, the authors attempted Run No. 12-14, expecting that the formation of propylene would be suppressed, whereas that of methylacetylene and allene would be promoted, if suitable amounts of propylene were added to allyl halides previously. When propylene was added, the total yield of methylacetylene and allene increased in the reaction of all allyl halides, and decreased in this order; iodide > chloride > bromide. This trend is similar to that without added propylene. Making the comparison of the cases where the added propylene is present or absent, the rate of increase in the total yield by adding propylene decreased in the order; chloride > bromide > iodide. As shown in Table 1, the formation of propylene is suppressed in the order; chloride > bromide > iodide, and this order is in good agreement with the rate of increase of the yield by adding propylene. Finally, the kinds of the products scarcely changed when propylene was added, but the yields of hydrogen, methane and ethylene, especially in allyl chloride, increased considerably.

The increase of allene-methylacetylene yield by adding propylene is explained on the basis of  $\alpha$ -hydrogen abstraction from propylene by halogen atoms.<sup>1c,7,29b)</sup> Namely, when propylene is added,



reaction 47, especially where X is Cl and Br, proceeds to form allyl radical, which yields allene and methylacetylene. It may be further concluded that considerable increase of the yields of hydrogen, methane, acetylene, ethylene, 1-butene, and butadiene results from the decomposition of propylene added.<sup>1)</sup> Since the large quantity of propylene added is decomposed in the pyrolysis of allyl chloride (Table 1), good yields of allene and methylacetylene in the absence of added propylene can be explained by the secondary decomposition of propylene formed. In the case of allyl iodide, since added propylene is scarcely decomposed, good yields of allene and methylacetylene may be illustrated by catalytic action of iodine or iodine atoms on the hydrogen abstraction of allyl radical.

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