The Synthesis of Methylacetylene by the Pyrolysis of Propylene. (VIII) The Pyrolysis of Allyl Bromide

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Allyl bromide has been pyrolysed in a flow system with a nitrogen dilution over a wide range of conditions (temperature, 800–1200°C; contact time, 0.188×10^{-3}—2.30×10^{-3} sec; concentration, 3.2–9.5 mol% ; pressure, atmospheric pressure) in order to elucidate the pyrolytic behaviors of allyl bromide at high temperatures.   The main products in the pyrolysis were found to be hydrogen, methane, ethane, ethylene, acetylene, allene, methylacetylene, propylene, butadiene, benzene, diallyl, n-propyl bromide, and 1-bromopropene.   By means of the zero-conversion method, it has been shown that, among them, hydrogen, ethylene, allene, propylene, butadiene, benzene, and diallyl are the major products in the early stage of the pyrolysis.   On the basis of the observed results, a free radical mechanism has been proposed for the main and the principal side reactions.   It has further been concluded that the pyrolysis is a radical decomposition initiated by the reaction $C_3H_5Br \rightarrow C_3H_5 \cdot + Br$ and that the mechanism in the early stage of the pyrolysis is explained essentially by the reactions of allyl radicals and bromoallyl radicals.

INTRODUCTION

In the course of our studies on the synthesis of methylacetylene,[1~7] we found that halogen and the halogen atom have a catalytic effect in converting the allyl radical into allene[4] and that there are considerable differences in the product distribution in the pyrolysis of three allyl halides.[6]   In this report, the result of pyrolysis of allyl bromide was described in detail.

The reaction products reported by previous investigators are summarised in Table 1.

From the kinetics for the pyrolysis and the reaction products, Szwarc *et al.*[8] and Maccoll[9] proposed a free radical mechanism involving an initial dissociation of allyl bromide into the allyl radical and the bromine atom.   The previous investigations have been carried out at low temperatures except for one by ourselves.[6]   In addition, product analysis has been limitted and little is known about the distribution of the pyrolysis products.

The purpose of the present investigation is to obtain data on the distribution of the pyrolysis products under various conditions.   On the basis of the observed results, an

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Table 1. Summary of Previous Investigations.

	Reference	Temperature range (°C)		Products
9)	Maccoll	320	to 380	benzene, 1-bromopropene, isopropyl bromide, *etc.*
8)	Szwarc, Ghosh and Sehon *	459	to 592	hydrogen, methane, dibenzyl, propylene, allene, *etc.*
10)	Brown and Throssell *	473	to 575	hydrogen, methane, propylene, ethylene, allene, cyclopropane, benzene, diallyl, dibenzyl, *etc.*
6)	Kunichika, Sakakibara and Taniuchi	800	to 1000	hydrogen, methane, acetylene, ethylene, ethane, propylene, allene, methylacetylene, butadiene, benzene, diallyl.

* toluene-carrier technique

effort was made to clarify the reaction mechanism for the pyrolysis at high temperatures (800–1200°C).

EXPERIMENTAL

Materials. The allyl bromide was prepared from allyl alcohol.[11] b.p. 69.5–

Table 2. Pyrolysis of Allyl Bromide at Various Temperatures

Run. No.	57	76	58	55	54	59	61	65
Temp., °C	800	800	900	1000	1000	1100	1200	1200
Contact time, 10^{-3} sec	2.02	2.60	1.34	0.905	0.870	0.634	0.391	0.403
Composition of reactant gas mol%								
Nitrogen	94.2	94.7	94.8	94.7	94.9	95.2	95.3	95.2
Allyl bromide	5.8	5.3	5.2	5.3	5.1	4.8	4.7	4.8
Rate of expansion	1.02	1.02	1.01	1.00	0.990	1.00	1.00	1.01
Conversion, %	24.6	32.8	25.3	31.4	29.3	31.3	28.0	27.0
Yield, mol/100 mol of allyl bromide pyrolyzed								
Hydrogen	10.2	7.5	10.3	13.8	13.9	13.8	15.7	15.4
Methane	tr.	0.2	tr.	0.8	0.6	0.6	0.6	0.9
Ethane	0.4	0.4	0.3	0.2	0.2	0.2	0.2	0.2
Ethylene	2.2	1.8	2.4	3.1	2.6	2.9	3.1	3.3
Acetylene	0.1	0.1	0.1	0.6	0.4	1.0	1.6	1.5
Propylene	23.9	21.7	20.6	16.9	16.0	15.2	14.2	15.0
Allene	1.8	1.3	1.7	1.7	1.6	1.9	2.4	2.4
Methylacetylene	0.5	0.3	0.7	1.0	0.8	1.6	2.0	1.9
Butadiene	0.9	0.5	1.0	1.0	1.0	1.0	1.0	0.9
Diallyl	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
Benzene	17.5	17.4	19.4	18.8	18.0	18.1	17.8	17.6
1-bromopropene	2.9	3.2	2.9	2.7	2.6	2.9	3 2	2.1
n-propyl bromide	2.5	2.2	6.2	7.5	7.4	8.5	6.0	3.6
Percentage of hydrogen and carbon accounted for in products								
Hydrogen	69.6	65.8	74.1	72.3	68.1	70.6	68.3	65.1
Carbon	69.3	60.3	69.2	69.0	65.5	67.8	64.9	61.1

70.5°C, n_D^{21} 1.4688. Cylinder nitrogen of 99.99 mol% purity was used as a diluent and carrier gas. Toluene used as an absorbent was reagent grade.

Apparatus and Procedure. The apparatus and the technique were essentially the same as that of previous paper[5] on the pyrolysis of allyl chloride, except for the use of toluene as an absorbent.

Analysis. The analysis of the pyrolysis products was made according to that described previously.[5]

RESULTS

The pyrolysis products obtained are as follows: hydrogen, methane, ethane, ethylene, acetylene, allene, methylacetylene, propylene, butadiene, n-propyl bromide, 1-bromopropene, diallyl, benzene.

Butene-1 and 1,3-cyclohexadiene in the pyrolysis products of allyl chloride were not detected in the case of allyl bromide under the present conditions.

Some of the experimental results are shown in Tables 2 and 3. The yield of each product was given by moles per 100 moles of allyl bromide pyrolyzed. In order to examine the hydrogen and carbon balance, the percentage of hydrogen and carbon accounted for in the reaction products (H_2 and C_1-C_6 hydrocarbons) was calculated from their yields.

Table 3. Pyrolysis of Allyl Bromide at Various Conversions and Concentrations

| Run. No.	49	47	28	80	32	71	68	53
Temp., °C	1000	1000	1000	1000	1000	1000	1000	1000
Contact time, 10^{-3} sec	0.188	0.265	1.17	1.41	2.30	0.933	0.870	0.943
Composition of reactant gas, mol%								
Nitrogen	95.3	94.5	94.7	95.7	94.5	96.7	92.6	90.5
Allyl bromide	4.7	5.5	5.3	4.3	5.5	3.3	7.4	9.5
Rate of expansion	1.05	1.03	1.01	1.00	1.01	1.00	1.01	1.02
Conversion, %	6.2	17.5	39.4	58.0	76.3	32.4	27.2	26.7
Yield, mol/100 mol of allyl bromide pyrolyzed								
Hydrogen	16.9	15.2	15.4	14.7	15.5	12.5	12.9	13.3
Methane	tr.	0.9	1.6	1.6	1.8	0.5	1.1	1.2
Ethane	0.7	0.4	tr.	0.2	tr.	0.2	0.3	0.4
Ethylene	4.7	4.0	2.8	2.9	2.7	3.0	2.9	3.1
Acetylene	0.3	0.6	0.4	0.6	1.0	0.7	0.6	0.5
Propylene	38.4	30.2	18.8	17.8	17.4	17.3	18.8	18.5
Allene	6.0	4.2	1.5	1.6	1.0	2.1	1.7	1.4
Methylacetylene	1.0	1.0	1.1	1.5	1.2	1.2	1.3	0.9
Butadiene	3.2	1.9	1.2	1.0	0.7	1.1	1.1	0.9
Diallyl	3.1	0.9	tr.	tr.	tr.	tr.	tr.	tr.
Benzene	18.7	22.5	19.4	17.4	21.6	17.9	19.3	18.7
1-bromopropene	1.6	2.6	3.1	2.8	3.9	2.1	3.0	3.2
n-propyl bromide	1.3	9.0	8.4	7.6	7.0	4.6	7.1	7.1
Percentage of hydrogen and carbon accounted for in products								
Hydrogen	100	100	76.0	70.5	77.7	67.4	74.9	72.8
Carbon	99.0	97.5	74.0	69.3	73.3	63.0	71.4	70.2
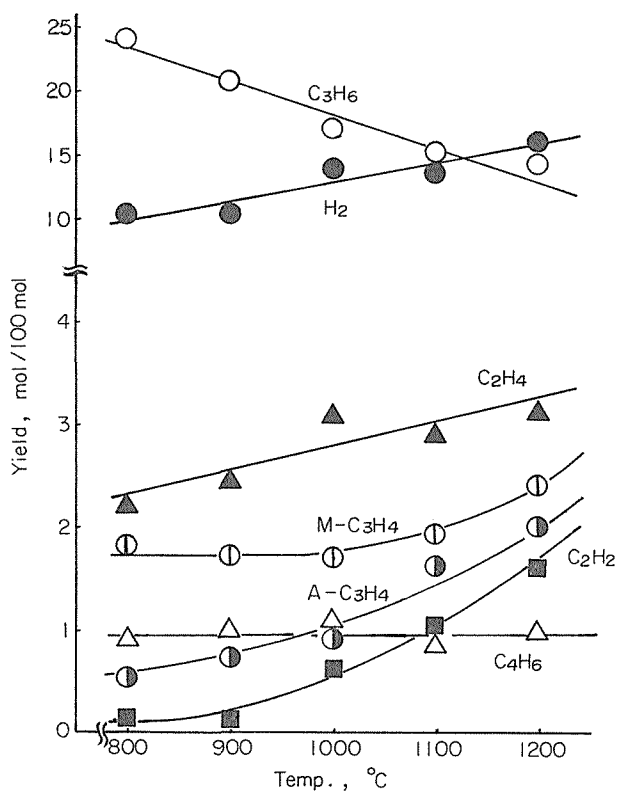
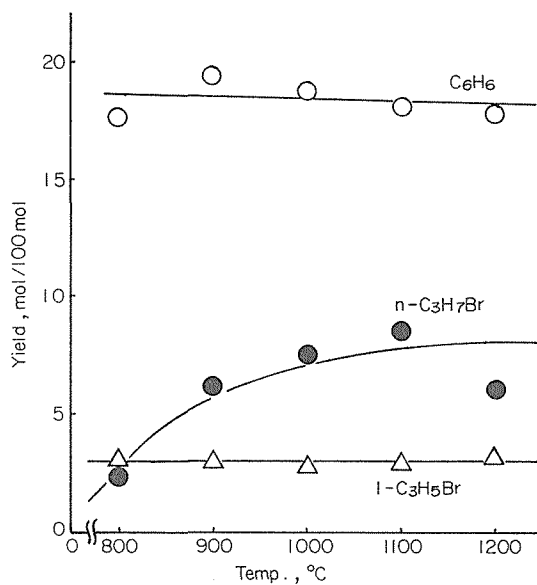Fig. 1. Effect of temperature on gaseous product yields.
Conversion, 25–33 %

Fig. 2. Effect of temperature on liquid product yields.
Conversion, 25–33 %

The Effect of the Temperature on the Product Yields. For the gaseous products, the results in the conversion range from 25 to 33% are shown in Table 2 and Fig. 1. The yield of propylene decreased with an increase in the temperature from 24 mol at 800°C to 14 mol at 1200°C and that of hydrogen increased from 10 mol to 16 mol. The yields of ethylene, allene, methylacetylene, and acetylene increased gradually with an increase in the temperature, while the yield of butadiene was almost constant at about 1 mol through the temperature examined.

For the liquid products, the results in the same conversion range are shown in Table 2 and Fig. 2. In the temperature range, the yield of benzene was almost constant at about 18 mol. The yield of n-propyl bromide increased with the increasing temperature, while that of 1-bromopropene was almost constant, being about 3 mol, in this temperature range.

The Effect of Conversion on the Yields. For the gaseous products, the results of the pyrolysis at 1000°C are shown in Table 3 and Figs. 3 and 4. The yield of propylene decreased rapidly with an increase in the conversion, ranging from 38 mol at 6% conversion to 17 mol at 76% conversion, while that of hydrogen was almost constant at 16 mol. (Fig. 3) The yield of allene decreased with the increasing conversion, ranging from 6 mol at 6% conversion to 1 mol at 76% conversion. Its yield decreased quickly at low conversions, and the decrease was much slower at high conversions. Methylacetylene was almost constant at 1 mol. The yields of ethylene and butadiene decreased rapidly with an increase in the conversion, and fell from 5 mol to 3 mol and from 3 mol to 1 mol, respectively. Moreover, the ratio of the yield of butadiene to that of ethylene approached to unity with the decreasing conversion. (Fig. 4) The yields of methane and acetylene increased with the increasing conversion, reaching 2 mol and 1 mol, respectively, at 76% conversion. (Fig. 4)
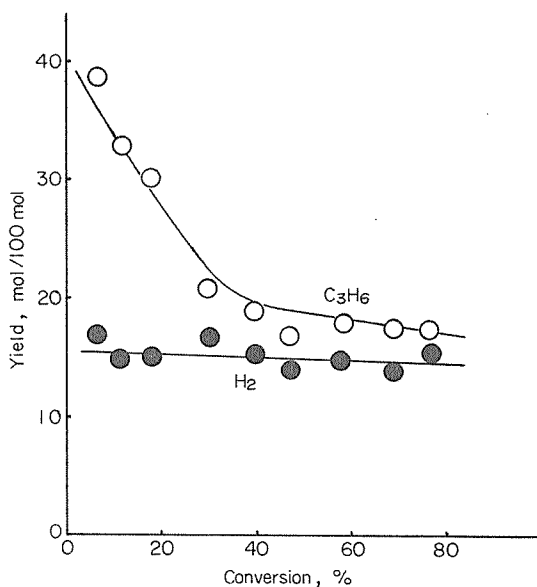

Fig. 3. Effect of conversion on gaseous product yields. (1)
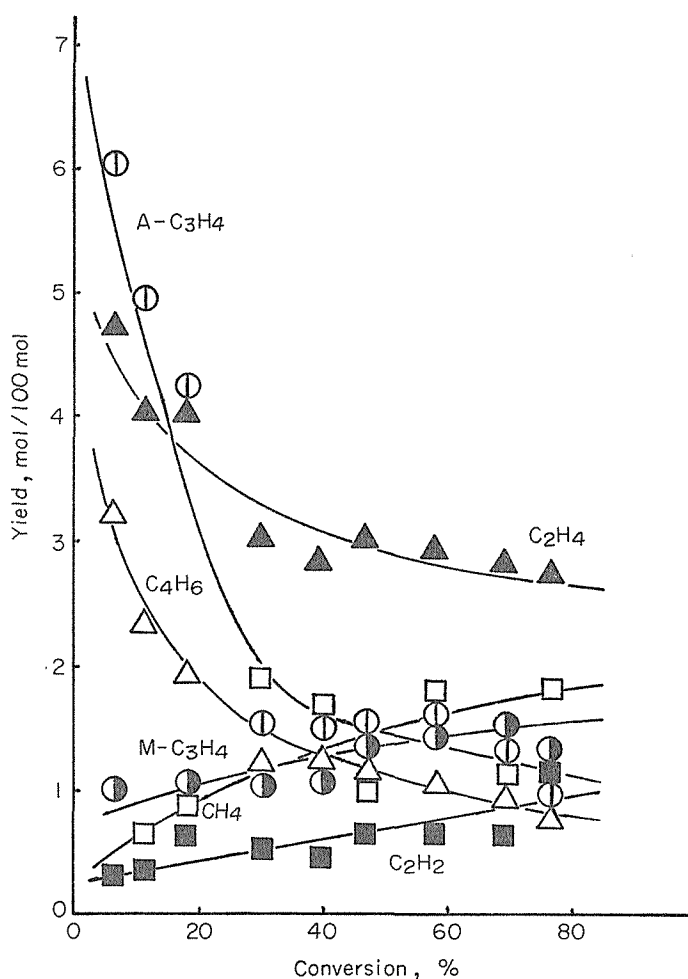Temp., 1000°C

Fig. 4. Effect of conversion on gaseous product yields. (2)
Temp., 1000°C

The results for the liquid products at the same temperature, 1000°C, are shown in Table 3 and Fig. 5. The yield of benzene was almost constant at about 20 mol through the conversion examined, while those of 1-brompropene and n-propyl bromide increased gradually with the increasing conversion to reach 4 mol and 7 mol respectivery at 76% conversion. In addition, diallyl decreased quickly with the increasing conversion and was hardly detected at higher conversions than 20%.

Furthermore, it was inferred from the zero conversion method that the main products in the early stage of the pyrolysis were propylene, hydrogen, allene, ethylene, butadiene, benzene, and diallyl, and that the yields at zero conversion were 40, 16, 7, 5, 4, 19 and 5 mol, respectively. (Figs. 3, 4, and 5)

The Effect of Concentration on the Yields. The yields of products obtained in a concentration range of 3 to 10 mol% at 1000°C are shown in Figs. 6 and 7 (also in Table 3). As the concentration increased, the yield of methane increased gradual-
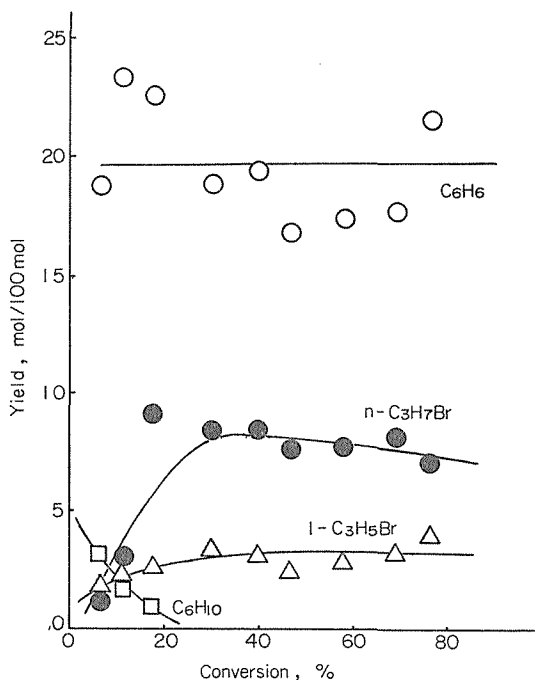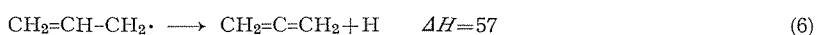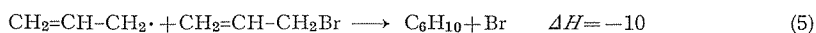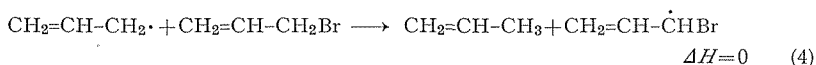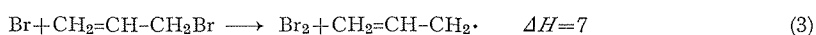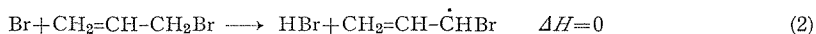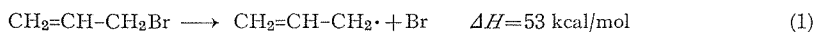
Pyrolysis of Allyl Bromide

Fig. 5. Effect of conversion on liquid product yields.
Temp., 1000°C

ly, while the yield of allene decreased.   The change of the concentration had no remarkable influence on the yields of any other gaseous products. (Fig. 6)   As to the liquid products, the yields of n-propyl bromide and 1-bromopropene increased slightly with the increasing concentration and that of benzene was almost constant at 19 mol.

DISCUSSION

On the basis of the experimental results, a mechanism for the pyrolysis of allyl bromide may be proposed.   The heats of reaction for the main reactions mentioned below are also given when available.[12~14]   The heats of reaction for the reaction (2) and (4) are calculated by assuming that the α(C-H) bond energies of propylene and allyl bromide are essentially the same.
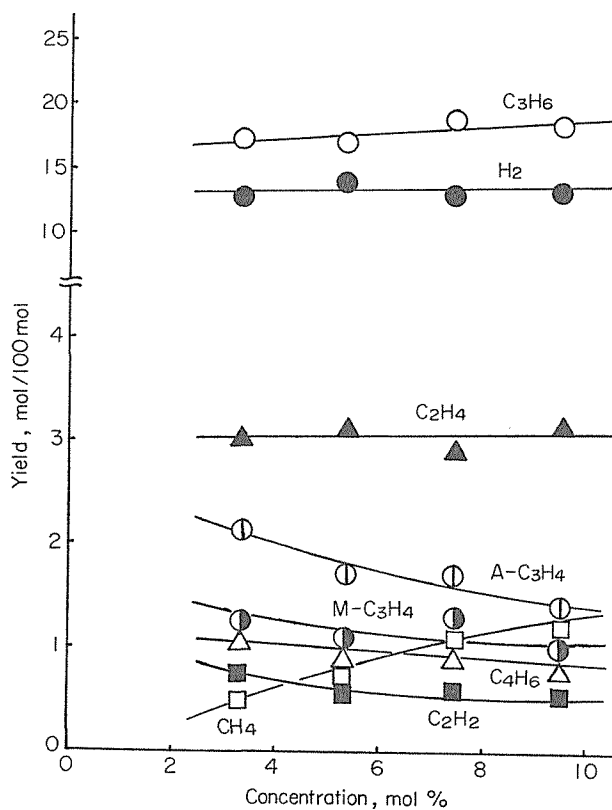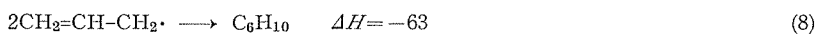
Main Reaction

$$CH_2=CH-CH_2Br \longrightarrow CH_2=CH-CH_2\cdot + Br \quad \Delta H = 53 \text{ kcal/mol} \tag{1}$$

$$Br + CH_2=CH-CH_2Br \longrightarrow HBr + CH_2=CH-\dot{C}HBr \quad \Delta H = 0 \tag{2}$$

$$Br + CH_2=CH-CH_2Br \longrightarrow Br_2 + CH_2=CH-CH_2\cdot \quad \Delta H = 7 \tag{3}$$

$$CH_2=CH-CH_2\cdot + CH_2=CH-CH_2Br \longrightarrow CH_2=CH-CH_3 + CH_2=CH-\dot{C}HBr$$
$$\Delta H = 0 \tag{4}$$

$$CH_2=CH-CH_2\cdot + CH_2=CH-CH_2Br \longrightarrow C_6H_{10} + Br \quad \Delta H = -10 \tag{5}$$

$$CH_2=CH-CH_2\cdot \longrightarrow CH_2=C=CH_2 + H \quad \Delta H = 57 \tag{6}$$

(399)

Fig. 6. Effect of concentration on gaseous product yields.
Temp.,   1000°C
Conversion,   27–32%

$$H + CH_2=CH-CH_2Br \longrightarrow H_2 + CH_2=CH-\dot{C}HBr \qquad \Delta H = -16 \tag{7}$$
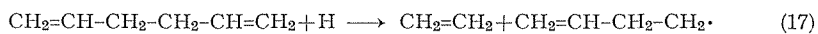
$$2CH_2=CH-CH_2 \cdot \longrightarrow C_6H_{10} \qquad \Delta H = -63 \tag{8}$$

$$2CH_2=CH-\dot{C}HBr \longrightarrow C_6H_6 + 2HBr \tag{9}$$

Principal Side Reactions

$$CH_2=C=CH_2 + Br \longrightarrow CH_2=C=\dot{C}H + HBr$$
$$\Updownarrow$$
$$\cdot CH_2-C\equiv CH \xrightarrow[RH]{} CH_3-C\equiv CH + R \cdot \tag{10}$$

$$CH_3-C\equiv CH + H \longrightarrow CH_3 \cdot + CH\equiv CH \tag{11}$$

$$CH_3 \cdot + RH \longrightarrow CH_4 + R \cdot \tag{12}$$

$$CH_2=CH-CH_2 \cdot + HBr \longrightarrow CH_2=CHCH_3 + Br \tag{13}$$

$$CH_2=CH-CH_3 + H \longrightarrow CH_2=CH_2 + CH_3 \cdot \tag{14}$$

$$CH_2=CH_2 + H \longrightarrow CH_3CH_2 \cdot \tag{15}$$

$$CH_3CH_2 \cdot + RH \longrightarrow CH_3CH_3 + R \cdot \tag{16}$$

$$CH_2=CH-CH_2-CH_2-CH=CH_2 + H \longrightarrow CH_2=CH_2 + CH_2=CH-CH_2-CH_2 \cdot \tag{17}$$

$$CH_2=CH-CH_2-CH_2 \cdot \longrightarrow CH_2=CH-CH=CH_2 + H \tag{18}$$
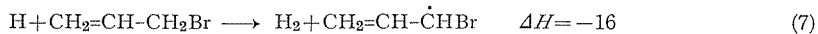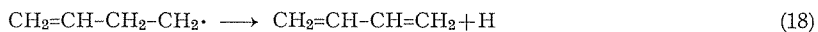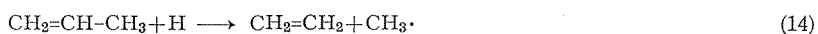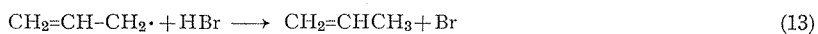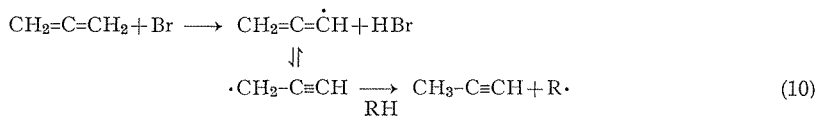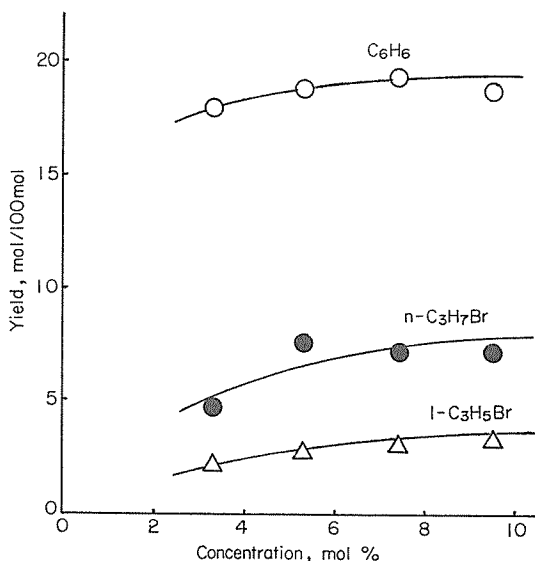
Fig. 7.   Effect of concentration on liquid product yields.
Temp.,   1000°C
Conversion,   27–32 %
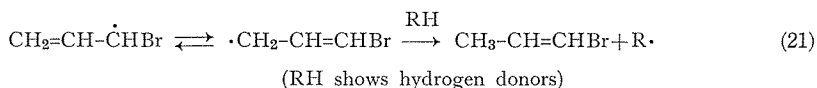
$$CH_2=CH-CH_3+Br \longrightarrow CH_2Br-\overset{\cdot}{C}H-CH_3 \tag{19}$$

$$CH_3-\overset{\cdot}{C}H-CH_2Br+RH \longrightarrow CH_3CH_2CH_2Br+R\cdot \tag{20}$$

$$CH_2=CH-\overset{\cdot}{C}HBr \underset{\longleftarrow}{\overset{\longrightarrow}{}} \cdot CH_2-CH=CHBr \overset{RH}{\longrightarrow} CH_3-CH=CHBr+R\cdot \tag{21}$$

(RH shows hydrogen donors)
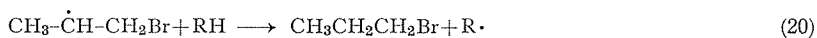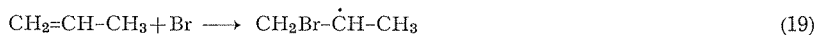
Reaction (1) is the initial step which indicates the dissociation of allyl bromide into the allyl radical and the bromine atom.   The bromine atom would then abstract the α-hydrogen atom (the allylic hydrogen) or the bromine atom from allyl bromide by subsequent reaction (2) or (3), respectively.   As there is no significant difference in the $\varDelta H$ values between reactions (2) and (3), both reactions are considered to proceed competitively under our experimental conditions.   The main products, propylene, allene, diallyl, benzene, and hydrogen are formed largely by subsequent reactions (4). (6), (5) and (8), (9) and (7), respectively.   Reactions (4), (5), (6) and (8) involving the allyl radical proceed competitively with each other.   Of these reactions, reaction (6) appears to become predominant at higher temperatures and lower concentration, as be evidenced by the experimental result that the total yield of allene and methylacetylene increases with an increase in the temperature. (Figs. 1 and 6)   Judging from the theoretical foundation that reaction (6) only is a unimolecular reaction which requires a high activation energy of about 62 kcal/mol,[5] such tendency would be reasonable.   Reaction (9) is a complicated reaction which includes combination of two bromoallyl radicals followed by cyclization.[15,16]

Giving our attention to reactions (1) to (3), the overall reaction in the early stage of the pyrolysis will be represented by the following equation:

$$a C_3H_5Br \longrightarrow b\overset{\cdot}{C}_3H_5+c\overset{\cdot}{C}_3H_4Br+d HBr+e Br_2 \tag{22}$$
$$(a=b+c, \ b>c)$$
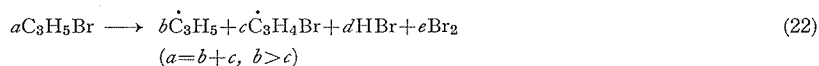
When there is no contribution of reaction (3), the amounts of allyl and bromoallyl radicals formed must be equal ($b = c$). Among the main products in the early stage of the pyrolysis, propylene, allene, diallyl, ethylene, and butadiene are derived certainly from allyl radical though the last two being *via* diallyl, as mentioned below, similarly benzene from bromoallyl radical. As a result, in the early stage of the pyrolysis the amounts of allyl radical should be approximately equal to the sum of the amounts of propylene, allene, ethylene, butadiene, and twice the amounts of diallyl. while the amounts of the bromoallyl radical should be equal to twice the amounts of benzene. The ratio of the allyl radical to the bromoallyl radical at zero conversion can be estimated from Figs. 3, 4, and 5. The observed ratio was approximately 7 to 4 ($b : c = 7 : 4$). This result suggests that reactions (2) and (3) proceed competitively under our experimental conditions. On the basis of this result, comparison of three allyl halides in the overall reaction in the early stage of the pyrolysis may be made.

$$C_3H_5X \longrightarrow \dot{C}_3H_5 + X \tag{23}$$

$$X + C_3H_5X \longrightarrow \dot{C}_3H_4X + HX \tag{24}$$

$$X + C_3H_5X \longrightarrow \dot{C}_3H_5 + X_2 \tag{25}$$

(X shows halogen atom)

In the case of allyl chloride, reaction (24) is more favorable than reaction (25), while the reverse is the case with allyl iodide in analogy with the alkyl halides.[17] These facts have been confirmed in the previous investigations.[5,7] In the pyrolysis of allyl chloride,[5] the amount of products derived from allyl radicals was approximately equal to the amount of products derived from the chloroallyl radical. While, in the case of allyl iodide,[7] the pyrolysis products were derived only from allyl radical. In this respect, the mechanism for the pyrolysis of allyl bromide is situated between those of allyl chloride and allyl iodide under the present conditions.

Though ethylene and butadiene appear to be the primary products from Fig. 4, these products are considered to be derived from diallyl by reactions (17) and (18). In fact, it was confirmed by our reference experiment[6] that almost the same amounts of C_2 and C_4 compounds were formed in the pyrolysis of diallyl. Moreover, this may be supported by the experimental result that the ratio of butadiene to ethylene formed approached to unity with the decreasing conversion (Fig. 4). It thus appears that diallyl exists in considerably high yields in the very early stage of the pyrolysis. By the way, diallyl is formed by reactions (5) and (8) which are competitive ones, as has been proposed in the pyrolysis of allyl iodide.[7] Reaction (5), however, is considered to be predominant in the early stage of the pyrolysis in view of a high concentration ratio of allyl bromide to the allyl radical and low ΔH for both reactions.

Reaction (10) is considered as the main course for the formation of methylacetylene on the basis of the observation that the yield of allene decreased quickly with the increasing conversion, while that of methylacetylene was almost constant (Fig. 4). 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.[1~3]

Except for the products mentioned above, the gaseous products, acetylene, methane,

and ethane are assumed to be formed largely by reactions (11), (12) and (16), respectively. Propylene and ethylene would probably be formed also by reactions (13) and (14) in addition to the reactions (4) and (17), respectively.

As *n*-propyl bromide appears to be the secondary product according to the zero–conversion method (Fig. 5), reactions (19) and (20) are considered as a route to the formation of *n*-propyl bromide. Reaction (21), proposed by Maccoll[9] for the formation of 1-bromopropene, is included also in this mechanism.

As the conversion increases, the pyrolysis reaction would become complex since the participation of various secondary reactions *i.e.,* hydrogen abstraction, dissociation, polymerization, and isomerization increases remarkably. Thus, it is difficult to account for the experimental results at high conversions.

REFERENCES

(1) Y. Sakakibara, *Bull. Chem. Soc. Japan*, **37**, 1262 (1964).

(2) Y. Sakakibara, *Bull. Chem. Soc. Japan*, **37**, 1268 (1964).

(3) S. Kunichika and Y. Sakakibara, *This Bulletin*, **42**, 270 (1964).

(4) S. Kunichika, Y. Sakakibara and M. Taniuchi, *This Bulletin*, **43**, 469 (1965).

(5) S. Kunichika, Y. Sakakibara and M. Taniuchi, *Bull. Chem. Soc. Japan*, **42**, 1082 (1969).

(6) S. Kunichika, Y. Sakakibara and M. Taniuchi, *This Bulletin*, **47**, 437 (1969).

(7) S. Kunichika, Y. Sakakibara and M. Taniuchi, *Bull. Chem. Soc. Japan*, **44**, 1388 (1971).

(8) M. Szwarc, B. N. Ghosh and A. H. Sehon, *J. Chem. Phys.*, **18**, 1142 (1950).

(9) A. Maccoll, *J. Chem. Soc.*, **1955**, 965.

(10) A. W. Brown and J. J. Throssell, *Chem. Ind.*, **1965**, 1868.

(11) O. Kamm and C. S. Marrel, "Organic Syntheses," Coll. Vol. I, 1956, p. 27.

(12) S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill Book Company, Inc., New York, Toronto, London 1960, p. 670.

(13) S. W. Benson, "Thermochemical Kinetics, "J. Wiley and Sons, Inc., New York, London, Sydney 1968, p. 196.

(14) R. J. Akers and J. J. Throsell, *Trans. Faraday Soc.*, **63**, 124 (1967).

(15) L. M. Porter and F. F. Rust, *J. Amer. Chem. Soc.*, **78**, 5571 (1956).

(16) L. J. Hughes and W. F. Yates, *J. Phys. Chem.*, **64**, 1789 (1960).

(17) N. N. Semenoff. "Some Problem in Chemical Kinetics and Reactivity," (translated into Japanese) Vol. I, Moscow 1954, p. 43.