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The Synthesis of Methylacetylene by the Pyrolysis of Propylene. IV. The Pyrolysis of Allyl Chloride

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Allyl chloride has been pyrolyzed in a flow system over a wide range of conditions (temperature, 800—1200°C; contact time, 0.665×10^{-3}—78.9×10^{-3} sec; concentration, 4.0—13.5 mol%; pressure, atmospheric pressure) to find suitable conditions for producing methylacetylene and allene. In addition, a study on the mechanism of pyrolysis of allyl chloride at high temperatures (800—1200°C) has been made. A total yield of allene and methylacetylene of 14 mol per 100 mol of allyl chloride pyrolyzed was obtained under suitable conditions. By means of the zero conversion method, hydrogen, propylene, allene, diallyl, 1,3-cyclohexadiene, and benzene have been found to be the main reaction products in the early stage of the pyrolysis, while methane, acetylene, ethylene, methylacetylene, butene-1, and butadiene have been found to be the side reaction products. The over-all activation energy of decomposition was 39.4 kcal/mol for an A factor of $10^{8.7}$ sec^{-1}. On the basis of the observed results, a free-radical mechanism has been proposed for the main reactions and the principal side reactions. It was further concluded that the pyrolysis was a radical decomposition initiated by the reaction $C_3H_5Cl \rightarrow C_3H_5\cdot + Cl$ and that the over-all mechanism in the early stage of the pyrolysis was represented essentially by the reaction $2C_3H_5Cl \rightarrow C_3H_5\cdot + \dot{C}_3H_4Cl + HCl$.

In previous papers,[1,2] the authors reported the synthesis of methylacetylene and allene by the pyrolysis of propylene at high temperatures. High temperatures, low conversions, and low pressures

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[1] a) Y. Sakakibara, This Bulletin, **37**, 1262 (1964); S. Kunichika and Y. Sakakibara, *Bull. Inst. Chem. Res., Kyoto Univ.*, **42**, 270 (1964). b) Y. Sakakibara, This Bulletin, **37**, 1268 (1964).

[2] S. Kunichika, Y. Sakakibara and M. Taniuchi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **43**, 469 (1965).

were found to be required for the good production of allene and methylacetylene. Since the C–Cl bond dissociation energy of allyl chloride[3] (58 kcal/mol) is considerably lower than that of α-(C–H) of propylene[4] (85 kcal/mol), the pyrolysis of allyl chloride would be expected to bring about better results under moderate conditions and to give available information about the behavior of allyl radical at high temperatures. In this report, the pyrolysis of allyl chloride under low pressure and high temperature was investigated with the aim of the production of allene and methylacetylene. Although several papers[5–8] have been published on the pyrolysis of allyl chloride, the investigations are mainly carried out below 800°C. Up to the present, it is known that only small amounts of allene and methylacetylene are obtained and that certain products seem to be produced through allene. The reaction products reported by previous investigators are summarized in Table 1.

TABLE 1. SUMMARY OF PREVIOUS INVESTIGATIONS

Reference	Temperature range (°C)	Products
5) Goodall and Howlett	370 to 475	Allene, allene polymers, acetylene, *etc.*
6) Shilov*	594 to 709	Allene, propylene, diallyl, dibenzyl, 4-phenyl-1-butene, *etc.*
7) Porter and Rust	550	Propylene, benzene, C_3H_4, 1,3-cyclohexadiene, hydrogen, methane, ethylene, diallyl, *etc.*
8) Hughes and Yates	540 to 765	Propylene, diallyl, 1,3-cyclohexadiene, benzene, *etc.*

* toluene-carrier technique

Goodall and Howlett first studied the pyrolysis of allyl chloride and concluded that the reaction was a complex homogeneous, heterogeneous process to yield, initially, allene and hydrogen chloride. They found the over-all activation energy of 42.5 kcal/mol for an A factor of $10^{9.10}$ sec^{-1}. They obtained large amounts of allene polymers, but only small amounts of allene were identified, presumably because of the rapid polymerization reaction under the reaction conditions. Shilov, on the other hand, found an activation energy of 59.3 kcal/mol at 623°C for the primary decomposition of allyl chloride in a stream of toluene and proposed that the first step in the pyrolysis was the splitting of the C–Cl bond leading to the formation of Cl atoms and allyl radicals. He obtained allene as the minor reaction product, and the amount of allene was less than 3% of hydrogen chloride.[6b] On the basis of the identification of the products, Porter and Rust, and Hughes and Yates also proposed a mechanism which involved the formation of Cl atoms and allyl radicals in the primary step of the reaction. Both of these authors indicated that allene and methylacetylene were only trace amounts of the pyrolysis products. Moreover, Hughes and Yates obtained 34.7 kcal/mol as the over-all activation energy of the pyrolysis.

The purpose of the present investigation is to determine suitable conditions for the production of methylacetylene and allene by the pyrolysis of allyl chloride and to obtain data on the distribution of the pyrolysis products. Based on the observed experimental results, an effort was made to clarify the reaction mechanism for the pyrolysis at higher temperatures (800—1200°C).

Experimental

Materials. Allyl chloride was prepared from allyl alcohol.[9] Bp 44—45°C; n_D^{22} 1.4135. Cylinder nitrogen of 99.9 mol% purity was used as a diluent.

Apparatus and Procedure. The apparatus is shown in Fig. 1. Dry nitrogen was passed through a rotameter to an allyl chloride mixing bottle which was immersed in a constant temperature oil bath set at about 120°C. Allyl chloride was added to the

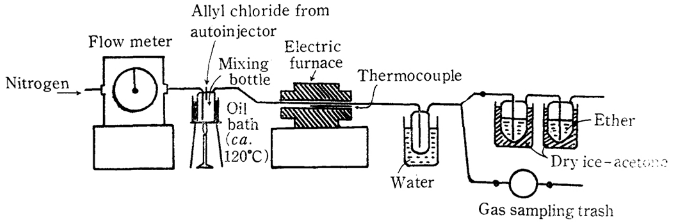

Fig. 1. Apparatus for pyrolysis.

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[3] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

[4] J. A. Kerr, *ibid.*, **66**, 465 (1966).

[5] A. M. Goodall and K. E. Howlett, *J. Chem. Soc.*, **1954**, 2596.

[6] A. E. Shilov, a) *Chem. Abstr.*, **49**, 11605f (1955); b) *J. Phys. Chem.*, **65**, 1088 (1961).

[7] L. M. Porter and F. F. Rust, *J. Am. Chem. Soc.*, **78**, 5571 (1956).

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

[9] A. I. Vogel, "A Text-book of Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., London - New York - Toronto (1956), p. 276.

Columns and conditions	Carrier gas	Products analyzed
Activated charcoal, 2.5 m, 60°C, 25 m*l*/min	Nitrogen	Hydrogen
Molecular sieve 5-A, 2.5 m, 60°C, 25 m*l*/min	Hydrogen	Methane, (nitrogen)
30-wt% Dioctyl phthalate, 5.0 m, room temperature, 50 m*l*/min	Hydrogen	Acetylene, propylene, allene, methylacetylene, butene-1, butadiene
8.0-wt% *β,β'*-Oxydipropionitrile on silica gel, 2.5 m, 60°C, 25 m*l*/min	Hydrogen	Ethylene
30-wt% Dioctyl phthalate, 2.5 m, 60°C, 50 m*l*/min	Hydrogen	(Allyl chloride)
30-wt% Squalane, 2.5 m, 90°C, 50 m*l*/min	Hydrogen	Diallyl, benzene, 1,3-cyclohexadiene

bottle at a constant rate using an automatic injector. The resulting mixture, containing 4.0—13.5 mol% of allyl chloride, was passed through a short preheater maintained at *ca.* 100°C and then pyrolyzed in a silica reaction tube under the specified conditions at atmospheric pressure. The reactor was heated to the desired temperature while a stream of dry nitrogen was passed through. The electric furnace was made of "Siliconit," and is the same as the one used in a previous investigation.[1a] After the temperature had become stationary the reactant mixture was passed through the reaction tube. The liquid products were collected in a water-trap and then in two dry ice-acetone traps containing 150 m*l* of ether as an absorbent. After that the gaseous products were collected in a 500 m*l* sampling flask to which the effluent was bypassed. The water trap was washed twice with 25 m*l* ether, and then a portion of the ether washed was taken up according to the collection time of the liquid products and was combined with the ether of two dry ice-acetone traps. The pyrolysis was performed under conditions varying over the following wide range; temperature, 800—1200°C; contact time, 0.665×10^{-3}—78.9×10^{-3} sec; concentration of allyl chloride, 4.0—13.5 mol%.

Analysis. Reaction products, consisting of hydrogen and hydrocarbons (mainly from methane up to C_6's), were analyzed by gas chromatography (g.l.c) using six different columns. The columns and their operating conditions are shown in the above table.

Product identification followed careful comparison of the retention behavior of standard hydrocarbons with the unknown products, employing two or more columns with different polarity.

Results

A part of the experimental results is shown in Tables 2 and 3. The yield of each product was given by moles per 100 mol of allyl chloride pyrolyzed. Since methylacetylene and allene are equilibrated rapidly over the isomerization catalysts,[10] their total yield 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 the reaction products (H_2 and C_1–C_6 hydrocarbons) was calculated from their yields. Though we tried to identify C_5 components (for example, cyclopentadiene, *etc.*), they were not produced in our experimental conditions.

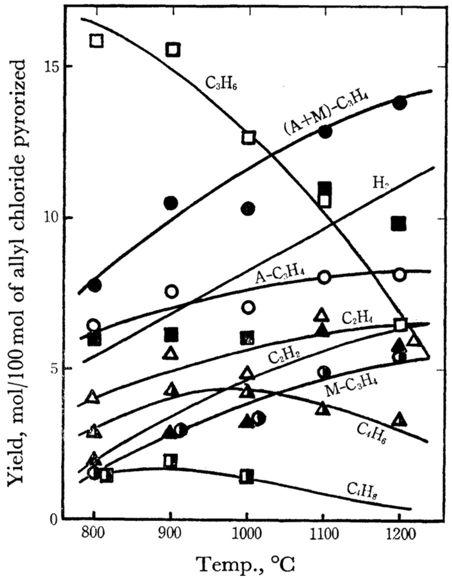

Fig. 2. Effect of temperature on gaseous product yields. Conversion, 18—26%

The Effect of Temperature on Product Yields. For the gaseous products, the results obtained in the conversion range from 18 to 26% are shown in Table 2 and Fig. 2. The yields of both methylacetylene and allene increased with the increase of temperature from 800 to 1200°C; the total yield of methylacetylene and allene ranged from 8 mol at 800°C up to 14 mol at 1200°C. Although the total yield increased rapidly at the lower temperatures, the increase was much slower at higher temperatures, ranging from 1100 to 1200°C. Propylene, on the other hand, decreased with an increase in the temperature from 16 mol to 7 mol. At 1000°C, the yield of propylene was much the same as the total yield of allene and methylacetylene. The other main products through C_4 hydrocarbons were hydrogen, methane, acetylene, ethylene, butene-1, and butadiene. The yields of hydrogen, acetylene, and ethylene increased

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[10] J. F. Cordes and H. Gunzler, *Chem. Ber.*, **92**, 1055 (1959).

TABLE 2. PYROLYSIS OF ALLYL CHORIDE AT VARIOUS TEMPERATURES

Run No.	1	2	3	4	5	6	7	8	9	10
Temp., °C	800	800	900	900	1000	1000	1100	1100	1200	1200
Contact time, 10^{-3} sec	34.7	42.6	11.3	16.3	2.22	2.58	1.27	1.71	0.665	0.812
Composition of reactant gas, mol %										
Nitrogen	88.7	87.2	92.8	89.8	89.1	87.3	92.9	94.8	96.0	95.2
Allyl chloride	11.3	12.8	7.2	10.2	10.9	12.7	7.9	5.2	4.0	4.8
Rate of expansion	0.962	1.00	0.986	0.974	0.994	0.995	0.985	0.983	0.974	0.975
Conversion, %	25.4	41.2	18.1	34.9	25.7	34.9	25.6	30.6	24.4	36.6
Yield, mol/100 mol of allyl chloride pyrolyzed										
Hydrogen	5.9	4.1	6.1	7.5	6.0	8.2	10.9	10.7	9.8	14.4
Methane	trace	trace	trace	trace	trace	trace	—	trace	—	trace
Acetylene	1.9	1.5	2.8	2.6	3.2	3.6	6.2	5.5	5.8	7.9
Ethylene	3.9	3.8	5.5	5.2	4.7	5.4	6.5	6.2	5.9	3.9
Propylene	15.8	13.8	15.5	13.4	12.6	11.1	10.7	8.5	6.5	5.7
Allene	6.2	4.4	7.5	5.0	7.0	5.5	8.0	8.0	8.1	6.0
Methylacetylene	1.5	1.2	2.9	2.2	3.2	3.2	4.8	5.1	5.7	5.0
1-Butene	1.4	1.0	1.8	1.3	1.4	1.2	trace	trace	trace	trace
Butadiene	2.8	2.2	4.3	3.3	4.2	3.3	3.7	3.4	3.3	2.3
Diallyl	1.3	1.5	2.5	1.7	2.3	1.8	1.1	3.3	1.7	trace
1,3-Cyclohexadiene	6.7	4.3	3.1	3.0	2.4	1.6	1.6	trace	trace	trace
Benzene	19.8	19.1	21.1	20.0	13.2	14.3	12.5	14.8	10.3	9.7
Total yield of methylacetylene and allene	7.7	5.6	10.4	7.2	10.2	8.7	12.8	13.1	13.8	11.0
Total yield of C_6 components	27.8	24.9	26.7	24.7	17.9	17.7	15.2	18.1	12.0	9.7
Percentage of hydrogen and carbon accounted for in products through C_6 components										
Hydrogen	74.0	63.4	77.9	69.4	62.4	59.0	59.2	60.6	49.4	42.0
Carbon	88.5	76.5	92.5	81.7	71.5	67.5	67.2	70.2	56.5	46.9

gradually with an increase in the temperature, reaching 10 mol, 6 mol, and 6 mol, respectively, while the yield of butadiene showed a maximum near 1000°C, and then decreased to 3 mol at 1200°C. The yield of butene-1 decreased gradually from 2 mol at 800°C to the trace amount at 1200°C.

For the liquid products (C_6 components), the results obtained in the conversion range from 18 to 26% are shown in Table 2 and Fig. 3. The yield of benzene decreased with the increase of temperature from 20 mol at 800°C to 10 mol at 1200°C. The yield of 1,3-cyclohexadiene decreased fairly rapidly until 1000°C, and then decreased gradually, ranging from 7 mol at 800°C to 2 mol at 1100°C, while the yield of diallyl was almost constant at about 2 mol all through the temperature examined. Consequently the total yields of C_6 components fell gradually from 28 mol at 800°C to 12 mol at 1200°C.

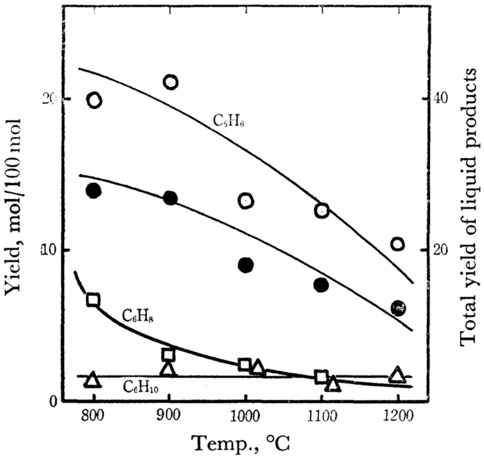


Fig. 3. Effect of temperature on liquid product yields. Conversion, 18—26%

●: total yield of liquid products

On the whole, the polymerization products, C_6 compounds, decreased with the increase in temperature, as is generally known for the decomposition of hydrocarbons (Fig. 3). The carbon and hydrogen balance, however, became remarkably worse at higher temperatures, owing to the increase of tarry and carbonaceous products (Table 2).

The Effect of Conversion on Yields. For the gaseous products, the results of the pyrolysis at 1000°C are shown in Table 3 and Fig. 4. The total yield of methylacetylene and allene decreased with the increasing conversion, ranging from 15 mol at 10% conversion to 4 mol at 90% conversion. In this connection, as the conversion was increased, the yield of allene fell at a considerable rate from 11 mol at 10% conversion to 2 mol at 90% con-

TABLE 3. PYROLYSIS OF ALLYL CHLORIDE AT VARIOUS CONVERSIONS AND CONCENTRATIONS

Run No.	11	12	13	14	15	16	17	18	19	20
Temp., °C	800	1000	1000	1000	1000	1000	1000	1000	1000	1000
Contact time, 10^{-3} sec	21.5	1.36	2.24	9.42	13.7	21.8	23.9	2.44	2.25	2.36
Composition of reactant gas, mol %										
Nitrogen	88.6	93.3	93.3	94.1	91.0	92.1	91.1	95.9	93.3	88.3
Allyl chloride	11.4	6.7	6.8	5.9	9.0	7.9	8.9	4.1	6.7	11.7
Rate of expansion	0.959	0.993	1.00	0.948	1.00	1.00	0.966	1.00	1.00	1.00
Conversion, %	7.1	11.0	21.3	40.1	58.7	86.9	93.5	32.7	29.9	29.1
Yield, mol/100 mol of allyl chloride pyrolyzed										
Hydrogen	—	4.6	6.1	11.8	15.4	21.3	17.9	5.9	4.7	4.6
Methane	—	—	trace	trace	trace	2.0	1.8	—	trace	trace
Acetylene	1.8	3.4	3.3	4.7	4.9	5.3	4.5	3.2	3.3	2.7
Ethylene	2.8	4.4	4.0	4.5	7.3	8.0	7.2	3.7	4.0	4.1
Propylene	17.9	15.5	10.3	9.7	9.4	8.5	7.9	10.9	10.3	10.8
Allene	8.1	10.8	9.6	4.4	3.5	2.3	1.9	7.9	7.2	5.9
Methylacetylene	trace	3.9	3.8	3.5	2.7	2.4	2.0	3.4	3.6	2.6
1-Butene	trace	trace	trace	0.9	0.8	0.7	0.6	—	1.6	1.2
Butadiene	3.4	4.3	4.6	2.8	2.2	1.8	1.5	3.6	4.2	3.4
Diallyl	6.7	6.6	4.2	1.4	trace	trace	trace	2.2	1.9	2.6
1,3-Cyclohexadiene	11.0	6.1	3.0	trace	trace	trace	trace	2.8	2.1	2.3
Benzene	17.9	14.5	15.0	16.6	16.3	20.6	19.2	12.7	15.4	15.7
Total yield of methylacetylene and allene	8.1	14.7	13.4	7.9	6.2	4.7	3.9	11.3	10.8	8.5
Total yield of C_6 components	35.6	27.2	22.2	18.0	16.3	20.6	19.2	17.7	19.4	20.6
Percentage of hydrogen and carbon accounted for in products through C_6 components										
Hydrogen	87.5	86.9	66.6	55.8	54.6	62.6	54.6	57.0	60.6	59.7
Carbon	104.0	95.3	75.5	64.8	59.2	65.7	58.1	67.0	72.5	71.1

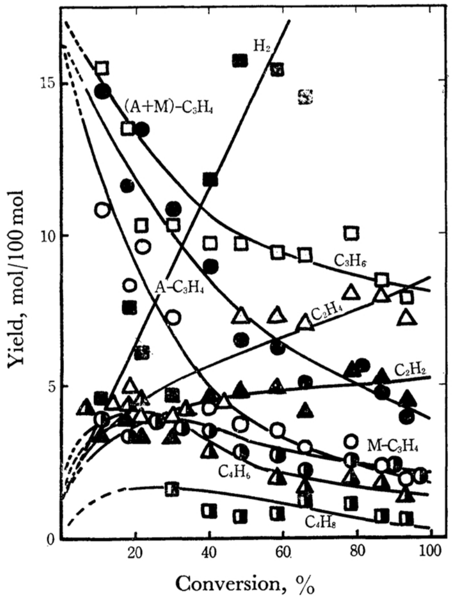


Fig. 4. Effect of conversion on gaseous product yields. Temp., 1000°C

version, while that of methylacetylene was fairly constant at 4 mol in a 10—30% conversion range, and beyond this conversion range, it decreased gradually from 4 mol to 2 mol at 90% conversion. Thus, taking account of an equilibrium relation between methylacetylene and allene, it seems probable that methylacetylene is not a primary product, but a secondary one produced by the isomerization of allene.[1b)] The yield of propylene decreased from 15 mol at 10% conversion to 8 mol at 90% conversion. Hydrogen increased from 4 mol at 10% conversion to 20 mol at 90% conversion. The yields of acetylene and ethylene increased gradually from 3 mol and 4 mol at 10% conversion to 5 mol and 8 mol at 90% conversion, respectively. The yield of butadiene decreased gradually from 4 mol at 10% conversion to 2 mol at 90% conversion.

The results for the liquid products at the same temperature are shown in Table 3 and Fig. 5. As the conversion increased, the yield of benzene increased gradually from 14 mol at 10% conversion to 18 mol at 80% conversion, while those of 1,3-cyclohexadiene and diallyl fell rapidly in the lower part of the conversion range from 6 mol at 10% conversion to trace amounts at 60% conversion. As a result, the total yields of C_6 components decreased gradually with the increasing conversion from 26 mol at 10% conversion to 18 mol at 80% conversion.

The amounts of tarry and carbonaceous products

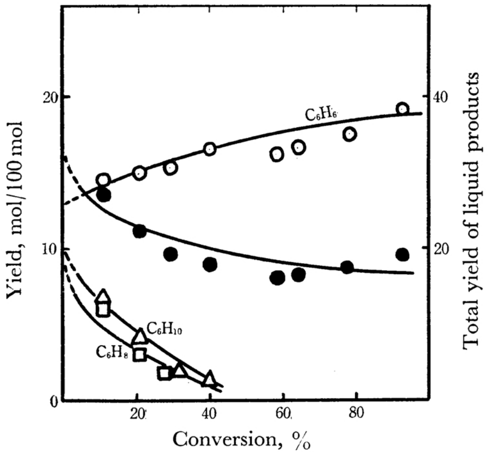


Fig. 5. Effect of conversion on liquid product yields. Temp., 1000°C

●: total yield of liquid products

increased with the increasing conversion to make the material balance remarkably worse, as described in Table 3. Furthermore, it was determined by the zero conversion method that the main products in the early stage of the pyrolysis were propylene, allene, hydrogen, benzene, 1,3-cyclohexadiene, and diallyl, as shown in Figs. 4 and 5.

The Effect of Concentration on Yields. The yields of products obtained in a concentration range of 4 to 12 mol% at 1000°C are shown in Fig. 6 (also in Table 3). When the concentration increased, the yield of propylene was almost constant, being about 11 mol, while the yields of allene and methylacetylene were influenced remarkably and fell from 8 mol to 6 mol and 4 mol to 3 mol, respectively. As a result, the total yield of allene and methylacetylene decreased at a considerable rate with the increasing concentration, ranging from 12 mol at 4 mol% to 9 mol at 12 mol%. The yield of benzene increased from 13 mol to 16 mol with an increase in the concentration. It was further observed that the change of the concentration had no remarkable influence on the yield of any other products, that is, hydrogen, methane, acetylene, ethylene, butene-1, butadiene, diallyl, and 1,3-cyclohexadiene.

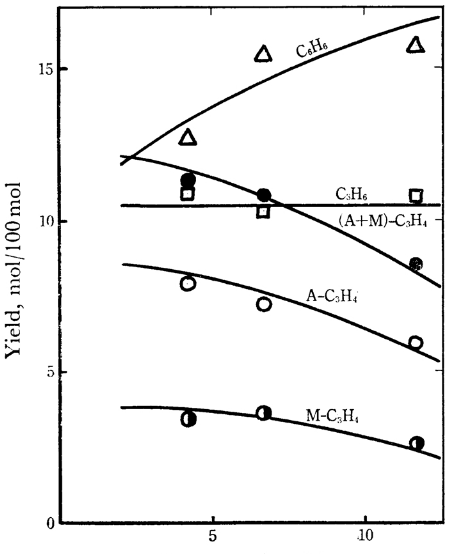


Fig. 6. Effect of concentration on product yields. Temp., 1000°C. Conversion, 29—33%

Kinetics. A rough estimate of the activation energy for the over-all process was made using our data at 800—1200°C. The pyrolysis was found to be first order at a given temperature range. An Arrhenius plot (Fig. 7) of first order rate constants based on gas chromatographic analysis for allyl chloride consumed gave a value of 39.4 kcal/mol for the over-all activation energy. This value is much lower than the dissociation energy of allyl chloride, $E_{C_3H_5\text{-}Cl}=58$ kcal/mol.[3] The corresponding A factor was $10^{8.7}$ sec^{-1}. The values of the activation energy and A factor obtained were in good agreement with the values of 42.5 kcal/mol and $10^{9.10}$ sec^{-1} found by Goodall and Howlett. In addition, the activation energy we found was intermediate between those reported by Goodall and Howlett, and Hughes and Yates who reported 34.7 kcal/mol as the over-all activation energy of the pyrolysis.

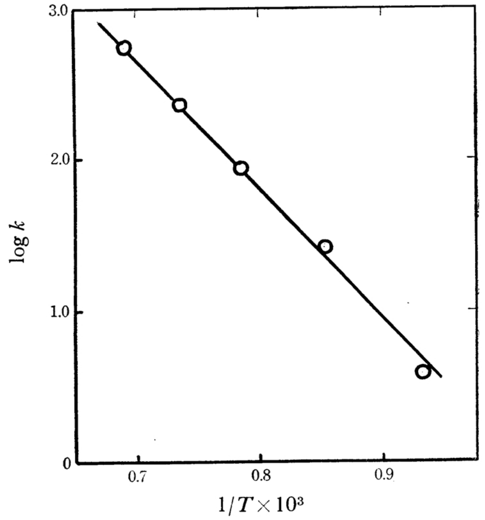


Fig. 7. Plot log k against $1/T$ for allyl chloride.

Discussion

Mechanism. In the present investigation, the reaction products were essentially identical with those of Porter and Rust, and Hughes and Yates, except that allene and methylacetylene were found as the major products. Thus, the mechanism proposed by both of these authors may be convenient for explaining the experimental results, taking into further consideration the formation steps of allene and methylacetylene. According to the zero conversion method (Figs. 4 and 5), it was concluded that propylene, allene, hydrogen, diallyl, 1,3-cyclohexadiene, and benzene were the main products in the early stage of the pyrolysis. Consequently, a following mechanism may be proposed for the pyrolysis of allyl chloride.

Main Reactions

$$CH_2{=}CH{-}CH_2Cl \rightarrow CH_2{=}CH{-}CH_2\cdot + Cl \tag{1}$$

$$CH_2{=}CH{-}CH_2\cdot + CH_2{=}CH{-}CH_2Cl \rightarrow CH_2{=}CH{-}CH_3 + CH_2{=}CH{-}\dot{C}HCl \tag{2}$$

$$Cl + CH_2{=}CH{-}CH_2Cl \rightarrow HCl + CH_2{=}CH{-}\dot{C}HCl \tag{3}$$

$$CH_2{=}CH{-}CH_2\cdot \rightarrow CH_2{=}C{=}CH_2 + H \tag{4}$$

$$H + CH_2{=}CH{-}CH_2Cl \rightarrow H_2 + CH_2{=}CH{-}\dot{C}HCl \tag{5}$$

$$CH_2{=}CH{-}CH_2\cdot + H \rightarrow CH_2{=}CH{-}CH_3 \tag{6}$$

$$2CH_2{=}CH{-}CH_2\cdot \rightarrow C_6H_{10} \tag{7}$$

$$CH_2{=}CH{-}CH_2\cdot + CH_2{=}CH{-}\dot{C}HCl \rightarrow C_6H_8 + HCl \tag{8}$$

$$2CH_2{=}CH{-}\dot{C}HCl \rightarrow C_6H_6 + 2HCl \tag{9}$$

Side Reactions

Methane

$$CH_3\cdot + RH \rightarrow CH_4 + R\cdot \tag{10}$$

Acetylene

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

$$\cdot CH{=}CH_2 \rightarrow CH{\equiv}CH + H \tag{12}$$

Ethylene

$$CH_3{-}CH{=}CH_2 + H \rightarrow CH_3\cdot + CH_2{=}CH_2 \tag{13}$$

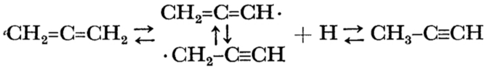
$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + H \rightarrow CH_2{=}CH_2 + \cdot CH_2{-}CH_2{-}CH{=}CH_2 \tag{14}$$

$$\cdot CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow CH_2{=}CH_2 + \cdot CH{=}CH_2 \tag{15}$$

Propylene

$$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + H \rightarrow CH_2{=}CH{-}CH_2\cdot + CH_2{=}CH{-}CH_3 \tag{16}$$

methylacetylene



$$CH_2{=}C{=}CH_2 \rightleftarrows \begin{matrix} CH_2{=}C{=}CH\cdot \\ \uparrow\downarrow \\ \cdot CH_2{-}C{\equiv}CH \end{matrix} + H \rightleftarrows CH_3{-}C{\equiv}CH \tag{17}$$

Butene-1

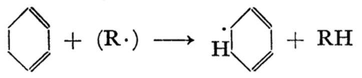
$$RH + \cdot CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow R\cdot + CH_3{-}CH_2{-}CH{=}CH_2 \tag{18}$$

Butadiene

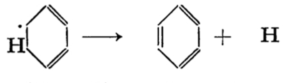
$$\cdot CH_2{-}CH_2{-}CH{=}CH_2 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H \tag{19}$$

Hydrogen

$$H + RH \rightarrow H_2 + R\cdot \tag{20}$$



(21)



(22)

Reactions (1) to (9) are the main reactions in the early stage of the pyrolysis. Reactions (10) to (22) are the principal side reactions, which would be predominant in the higher conversions. The compatibility of the proposed mechanism with the observed experimental data can now be explained.

Main Reactions. Reaction (1) is the initial step which indicates the dissociation of allyl chloride into an allyl radical and a chlorine atom. All the main products, propylene, allene, hydrogen, diallyl, 1,3-cyclohexadiene, and benzene are formed by subsequent Reactions (2) and (6), (4), (5), (7), (8), and (9), respectively. Reaction (4), being the step of the formation of allene from allyl radical,[11,12,1b] appears to be an important course 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 and lower concentration, as supported by the experimental results that allene and methylacetylene increase with an increase in the temperature, and propylene and all C_6 compounds decrease reversely (Figs. 2 and 3). This may be plausible judging from the theoretical foundation that Reaction (4) only is a unimolecular reaction which requires a high activation energy of about 62 kcal/mol.[12a,13] Reactions (8) and (9) are complicated reactions which include combination of allyl and chloroallyl radicals followed by cyclization.[7]

Keeping our mind on Reactions (1) and (3), the over-all reaction in the early stage of the pyrolysis will be represented by the reaction $2C_3H_5Cl \rightarrow C_3H_5 + C_3H_4Cl + HCl$. Consequently, when 100 mol of allyl chloride is decomposed, 50 mol of allyl radical and 50 mol of chloroallyl radical are formed, respectively. Among the reaction products, propylene, allene, methylacetylene, and diallyl are derived certainly from allyl radicals, similarly benzene from chloroallyl radicals, and 1,3-cyclohexadiene from both radicals. As a result, in the early stage of the pyrolysis, the amount of allyl radical should be approximately equal to the sum of the amounts of propylene, allene, methylacetylene, 1,3-cyclohexadiene, and twice of the amounts of diallyl, while the amount of chloroallyl radical should be equal to the sum of the amounts of 1,3-cyclohexadiene and twice of the amounts of benzene. The fact that this relationship is approximately correct can be confirmed from the following results taken from Run 11 at 800°C and Run 12 at 1000°C (Table 3). These observed values 50.4, 46.8, and

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12) a) A. Amano and M. Uchiyama, *J. Phys. Chem.*, **68**, 1133 (1964); b) K. J. Laidler and B. W. Wojciechowski, *Proc. Roy. Soc.*, **A259**, 257 (1960).

13) K. W. Egger, D. M. Golden and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964); R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, **1964**, 5578; D. M. Golden, A. S. Rodgers and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 3196 (1966).

49.5 are approximate to theoretical value 50.0.

Run 11

$$C_3H_5\cdot \rightarrow C_3H_6 + C_3H_4 + 2C_6H_{10} + C_6H_8$$

$$50.0 \risingdotseq 17.9 + 8.1 + 2 \times 6.7 + 11.0 = 50.4$$

$$\dot{C}_3H_4Cl \rightarrow C_6H_8 + 2C_6H_6$$

$$50.0 \risingdotseq 11.0 + 2 \times 17.9 = 46.8$$

Run 12

$$C_3H_5\cdot = 49.5, \quad \dot{C}_3H_4Cl = 35.1$$

The discrepancy between the value of Run 11 and that of Run 12 lies in the difference of temperature. The lower value of chloroallyl radical for Run 12 may be caused by the decomposition of chloroallyl radical to chloroallene and/or $CH_2{=}CH{-}\ddot{C}H$ that appears to be probable at higher temperature, though it is not shown in the reaction mechanism. Furthermore, the decrease of carbon and hydrogen balance with the increasing temperature (Table 2) may be discussed in connection with this. Namely, it seems reasonable to presume that the decompositions, followed by association, of allyl and chloroallyl radicals leading to tarry and carbonaceous products may increase remarkably at higher temperature, judging from the fact that benzene is fairly stable under our experimental conditions. From the results mentioned above, it is concluded that the decomposition products in the early stage of the pyrolysis are well accounted for by considering the mechanism comprised mainly reactions of allyl and chloroallyl radicals formed in the pyrolysis.

Side Reactions. Besides the main products, several side reaction products were obtained: methane, acetylene, ethylene, methylacetylene, butene-1, butadiene. The formations of these side reaction products are assumed to proceed largely by Reactions (10)—(15) and (17)—(19). In the experimental results, C_2 compounds, ethylene and acetylene, and C_4 compounds, butene and butadiene, were formed in considerable amounts (Table 2). This fact suggests that diallyl decomposed to give C_2 and C_4 compounds, as shown in Reaction (14). In fact, it was confirmed by our reference experiment that almost the same amounts of C_2 compounds, ethylene and acetylene, and C_4 compounds, butene and butadiene were formed in the pyrolysis of diallyl. Concerning thermal isomerization of allene to methylacetylene, it is reported also by the present authors that allene isomerizes to methylacetylene in fairly good yield at high temperatures.[1] Propylene, hydrogen, and benzene would probably be formed also by Reactions (16), (20), (21), and (22) in addition to the main Reactions (2) and (6), (5), and (9).

As the conversion increases, the pyrolysis reaction would become complex since the participation of hydrogen abstraction by chlorine atom in secondary reactions increases remarkably . Thus, it is difficult to account for the experimental results at high conversions. The rapid decrease in the yields of propylene and allene - methylacetylene with the increasing conversion (Fig. 4) may be responsible for the loss owing to various secondary decomposition and polymerization reactions; the extremely rapid decrease in allene appears to be plausible from the fact that allene is unstable, compared with propylene, and is apt to undergo various secondary reactions including the isomerization Reaction (17). On the other hand, the yield of benzene increases little by little with the increasing conversion (Fig. 5). This may be due mainly to the conversion of 1,3-cyclohexadiene into benzene by Reactions (21) and (22), and to large stability of benzene under our experimental conditions.

As the concentration of allyl chloride increases, bimolecular reactions become more advantageous than unimolecular reactions. The increase in the yield of benzene and the decrease in the yield of allene and methylacetylene with the increasing concentration correspond with this (Fig. 6).