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The Synthesis of Methylacetylene by the Pyrolysis of Propylene. VI. The Pyrolysis of Allyl Iodide

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Allyl iodide has been pyrolyzed in a flow system over a wide range of conditions (temperature, 800—1100°C; contact time, $1.44\times10^{-4}-14.0\times10^{-4}$ sec; concentration, 1.8—6.5 mol%; pressure, atmospheric pressure) in order to find suitable conditions for producing methylacetylene and allene and in order to elucidate the reactions of the allyl radical with iodine or the iodine atom at high temperatures. In addition, a study of the mechanism of the pyrolysis of allyl iodide at high temperatures (800—1100°C) has been made. A total yield of allene and methylacetylene of 10 mol per 100 mol of allyl iodide pyrolyzed was obtained under suitable conditions. In the pyrolysis, little cleavage of the C–C bonds of allyl iodide occurred, and propylene, allene, methylacetylene, diallyl, benzene, and an unidentified product were found to be the main products. By means of the zero-conversion method, diallyl alone has been found to be the major product in the early stage of the pyrolysis, while propylene, allene, methylacetylene, and benzene have been found to be the chief products at higher conversions. On the basis of the observed results, a free-radical mechanism has been proposed for the main reactions. It has further been concluded that the pyrolysis is a radical decomposition initiated by the $C_3H_5I \rightarrow C_3H_5\cdot + I$ reaction and that the overall mechanism in the early stage of the pyrolysis may be represented essentially by the $2C_3H_5I \rightarrow C_6H_{10} + I_2$ reaction.

In previous papers, the present authors reported the synthesis of methylacetylene by the pyrolysis of propylene[1] and allyl halides.[2] Since the C–I bond dissociation energy of allyl iodide[3] (43.5 kcal/mol) is considerably lower than that of the α(C–H) of propylene[3] (87.5 kcal/mol), the pyrolysis of allyl iodide may be expected to bring about better results under moderate conditions and to give information about the reactions of the allyl radical with iodine and the iodine atom at high temperatures. It was further found, by the pyrolysis of allyl halides,[2b] that iodine or the iodine atom has a catalytic effect in converting the allyl radical into allene. Therefore, the pyrolysis of allyl iodide was investigated with the aim of producing methylacetylene and allene and elucidating the catalytic action of iodine on the allyl radical.

Although several papers[2b,4–7] have been published on the pyrolysis of allyl iodide, the investigations have been generally concerned with the strength of the C–I bond and have been carried out at low temperatures, except for our own study[2b] and that of Lossing, Ingold, and Henderson.[6] With the exception of our study,[2b] product analyses have been limited and little is known about the decomposition products. Diallyl alone was positively identified in the pyrolysis products; there was no data for the identification of other pyrolysis products. Of course, methylacetylene and allene were not found in the products. The reaction products reported by previous investigators are summarized in Table 1.

Table 1. Summary of previous investigations

	Reference	Temperature range (°C)	Product
4)	Szwarc	a)	diallyl
6)	Lossing, Ingold and Henderson,	750 to 915	diallyl
7)	Benson	a)	C_6H_{10}[b]
2b)	Kunichika, Sakakibara and Taniuchi	800 to 1100	propylene, allene, methylacetylene, diallyl, and benzene

a) No accurate information was obtained about the temperature range of the pyrolysis.
b) Benson says that the C_6H_{10} is undoubtedly cyclohexene or methylcyclopentene.[7]

Butler and Polanyi[5] first studied the pyrolysis of allyl iodide kinetically. From the kinetics of the pyrolysis, Szwarc[4] and Benson[7] proposed a simple radical mechanism involving an initial dissociation of allyl iodide into the iodine atom and the allyl radical. Lossing *et al.*[6] found that the production of the allyl radical appeared to be almost quantitative in the high-temperature pyrolysis of allyl iodide, the only hydrocarbon product of any importance being the dimerization product, diallyl.

The purpose of the present investigation is to determine suitable conditions for the production of methylacetylene and allene by the pyrolysis of allyl iodide, and to obtain data on the distribution of the pyrolysis products. On the basis of the observed experimental results, an effort will be made to clarify the reaction mechanism for the pyrolysis at high temperatures (800—1100°C) and the reactions of the allyl radical with iodine and the iodine atom.

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

[2] S. Kunichika, Y. Sakakibara, and M. Taniuchi, a) This Bulletin, **42**, 1082 (1969); b) *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 437 (1969).

[3] S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York·London Sydney (1968), p. 215.

[4] M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

[5] E. T. Butler and M. Polanyi, a) *Nature*, **146**, 129 (1940); b) *Trans. Faraday Soc.*, **39**, 19 (1943).

[6] F. P. Lossing, K. U. Ingold, and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

[7] S. W. Benson, *ibid.*, **38**, 1945 (1963).

Table 2. Pyrolysis of allyl iodide at various temperatures

Run No.	20	3	18	4	9	17	28	29
Temp., °C	800	800	900	900	1000	1000	1100	1100
Contact time, 10^{-4} sec	3.89	12.3	2.49	6.59	1.81	2.86	1.44	1.60
Composition of reactant gas, mol%								
Nitrogen	95.9	96.5	95.5	96.9	96.3	96.3	97.1	96.7
Allyl iodide	4.1	3.5	4.5	3.1	3.7	3.7	2.9	3.3
Rate of expansion	0.984	0.995	0.994	0.980	0.968	0.995	1.00	1.00
Conversion, %	12.8	27.6	14.5	32.2	15.7	34.8	33.5	37.2
Yield, mol/100 mol of allyl iodide pyrolyzed								
Propylene	14.5	41.4	24.8	41.4	26.9	38.2	38.2	39.9
Allene		4.6	3.7	5.2	5.5	6.8	10.2	9.4
Methylacetylene								
Diallyl	39.4	9.7	26.7	10.8	27.9	9.4	4.5	5.5
Unidentified product		6.4		6.1		7.2	4.6	5.1
Benzene	3.2	5.6	4.6	8.9	6.4	6.4	6.8	7.0
Total yield of methylacetylene and allene		4.6	3.7	5.2	5.5	6.8	10.2	9.4
Percentage of hydrogen and carbon accounted for in products								
Hydrogen	100.0	94.7	91.6	98.2	99.9	92.3	80.4	85.0
Carbon	99.5	89.4	91.0	98.1	101.0	91.0	80.0	84.6

Experimental

Materials. The allyl iodide was prepared from allyl chloride.8) Bp 101—102°C; n_D^{22}1.5540. Cylinder nitrogen of a 99.9 mol% purity was used as diluent and carrier gas.

Apparatus and Procedure. The apparatus and the technique were essentially the same as had been used previously for the pyrolytical study of allyl chloride,2a) except for the use of toluene as an absorbent. 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 a 200-m*l* portion of an aq. 2 N NaOH solution which had been put in two washing bottles. The alkaline solution was extracted twice with 50-m*l* portions of toluene, and then a portion of the toluene extract was taken up as has been described previously.2a)

Analysis. The analytical method for the pyrolysis products was essentially the same as that described previously.2a)

Results

Some of the experimental results are shown in Tables 2 and 3. In the pyrolysis, little cleavage of the C–C bonds of allyl iodide occurred. Consequently, all the decomposition products possessed C_3 and C_6 skeletons derived from the allyl and iodoallyl radicals; the C_1, C_2, and C_4 hydrocarbons were detected in only small amounts. Propylene, allene (A-C_3H_4), methylacetylene (M-C_3H_4), diallyl, benzene, and an unidentified product were found to be the main products. Except for the products mentioned above, no other products, not even hydrogen, were detected in any considerable amount. The kinds of the decomposition products were appreciably fewer than those in the pyrolyses of allyl chloride and bromide.2b) In addition, larger amounts of propylene and diallyl were obtained, but smaller amounts of benzene were found.

The Effect of the Temperature on the Product Yields. The results obtained in the conversion range from 13 to 16% are shown in Table 2 and Fig. 1. As the temperature was increased, the yield of allene gradually increased to reach 6 mol at 1000°C, and that of propylene increased from 15 mol at 800°C to 27 mol at 1000°C. The yield of diallyl decreased from 39 mol to 28 mol, while that of benzene increased slowly from 3 mol to 6 mol. At a higher conversion range from 27 to 34%, the yield of allene increased from 5 mol at 800°C to 10 mol at 1100°C, while that of propylene decreased from 41 mol to 38 mol. The yield of diallyl

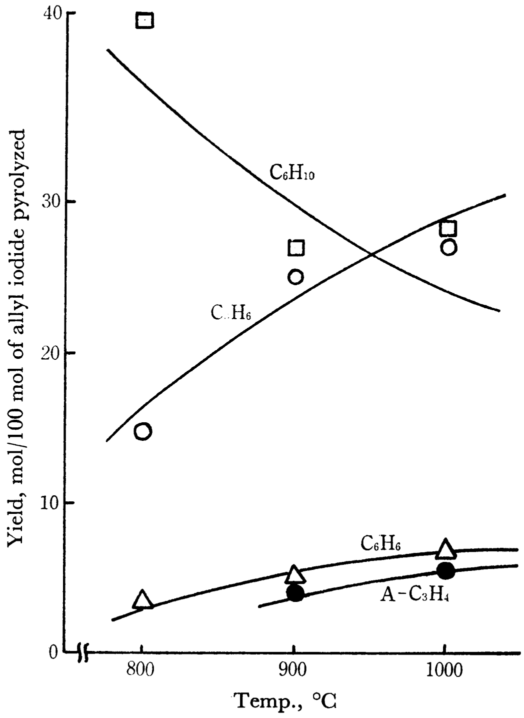

Fig. 1. Effect of temperature on product yields. conversion, 13—16%

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8) R. L. Letsinger and J. G. Traynham, *J. Amer. Chem. Soc.*, **70**, 2818 (1948).

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

Run No.	8	13	23	22	14	26	16	25
Temp., °C	1000	1000	1000	1000	1000	1000	1000	1000
Contact time, 10^{-4} sec	1.48	2.24	3.06	3.11	6.95	3.06	2.97	3.18
Composition of reactant gas, mol%								
Nitrogen	97.0	95.5	94.2	96.4	96.3	98.1	96.3	93.5
Allyl iodide	3.0	4.5	5.8	3.6	3.7	1.9	3.7	6.5
Rate of expansion	0.979	0.967	0.984	0.990	0.980	0.994	0.985	0.974
Conversion, %	10.8	21.8	50.2	58.0	68.4	40.2	40.5	40.4
Yield, mol/100 mol of allyl iodide pyrolyzed								
Propylene	21.7	34.5	39.4	43.6	44.4	30.9	39.4	42.0
Allene	3.9	6.3	5.9	9.4	7.1	9.5	6.7	6.7
Methylacetylene			0.8	trace	2.6			
Diallyl	33.3	19.2	2.0	2.0	6.3	5.2	7.1	3.5
Unidentified product			4.3	4.7	4.6	6.6	6.8	6.4
Benzene	4.1	7.1	7.7	6.3	5.7	5.7	5.0	8.4
Total yield of methylacetylene and allene	3.9	6.3	6.7	9.4	9.7	9.5	6.7	6.7
Percentage of hydrogen and carbon accounted for in products								
Hydrogen	100.0	93.3	74.4	80.7	80.5	75.2	86.4	85.5
Carbon	100.0	93.2	74.0	79.0	77.9	75.5	84.0	85.0

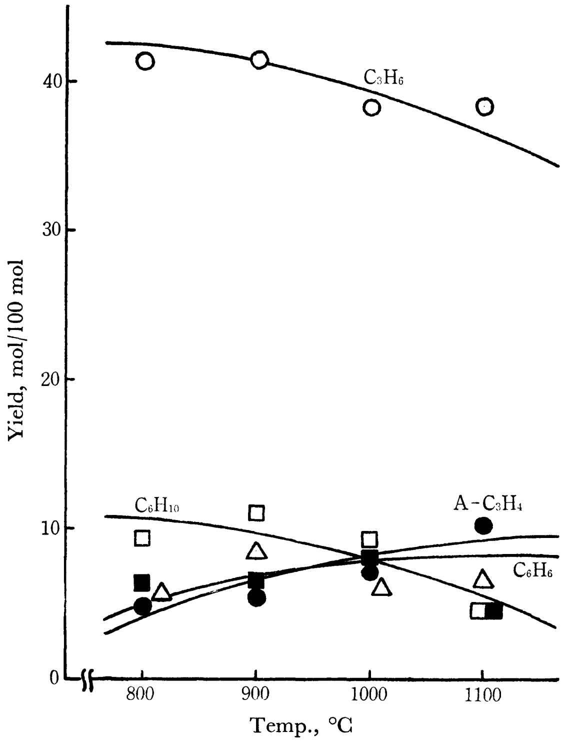

Fig. 2. Effect of temperature on product yields. conversion, 27—34%
■: unidentified product

decreased from 10 mol to 5 mol. On the contrary, the yield of benzene was almost constant at 7 mol (Fig. 2).

The yield of methylacetylene was very small over the conversion range studied, and so the effect of temperature on its yield could not be examined. The carbon and hydrogen balance became remarkably worse at higher temperatures as a result of the increase in tarry and carbonaceous products (Table 2).

The Relation between the Conversion and the Yields.

The results of the pyrolysis at 1000°C are shown in Table 3 and Fig. 3. The total yields of methylacetylene and allene increased with an increase in the conversion, ranging from 4 mol at 10% conversion to 10 mol at 70% conversion. As the conversion was increased, the yield of allene increased from 4 mol at 10% conversion to 7 mol at 70% conversion, while that of methylacetylene increased slowly in the 50—70% conversion range, reaching 2 mol at 70% conversion. The yield of propylene increased from 22 mol

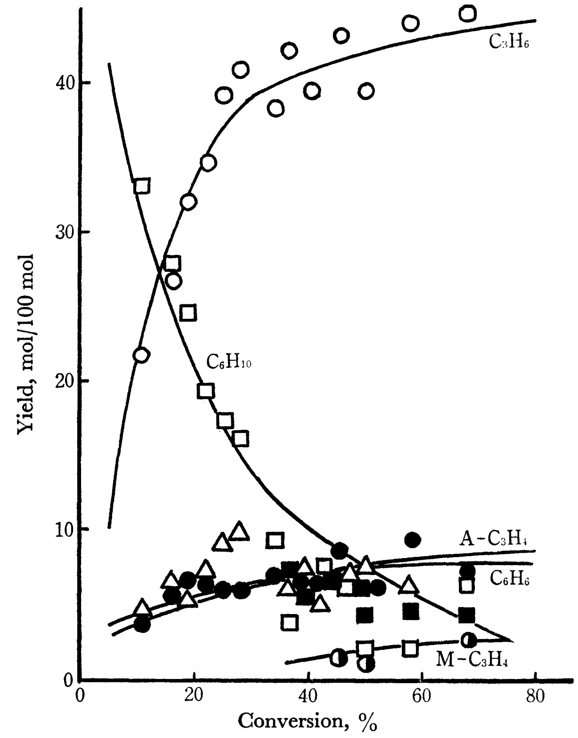

Fig. 3. Relation between conversion and product yields. temp., 1000°C
■: unidentified product

at 10% conversion to 44 mol at 70% conversion. Although its yield increased rapidly at lower conversions, the increase was much slower at higher conversions (ranging from 30% conversion to 70% conversion). The yield of diallyl, on the other hand, decreased from 33 mol at 10% conversion to 6 mol at 70% conversion. Though its yield decreased quickly at lower conversions, the decrease was much slower at higher conversions. Thus, the tendency of change in diallyl was found to be nearly the reverse of that in propylene. The yield of benzene increased from 4 mol at 10% conversion to 7 mol at 70% conversion. The yield of an unidentified product increased in the 30—70% conversion range, reaching 5 mol at 70% conversion. The amount of tarry and carbonaceous products increased with the increasing conversion to make the material balance remarkably worse, as is described in Table 3. Moreover, it was determined by the zero-conversion method that the major product in the early stage of the pyrolysis was diallyl, as is shown in Fig. 3.

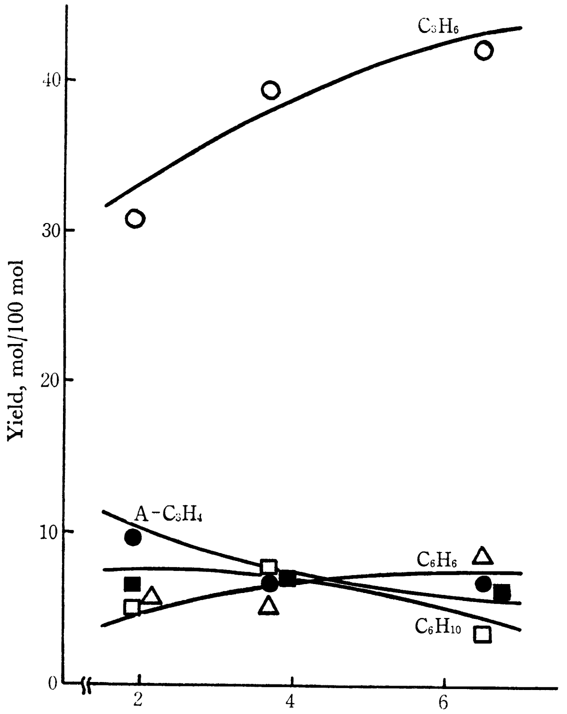

Fig. 4. Effect of concentration on product yields.
conversion, *ca.* 40%
■: unidentified product

The Effect of the Concentration on the Yields. The yields of products obtained in a concentration range from 2 to 7 mol% at 1000°C are shown in Fig. 4 (also in Table 3). As the concentration was increased, the yield of propylene gradually increased from 31 mol to 42 mol, while that of allene slowly decreased from 10 mol to 7 mol. The yield of benzene increased from 6 mol to 8 mol, and that of diallyl decreased from 6 mol to 4 mol. The yield of an unidentified product was almost constant at about 6 mol over the concentration range studied.

In closing, it is worthy of special mention that all the decomposition products possess C_3 and C_6 skeletons derived from the allyl and iodoally radicals. It was further found that the amount of propylene was approximately equal to the sum of the amounts of allene, methylacetylene, and four times the amounts of benzene (Fig. 3 and Table 3).

Discussion

Mechanism. On the basis of the experimental results, a mechanism for the pyrolysis of allyl iodide may be proposed. The heats of reaction for the reactions mentioned below are also given when available. The values of the heats of formation of the various materials used in their computation are shown in Table. 4.

TABLE 4. HEATS OF FORMATION OF GASES AT 298°K AND 1 atm(kcal/mol)

C_3H_5I[9a)]	21.5	I_2[9b)]	14.9
C_3H_6[9b)]	4.9	HI[9c)]	6.2
A-C_3H_4[9b)]	45.9	I[9b)]	25.5
M-C_3H_4[9c)]	44.3	$C_3H_5\cdot$[9b)]	40.6
C_6H_{10}[9d)]	17.8	H[9b)]	52.1

A possible explanation may be offered for the formation of allene and methylacetylene in the pyrolysis of allyl iodide.

$$\begin{array}{lll}
C_3H_5I \longrightarrow C_3H_5\cdot + I & \Delta H = 44.6 & (1) \\
I + C_3H_5I \longrightarrow C_3H_5\cdot + I_2 & \Delta H = 8.5 & (2) \\
I + C_3H_5I \longrightarrow HI + \cdot C_3H_4I & & (3) \\
C_3H_5\cdot + C_3H_5I \rightleftarrows C_6H_{10} + I & \Delta H = -18.8 & (4) \\
C_3H_5\cdot + C_3H_5I \longrightarrow C_3H_6 + \cdot C_3H_4I & & (5) \\
C_3H_5\cdot + HI \longrightarrow C_3H_6 + I & \Delta H = -16.4 & (6) \\
C_3H_5\cdot + I \longrightarrow C_3H_4 + HI & \Delta H = -14.0 & (7) \\
C_3H_5\cdot + I_2 \longrightarrow C_3H_4 + HI + I & \Delta H = 22.1 & (8) \\
2C_3H_5\cdot \longrightarrow C_6H_{10} & \Delta H = -63.4 & (9) \\
2\dot{C}_3H_4I \longrightarrow C_6H_6 + 2HI & & (10) \\
A\text{-}C_3H_4 + I \longrightarrow M\text{-}C_3H_4 + I & \Delta H = -1.6 & (11) \\
2I + M \longrightarrow I_2 + M & \Delta H = -36.1 & (12)
\end{array}$$

Reactions (1) to (12) are the main reactions in the pyrolysis. Reaction (1) is the initiation step, which features the dissociation of allyl iodide into the allyl radical and the iodine atom. All the main products—propylene, allene, diallyl, benzene, and methylacety lene— except for an unidentified product, are formed largely by subsequent reactions— (5) and (6), (7) and (8), (4), and (9), (10), and (11) respectively. As the formation step of allene, the unimolecular decomposition of the allyl radical[1,10)] is also considered, but the

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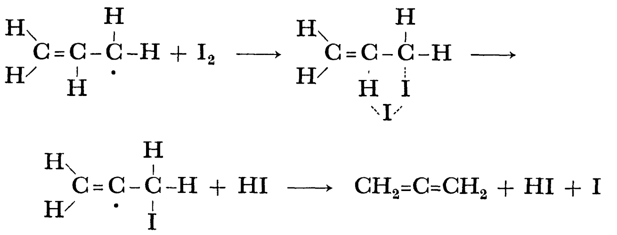
9) a) A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3194 (1966); b) See Ref. 3, p. 195; c) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Company, Inc., New York, Toronto, London (1960), p. 662; d) R. J. Akers and J. J. Throssell, *Trans. Faraday Soc.*, **63**, 124 (1967).

10) M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949); K. J. Laidler and B. W. Wojciechowski, *Proc. Poy. Soc., Ser. A*, **259**, 257 (1960); A. Amano and M. Uchiyama, *J. Phys. Chem.*, **68**, 1133 (1964).

activation energy of Reaction (13) (*ca.* 62 kcal/mol)[2a)]

$$C_3H_5\cdot \longrightarrow C_3H_4 + H \qquad (13)$$

is fairly high compared to that of Reaction (1). Therefore, Reaction (13) may be discounted energetically. Thus, two possible alternatives, Reactions (7) and (8), may be considered as the formation reactions of allene. The ΔH value of the overall process for Reaction (8) is *ca.* 22 kcal/mol. Although Reaction (7) should have a high specific rate in view of its exothermicity (*ca.* 14 kcal/mol), Reaction (8) may also be considered in view of the high ratio of molecular iodine to atomic iodine.[11)] The pathway of Reaction (8) can probably be written as follows:[12)]



The values of the activation energy for hydrogen abstraction from propane by the allyl radical and the iodine atom have been reported to be *ca.* 25 kcal/mol in both cases.[13)] It may, therefore, be presumed that the allyl radical and the iodine atom show almost the same reactivity for hydrogen abstraction. In addition, the corresponding value for an allylic hydrogen in propylene by the iodine atom has been estimated to be 18 kcal/mol.[14)] Consequently, assuming that the α (C–H) bond energies of propylene and allyl iodide are essentially the same, it may be considered that an allylic hydrogen in allyl iodide would be abstracted easily by the allyl radical (Reaction (5)) and the iodine atom (Reaction (3)) under the present conditions. Reactions (2) and (3) of the iodine atom with allyl iodide are in competition with each other since, although Reaction (2) is better than Reaction (3) from an energetic point of view, the latter reaction may also play an important role at higher temperatures. Reactions (4) and (5) of the allyl radical with allyl iodide will proceed competitively. In addition, Reactions (4) and (9) involving the allyl radical, leading to diallyl, will be competitive reactions under our reaction conditions.[7)] In Reaction (10), benzene would arise *via* the combination and cyclization of two iodoallyl radicals, formed by the α-hydrogen (allylic hydrogen) abstraction of allyl iodide, as in the cases of the other allyl halides.[2,15)] The isomerization of allene to methylacetylene (Reaction (11)) would proceed through the same mechanism as the iodine-catalyzed, positional isomerization of butene.[16)]

Figure 3 shows that the only major product in the early stage of the pyrolysis is diallyl. Hence, the stoichiometry of the reaction in the early stage is very well represented by the $2C_3H_5I \rightarrow C_6H_{10} + I_2$ reaction. This is fitted to the mechanism proposed by Szwarc[4)] and Benson[7)] in the pyrolysis of allyl iodide. It can, therefore, be presumed that Reactions (2) and (4) may play an important role in the early stage of the pyrolysis.[4,7)] From the relationship between the yield and the conversion (Fig. 3), diallyl in the pyrolyzed gas appears to reach an equilibrium state in the early stage of the pyrolysis and to exist thereafter in an equilibrium concentration. Thus, Reaction (4) is presumed to be an equilibrium.

As the temperature increases (Fig. 1), the yields of propylene and allene increase, while that of diallyl decreases. This may be explained by the following two reasons. First is temperature effect on the reaction rates; generally, subtituent reactions prevail over addition reactions at higher temperatures.[17)] Therefore, Reaction (5) would be relatively favored over Reaction (4) with an increase in the temperature. Thus, the yield of propylene increases, while that of diallyl decreases. Second is the temperature effect on the equilibrium constant of Reaction (4); the heat of formation of the forward reaction of Reaction (4) is negative. Consequently, the equilibrium constant of Reaction (4) decreases with an increase in the temperature. This leads to a decrease in the formation of diallyl, while an increase in the formation of propylene and allene results from Reactions (5) and (6), and (7) and (8), respectively, these being reactions consuming allyl radical. In the higher conversion range, from 27 to 34% (Fig. 2), more amounts of iodine and the iodine atom are considered to exist at an equilibrium concentration in the pyrolysis system than is the case with a lower conversion. Thus, the allyl radical formed is apt to be converted into allene through Reactions (7) and (8) in the higher conversion range with an increase in the temperature. Thus, the yield of propylene seemingly decreases, but the total yield of propylene and allene increases with an increase in the temperature.

As the conversion proceeds (Fig. 3), the yields of propylene and allene increase, while that of diallyl decreases. This may be explained by considering Reaction (4) to be a rapid equilibrium reaction; because its equilibrium constant is invariable with respect to the conversion, diallyl becomes the major product in the early stage of the pyrolysis. Thus, after the equilibrium was attained in the early stage of the pyrolysis, the yields of propylene and allene are increased by Reactions (5) and (6), and by Reactions (7) and (8), but that of diallyl decreases.

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11) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Voll. II, Longmans, Green and Co. Ltd., London, New York, Tronto (1927), p. 49.

12) J. H. Raley, R. D. Mullineaux, and C. W. Bittner, *J. Amer. Chem. Soc.*, **85**, 3174 (1963).

13) a) H. Tominaga, S. Abiko, and T. Kunugi, *Sekiyu Gakkai Shi*, **10**, 190 (1967); b) P. S. Nangia and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 2773 (1964); J. H. Knox and R. G. Musgrave, *Trans. Faraday Soc.*, **63**, 2201 (1967).

14) D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966).

15) a) A. Maccoll, *J. Chem. Soc.*, **1955**, 965; b) L. M. Porter and F. F. Rust, *J. Amer. Chem. Soc.*, **78**, 5571 (1956); L. J. Hughes and W. F. Yates, *J. Phys. Chem.*, **64**, 1789 (1960).

16) S. W. Benson and A. N. Bose, *J. Amer. Chem. Soc.*, **85**, 1385 (1963).

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

Besides, the amount of propylene is approximately equal to the sum of the amounts of allene, methylacetylene, and four times the amount of benzene, and the amount of hydrogen is very small. These experimental results may be well explained by the mechanism mentioned above.

Assuming that almost all the hydrogen iodide is consumed by Reaction (6), we obtain the following stoichiometric relations:

From Reactions (5), (10) and (6):

$$4C_3H_5\cdot + 2C_3H_5I \longrightarrow 4C_3H_6 + C_6H_6 + 2I$$

Similarly, from Reactions (3), (10), and (6):

$$4C_3H_5\cdot + 2C_3H_5I \longrightarrow 4C_3H_6 + C_6H_6 + 2I$$

From Reactions (7) and (6):

$$2C_3H_5\cdot \longrightarrow C_3H_6 + C_3H_4$$

From Reactions (8) and (6):

$$2C_3H_5\cdot + I_2 \longrightarrow C_3H_6 + C_3H_4 + 2I$$

Therefore, when 1 mol of benzene is formed, 4 mol of propylene is formed. In addition, when 1 mol of allene (methylacetylene) is formed, 1 mol of propylene is formed. The experimental data seem to confirm this (Fig. 3 and Table 3). Thus, it can be concluded that propylene is formed nearly exclusively by Reactions (5) and (6), and that the rate of Reaction (6) is very rapid, since the amount of hydrogen is very small.

As the conversion increases (Fig. 3), the yield of benzene increases, while that of diallyl decreases. As a result, it may be presumed also that benzene will be formed to some extent through diallyl.[7,18] With the increasing conversion, the pyrolysis reaction would become more complex, since the participation of hydrogen abstraction by the allyl radical or the iodine atom in secondary reactions increases remarkably. Consequently, it is difficult to account for the experimental results at higher conversions.

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[18] R. D. Mullineaux and J. H. Raley, *J. Amer. Chem. Soc.*, **85**, 3178 (1963).