

The Synthesis of Methylacetylene by the Pyrolysis of Propylene. (VII). The Catalysis of Iodine

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The pyrolysis of propylene in the presence of iodine was studied in a flow system with a nitrogen dilution over a wide range of conditions (temperature, 800–1200°C; contact time, 0.774×10^{-3} – 490×10^{-3} sec; pressure, atmospheric pressure) in order to find suitable conditions for producing methylacetylene and allene, and to obtain data concerning the distribution of the pyrolysis products. Iodine promoted the rate of propylene pyrolysis and the concentration of iodine affected the product distribution. The main products of the pyrolysis were found to be hydrogen, methane, acetylene, ethylene, allene, methylacetylene, butadiene, benzene, and isopropyl iodide. The total yield of methylacetylene and allene of 46 mol per 100 mol of propylene pyrolyzed was attained under suitable conditions. It was further found that small amounts of iodine (*ca.* 0.3 mol% of iodine for 13 mol% of propylene) were very effective for the synthesis of methylacetylene and allene at high temperatures (around 1200°C) and that the catalytic effect of iodine was considerably remarkable even at higher conversions. A brief discussion is given of the formation of methylacetylene and allene and the catalytic effect of iodine.

INTRODUCTION

In previous papers,¹⁾ high temperatures (1200–1300°C), short contact times (1.0×10^{-3} – 2.5×10^{-3} sec), and low pressures (below 100 mmHg) were found to be required for the efficient formation of methylacetylene and allene by the pyrolysis of propylene. Subsequently, it was found that certain radical sources were suitable as the catalyst and that halogens such as chlorine and bromine were the most effective among them.²⁾ In addition, from the experimental results of the pyrolysis of allyl halides,³⁾ it was recognized that iodine or the iodine atom had the catalytic effect for the formation of allene through the allyl radical and that little cleavage of the C-C bonds of allyl iodide occurred in the pyrolysis of allyl iodide.^{3c)} Thus, iodine is expected to be the most appropriate as the catalyst among these halogens. Recently, the dehydrogenation process of hydrocarbons with iodine⁴⁾ is developed, but no report has been made of the reaction of propylene with iodine at high temperatures (800–1200°C).

The purpose of this report is to find suitable conditions for the production of methylacetylene and allene by the pyrolysis of propylene in the presence of iodine and to examine the effect of iodine on the distribution of the pyrolysis products. Based on the observed experimental results, a brief discussion is given of the catalytic effect of iodine on the synthesis of methylacetylene and allene.

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EXPERIMENTAL

Materials. Propylene (99.5 mol% pure) was purchased from the Takachiho Chemical Co. Cylinder nitrogen (99.99 mol% pure) was used as a diluent and carrier gas. Oxygen content as the impurity was less than 0.01 mol%. E.p. grade iodine was used without further purification.

Apparatus and Procedure. The apparatus is shown in Fig. 1. Nitrogen and propylene were introduced through feed regulating valves, flow meters, and a mixing bottle into an iodine evaporator which was immersed in a constant temperature oil bath. The feed amount of iodine was adjusted by regulating the temperature of oil bath and the flow rate of reactant gas. The resulting mixture, containing *ca.* 85 mol% nitrogen, *ca.* 13 mol% propylene, and 0.1–1.8 mol% iodine, was pyrolyzed in a silica reaction tube, from 1.0 to 2.0 mm in inside diameter, under the specified conditions at atmospheric pressure. The reaction tube was heated to the desired temperature by a spiral "Siliconit" heating element which was 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 exhausted gas was immediately bubbled through two washing bottles containing 100 ml of *aq.* 3N NaOH solution in order to prevent further reactions of the unsaturated hydrocarbon products (especially, methylacetylene and allene) with hydrogen iodide or the residual iodine after emergence from the pyrolysis zone. Then, it was passed through a 500 ml glass gas-sampling flask.

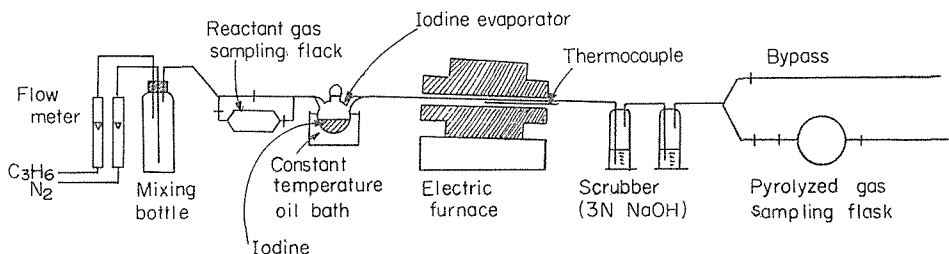


Fig. 1. Apparatus for pyrolysis.

The reaction temperature and contact time are measured as described in a previous paper.^{1a)} The amounts of iodine fed were determined from the weight loss in the evaporator during a run.

Analysis. The analytical method for hydrogen and hydrocarbons up to C_4 's in the pyrolysis products was essentially the same as that described previously.¹⁾ Benzene and isopropyl iodide were also analyzed by a gas chromatograph using a 30-wt.% β,β' -oxydipropionitrile column (2.5 m) at $60^\circ C$ with 72.5 ml/min of hydrogen as a carrier gas.

RESULTS

A part of the experimental results is shown in Table 1. The yield of each product is given by moles per 100 moles of propylene pyrolyzed. The main products through C_6

Table 1. Experimental data

Run No.	43	34	27	50	20	52	57	72	73	15	21	24
Temp., °C	800	900	1000	1100	1200	1200	1200	1200	1200	1200	1200	1200
Contact time, 10 ⁻³ sec	208	51.5	8.29	2.42	0.920	0.818	1.74	2.00	1.12	0.915	0.917	0.810
Composition of reactant gas, vol%												
Nitrogen	87.7	84.4	83.6	85.6	88.6	86.8	86.3	85.4	86.6	87.6	87.9	85.6
Propylene	11.7	15.0	15.9	13.7	10.7	12.9	13.3	14.6	13.4	12.2	11.3	13.1
Iodine	0.6	0.6	0.5	0.7	0.7	0.3	0.4			0.2	0.8	1.3
Conversion, %	18.5	19.2	22.0	21.3	25.5	14.1	58.4	52.4	26.2	22.6	21.8	25.0
Yield, mol/100 mol of propylene pyrolyzed												
Hydrogen	10.7	16.2	13.6	24.8	20.2	31.0	45.7	30.1	26.4	25.8	17.1	12.1
Methane	8.8	24.3	27.0	20.0	26.2	27.3	32.8	34.2	30.2	24.4	17.2	11.7
Acetylene	1.0	3.3	5.1	5.7	7.3	7.5	12.5	13.8	9.6	8.4	3.8	3.8
Ethylene	14.1	21.2	24.6	23.5	21.6	34.4	28.0	35.0	33.5	29.4	14.8	9.6
Ethane								1.0	0.8			
Allene	6.0	8.1	13.3	18.1	19.8	27.8	12.3	9.6	13.9	21.6	18.7	15.8
Methylacetylene	6.7	10.4	16.3	23.0	24.0	27.2	22.7	14.4	16.1	24.5	19.0	16.1
Butene-1								0.9	2.1			
Butadiene	tr.	tr.	tr.	tr.	tr.	tr.	1.3	2.8	3.6	tr.	tr.	tr.
Benzene	8.7	6.4	3.1	4.7	4.5	2.0	4.4	2.2	tr.	—	5.7	4.2
Isopropyl Iodide	8.2	5.1	0.9	5.7	6.1	2.2	tr.			tr.	11.1	13.0
Total yield of methylacetylene and allene	12.7	18.5	29.6	41.1	43.8	55.0	35.0	24.0	30.0	46.1	37.7	31.9
Total percentage of hydrogen and carbon accounted for in the reaction products described above												
Hydrogen	45.8	61.5	64.6	77.9	91.9	95.4	92.4	84.0	81.7	78.0	71.4	60.1
Carbon	51.2	60.9	65.5	82.4	87.0	98.4	83.5	78.0	78.0	79.5	78.0	65.4

hydrocarbons were methane, acetylene, ethylene, allene, methylacetylene, butadiene, and benzene, in addition to hydrogen and isopropyl iodide.

No other products (for example, methyl iodide, diallyl, and C_5 components, *etc.*) were detected in considerable amounts. Since methylacetylene and allene are equilibrated rapidly over the isomerization catalysts,⁵⁾ their total yield is also noted to evaluate suitable conditions for the synthesis of methylacetylene. In order to examine the hydrogen and carbon balance, the total percentage of hydrogen and carbon accounted for in the pyrolysis products (H_2 , C_1 - C_6 hydrocarbons, and isopropyl iodide) was calculated from their yields.

The Effect of the Temperature on the Product Yields. The results obtained in the conversion range from 19 to 26% and in the iodine concentrations ranging from 0.5 to 0.7 mol% are shown in Table 1 and Fig. 2. The yields of both methylacetylene (M- C_3H_4) and allene (A- C_3H_4) increased with an increase in the temperature, from 800 to 1200°C; the total yield ((A+M)- C_3H_4) ranged from 13 mol at 800°C up to 44 mol at 1200°C. The yields of methane and ethylene increased with an increase in the temperature from 9 mol to 26 mol and from 14 mol to 22 mol, respectively. The yields of

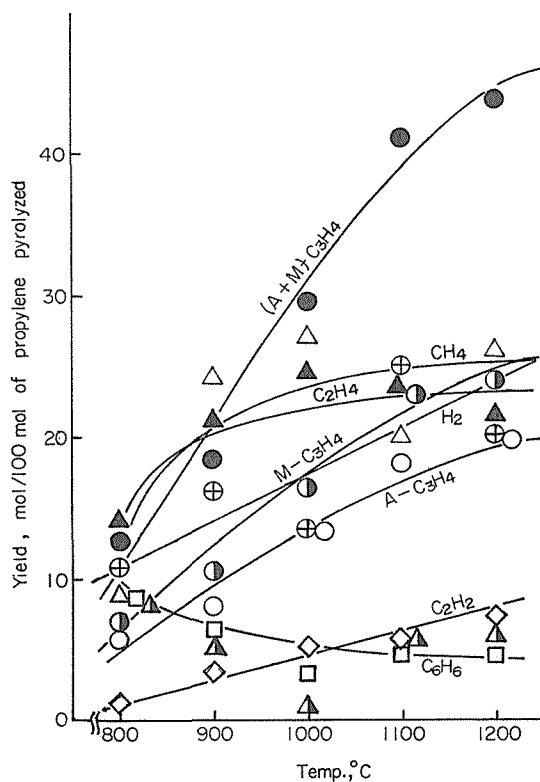


Fig. 2. Effect of temperature on product yields.

conversion, 19-26%; iodine, 0.5-0.7 mol%

In Figs. 2 to 5

- ; (A+M)- C_3H_4 , ○; A- C_3H_4 , ⊙; M- C_3H_4 , ⊕; H_2
 △; CH_4 , ▲; C_2H_4 , ▽; C_4H_8 , △; C_3H_7I , ◇; C_2H_2 ,
 ◆; C_2H_6 , □; C_6H_6 , ▨; C_4H_6

hydrogen and acetylene also increased to 20 mol and 7 mol, respectively, at 1200°C. On the contrary, the yield of benzene decreased to 5 mol at 1200°C. The yield of butadiene was very low over the conversion range studied.

The Relation between the Conversion and the Yields. The results of the pyrolysis at 1200°C and in the iodine concentrations ranging from 0.3 mol to 0.4 mol%, which were presumably a suitable iodine concentration range for the synthesis, are shown in Table I and Fig. 3. The total yield of methylacetylene and allene decreased with the increasing conversion, ranging from 55 mol at 14% conversion down to 35 mol at 58% conversion. In this conversion range, the yield of allene fell gradually as the conversion increased, while that of methylacetylene was roughly constant at 27 mol to 23 mol. The yield of methane increased from 27 mol at 14% conversion to 33 mol at 58% conversion, while that of ethylene decreased from 34 mol to 28 mol in the same conversion range. The yields of hydrogen and acetylene also increased to 46 mol and 13 mol at 58% conversion, respectively. In the conversion range from 30 to 60%, butadiene was obtained in a constant yield of about 1 mol. In addition, the yield of benzene was nearly constant at *ca.* 5 mol over the conversion range, and the yield of isopropyl iodide decreased gradually with the increasing conversion, reaching trace amounts at 58% conversion.

The Effect of the Iodine Concentration on the Yields. The product distribution was markedly influenced by the mole concentration of added iodine. Typical results obtained in the iodine concentrations ranging from 0 mol (no addition) up to 1.3 mol% and in the conversion range from 22 to 32% at 1200°C are shown in Table I and Fig. 4.

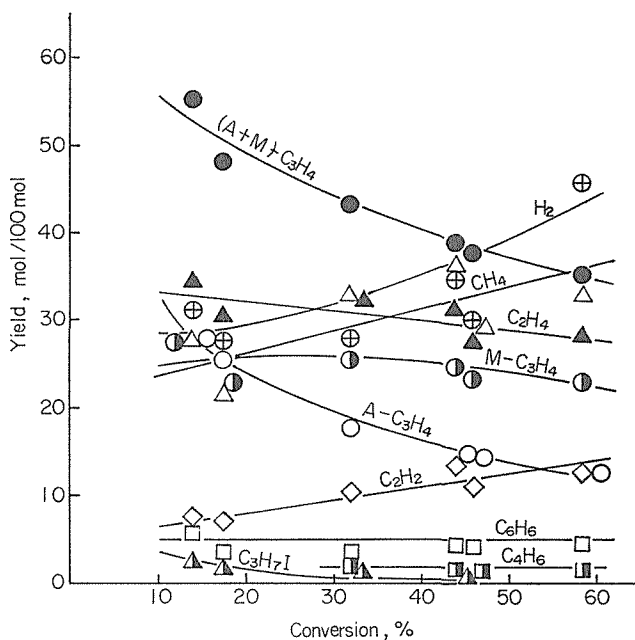


Fig. 3. Relation between conversion and yields.

temp., 1200°C; iodine, 0.3–0.4 mol%

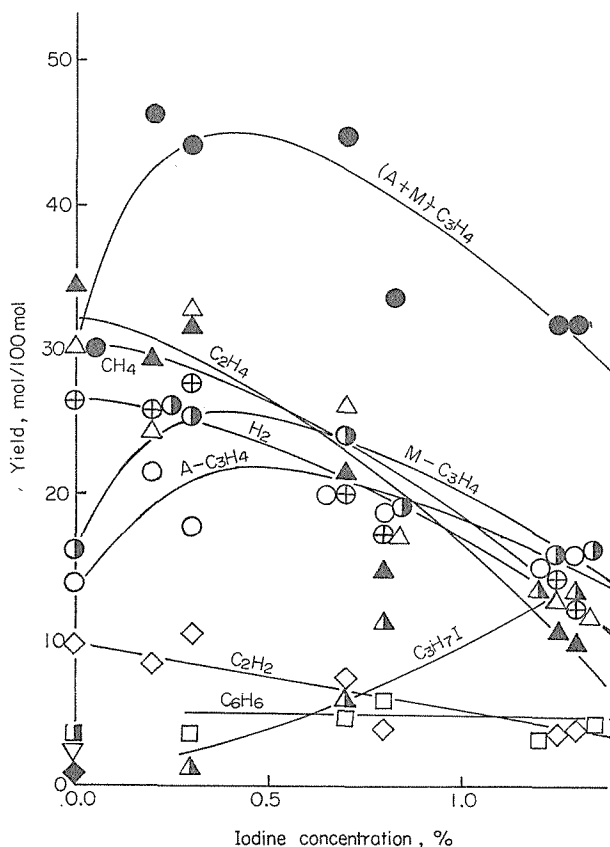


Fig. 4. Effect of iodine concentration on yields.
temp., 1200°C; conversion, 22–32 %.

The yields of both methylacetylene and allene showed the maximum values at 0.2 mol% of the iodine concentration. Thus, the total yield of methylacetylene and allene of 46 mol was attained at 0.2 mol%. As the iodine concentration increased, the yields of methane, ethylene, hydrogen, and acetylene decreased gradually, reaching 12 mol, 10 mol, 12 mol, and 4 mol at 1.3 mol%, respectively. In contrast to this, the yield of isopropyl iodide increased at a considerable rate, reaching 13 mol at 1.3 mol%, while that of benzene was nearly constant at *ca.* 5 mol. In addition, the addition of small amounts of iodine resulted in the promotion of the rate of propylene pyrolysis and suppressed the formation of ethane, butene-1, and butadiene.

The Pyrolysis of Propylene in the Absence of Iodine. In order to clarify the catalytic effect of iodine, propylene alone was pyrolyzed. The results of the pyrolysis at 1200°C are shown in Table I and Fig. 5. As the conversion increased, the yield of allene fell at a considerable rate from 21 mol at 9% conversion to 10 mol at 52% conversion, while that of methylacetylene was fairly constant at *ca.* 15 mol over the wide conversion range. Thus, the total yield of methylacetylene and allene decreased with the increasing conversion, ranging from 37 mol to 24 mol in the same conversion range. In this conversion range, the yield of methane increased gradually from 23 mol to 34 mol

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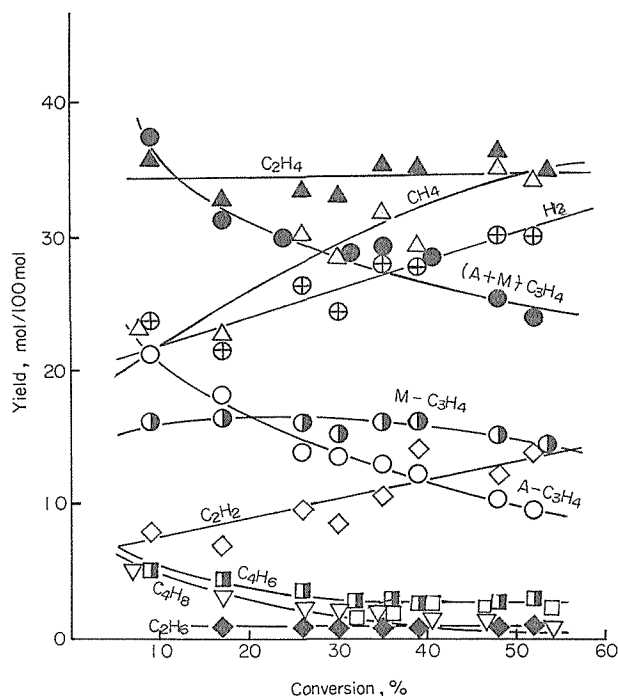


Fig. 5. Pyrolysis of propylene in the absence of iodine.
temp., 1200°C

with the increasing conversion, while that of ethylene was nearly constant at *ca.* 34 mol. As the conversion increased, the yields of hydrogen and acetylene increased to 30 mol and 14 mol at 52% conversion, respectively and the yields of butene-1 and butadiene decreased gradually to 1 mol and 3 mol at the same conversion. In the conversion range from 30 to 50%, the yield of benzene was almost constant at *ca.* 2 mol.

The Catalytic Effect of Iodine in the Synthesis of Methylacetylene and Allene.

The yields of methylacetylene and allene in the presence of iodine (*ca.* 0.3–0.4 mol%) were compared with those in its absence in the 10–60% conversion range. The results are shown in Fig. 6. Over the conversion range, the total yield of methylacetylene and allene in the presence of iodine was considerably higher than that in its absence; this difference was more remarkable in the lower conversion. It was further found that similar curves of the yields for each product were obtained in both cases.

DISCUSSION

The reaction of propylene with iodine at high temperatures is assumed to be a free radical decomposition involving hydrogen abstraction by the iodine atom.^{4a)} The reaction would be initiated by the equilibrium dissociation of iodine (reaction 1). The iodine atom,

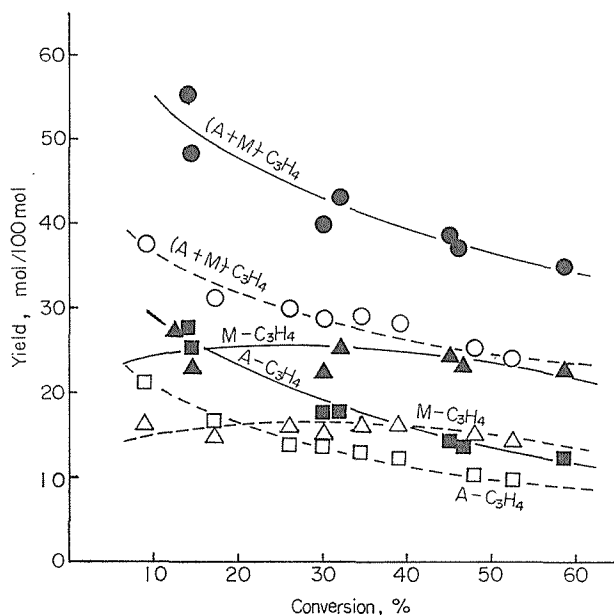


Fig. 6. Catalytic effect of iodine on the yields of methylacetylene and allene with conversion.

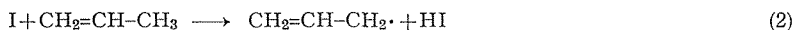
temp., 1200°C

With iodine,; 0.3-0.4 mol%

●; (A+M)-C₃H₄, ■; A-C₃H₄, ▲; M-C₃H₄

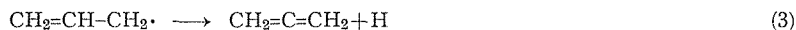
Without iodine

○; (A+M)-C₃H₄, □; A-C₃H₄, △; M-C₃H₄

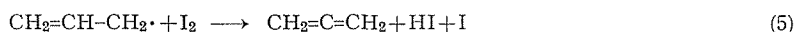
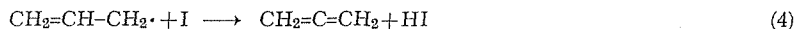


in reacting with propylene, attacks the allylic hydrogen atom exclusively, forming hydrogen iodide and the allyl radical (reaction 2).

In discussing the formation of allene, the allyl radical may undergo the unimolecular decomposition to allene (reaction 3)¹⁾ at very low iodine concentrations.

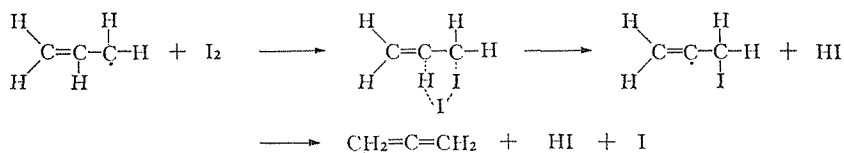


As the iodine concentration increases, two possible alternatives, reactions 4 and 5 may become important in addition to reaction 3,^{3c)} because the ΔH value for reaction 3 (ca. 57 kcal/mol) is fairly high compared with those of reactions 4 and 5. The exothermicity for reaction 4 is ca. 14 kcal/mol, and the heat of reaction of the overall process for reaction 5 is ca. 22 kcal/mol.



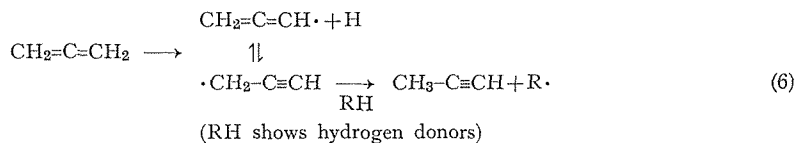
The pathway of reaction 5 can probably be written as follows.^{3c)}

Catalysis of Iodine

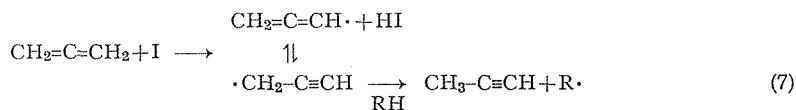


Thus, in the presence of iodine, it would be expected that the total yield of methylacetylene and allene becomes much higher than that without iodine. This is supported by the experimental results illustrated in Fig. 6.

At very low iodine concentrations, allene isomerizes mainly to methylacetylene according to reaction 6.^{1b)} As the iodine concentration increases, the iodine-catalyzed



isomerization of allene to methylacetylene (reaction 7)^{3c)} would come out predominant over reaction 6.



A rapid decrease in the total yield of methylacetylene and allene with the increasing conversion (Fig. 3) may be attributable to the loss due to various secondary reactions; a rapid decrease in allene appears to be plausible from the fact that allene is apt to undergo various secondary reactions including the isomerization reaction 7, while the approximate constancy in methylacetylene may be considered to be a result of the rapid isomerization of allene to methylacetylene (reaction 7) under the conditions used.^{3c)} The variation in the methylacetylene/allene ratio with conversion can be explained by this equilibrium (reaction 7). The experimental ratio (1.8 at 58% conversion) approached the calculated equilibrium constant (2.82 at 1200°C)^{1b)} with the increasing conversion (Table I and Fig. 3). Furthermore, the ratio in the presence of iodine was considerably higher than that in the absence (1.5 at 52% conversion) (Table I and Fig. 5). Thus, iodine is considered to be an effective catalyst for the isomerization of allene to methylacetylene.

In the pyrolysis of propylene in the presence of iodine, it was found that small amounts of iodine were very effective as the catalyst for the synthesis of methylacetylene and allene at high temperatures (around 1200°C) (Fig. 4) and that the catalytic effect of iodine was considerable even at higher conversions (Fig. 6). This may possibly be explained by considering the equilibrium as described below.



From the results of the investigations of the hydrogen iodide decomposition,^{6,7)} it seems

reasonable to assume that hydrogen iodide decomposes to give an equilibrium mixture of hydrogen, iodine, and hydrogen iodide at the high temperature (800–1200°C) according to the equilibrium (I). The dissociation of iodine into the iodine atom: $I_2 \rightleftharpoons 2I$ (the equilibrium (II)) increases with the increasing temperature.⁸⁾ The iodine atom formed would be consumed for abstracting the hydrogen atom mainly from propylene (reaction 2) at high temperatures, and the hydrogen iodide would be decomposed again to form hydrogen and iodine. Thus, the reaction would be always initiated by the further dissociation of the iodine reformed.

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