

The Synthesis of Methylacetylene by the Pyrolysis of Propylene (IX).

The Mechanism of the Iodine-catalyzed Pyrolysis of Propylene

Mamoru TANIUCHI*

Received November 17, 1972

A study has been made of the mechanism for the pyrolysis of propylene in the presence of iodine at high temperatures (800–1200°C). By means of the zero conversion method, hydrogen, methane, ethylene, and allene have been found to be the main primary products, while methylacetylene, acetylene, and benzene have been found to be the chief secondary products. On the basis of the observed results, a free radical chain mechanism has been proposed for the main reactions. The catalysis of iodine and the product distributions have been satisfactorily explained by this mechanism. The catalytic effect of iodine on the synthesis of methylacetylene and allene is attributable to (1) the reformation of iodine and the iodine atom by the reactions of hydrogen iodide: $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$, $\text{CH}_3 \cdot + \text{HI} \rightarrow \text{CH}_4 + \text{I}$; (2) the promotion of formation of the allyl radical from propylene and allene from the allyl radical: $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{I} \rightarrow \text{CH}_2=\text{CH}-\text{CH}_2 \cdot + \text{HI}$, $\text{CH}_2=\text{CH}-\text{CH}_2 \cdot + \text{I} \rightarrow \text{CH}_2=\text{C}=\text{CH}_2 + \text{HI}$, $\text{CH}_2=\text{CH}-\text{CH}_2 \cdot + \text{I}_2 \rightarrow \text{CH}_2=\text{C}=\text{CH}_2 + \text{HI} + \text{I}$; and (3) the suppression of decomposition of propylene to ethylene and the methyl radical: $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{H} \rightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3 \cdot$.

INTRODUCTION

In a previous paper,¹⁾ the present author investigated the pyrolysis of propylene in the presence of iodine at high temperatures (800–1200°C). It was found that small amounts of iodine were very effective as a catalyst for the synthesis of methylacetylene and allene at high temperatures around 1200°C and that the product distributions changed remarkably in the presence of iodine.

This paper deals with a discussion on the mechanism and the catalysis of iodine, based on the product distributions obtained from the pyrolysis under various conditions and on a few reference experiments.

EXPERIMENTAL

Some of the experimental results have been already described.¹⁾ In the reference experiments, the experimental methods were essentially the same as those for allyl chloride.²⁾ Allyl iodide was prepared from allyl chloride;³⁾ b. p. 101–102°C, n_D^{22} 1.5540. 1,5-Hexadiene was prepared similarly from allyl chloride;⁴⁾ b. p. 60°C, n_D^{20} 1.4034.

RESULTS AND DISCUSSION

Some of the experimental results are shown in Tables 1 and 2.

* 谷内 護: Laboratory of Organic Unit Reactions, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

Table 1. Experimental Data

Run No.	81	52	53	55	57	43	34	27	50	20	73	15	21	24	
Temp., °C	1200	1200	1200	1200	1200	800	900	1000	1100	1200	1200	1200	1200	1200	
Contact time, 10 ⁻³ sec	0.570	0.818	1.10	1.47	1.74	208	51.5	8.29	2.42	0.920	1.12	0.915	0.917	0.810	
Composition of reactant gas, vol%															
Nitrogen	84.0	86.8	85.9	85.6	86.3	87.7	84.4	83.6	85.6	88.6	86.6	87.6	87.9	85.6	
Propylene	15.7	12.9	13.8	13.9	13.3	11.7	15.0	15.9	13.7	10.7	13.4	12.2	11.3	13.1	
Iodine	0.4	0.3	0.3	0.4	0.4	0.6	0.6	0.5	0.7	0.7		0.2	0.8	1.3	
Conversion, %	5.2	14.1	31.8	45.4	58.4	18.5	19.2	22.0	21.3	25.5	26.2	22.6	21.8	25.0	
Yield, mol/100 mol of propylene pyrolyzed															
Hydrogen	24.4	31.0	27.7	34.4	45.7	10.7	16.2	13.6	24.8	20.2	26.4	25.8	17.1	12.1	
Methane	26.2	27.3	32.9	35.2	32.8	8.8	24.3	27.0	20.0	26.2	30.0	24.4	17.2	11.7	
Acetylene	4.9	7.5	10.4	13.1	12.5	1.0	3.3	5.1	5.7	7.3	9.6	8.4	3.8	3.8	
Ethylene	29.0	34.4	32.2	31.0	28.0	14.1	21.2	24.6	23.5	21.6	33.5	29.4	14.8	9.6	
Ethane											0.8				
Allene	38.8	27.8	17.7	14.4	12.3	6.0	8.1	13.3	18.1	19.8	13.9	21.6	18.7	15.8	
Methylacetylene	22.1	27.2	25.4	24.4	22.7	6.7	10.4	16.3	23.0	24.0	16.1	24.5	19.0	16.1	
Butene-1											2.1				
Butadiene	tr.	tr.	1.8	1.4	1.3	tr.	tr.	tr.	tr.	tr.	3.6	tr.	tr.	tr.	
Benzene	—	2.0	3.4	4.1	4.4	8.7	6.4	3.1	4.7	4.5	tr.	—	5.7	4.2	
Isopropyl Iodide*	—	2.2	1.2	0.5	tr.	8.2	5.1	0.9	5.7	6.1		tr.	11.1	13.0	
Total yield of methylacetylene and allene	60.9	55.0	43.1	38.8	35.0	12.7	18.5	29.6	41.1	43.8	30.0	46.1	37.7	31.9	
Total percentage of hydrogen and carbon accounted for in the reaction products described above															
Hydrogen	84.5	95.4	91.6	91.9	92.4	45.8	61.5	64.6	77.9	91.9	81.7	78.0	71.4	60.1	
Carbon	92.3	98.4	93.0	87.2	83.5	51.2	60.9	65.5	82.4	87.0	78.0	79.5	78.0	65.4	

* This substance is presumed to be the addition product of hydrogen iodide to propylene at the outlet of the reaction tube.

Table 2. Pyrolyses of Allyl Iodide and 1,5-Hexadiene temp., 1000°C

Composition of reactant gas, vol%					
Nitrogen	95.5	94.2	96.4	96.1	94.1
Allyl Iodide	4.5	5.8	3.6		
1,5-Hexadiene				3.9	5.9
Contact time, 10 ⁻³ sec	0.224	0.306	0.311	1.97	2.96
Conversion, %	21.8	50.2	58.0	22.1	48.6
Yield,* mol/100 mol of allyl compound pyrolyzed					
Hydrogen				1.1	2.6
Methane				tr.	tr.
Acetylene				0.8	0.8
Ethylene				5.9	6.1
Propylene	34.5	39.4	43.6	25.6	23.1
Allene	6.3	5.9	9.4	8.8	5.1
Methylacetylene		0.8	tr.	2.4	1.6
1-Butene				5.3	4.8
Butadiene				4.4	3.7
Cyclopentadiene				—	2.4
Methylcyclopentadiene				—	1.3
1,5-Hexadiene	19.2	2.0	2.0		
Unidentified product		4.3	4.7		
1,3-Cyclohexadiene				3.8	0.8
Benzene	7.1	7.7	6.3	3.5	2.7
Total yield of methylacetylene and allene	6.3	6.7	9.4	11.2	6.7
Total percentage of hydrogen and carbon accounted for in the reaction products described above					
Hydrogen	93.3	74.4	80.7	69.2	60.9
Carbon	93.2	74.0	79.0	68.9	59.4

* In the case of 1,5-hexadiene, the yield of each product is given by moles per 50 moles of 1,5-hexadiene pyrolyzed for comparison with that of allyl iodide.

Mechanism. The pyrolysis of propylene in the presence of iodine at high temperatures (800–1200°C) seems to proceed substantially by a free radical mechanism.^{1,5)} Because iodine and iodine atom would be reformed by the reactions of hydrogen iodide, as described later, the pyrolysis is considered to be a chain reaction catalyzed by iodine. Moreover, the product distributions changed remarkably according to the pyrolysis conditions, especially iodine concentrations.¹⁾ Therefore, it seems impossible to deduce a simple mechanism which would be valid over a wide range of iodine concentrations, temperatures, and conversions. However, from Fig. 1, which shows the extrapolation of the product yield to zero conversion, and the result of the pyrolysis of propylene alone,⁶⁾ it may be concluded that hydrogen, methane, ethylene, and allene are the primary products, and that methylacetylene, acetylene, and benzene are the secondary products. Thus, on referring to the mechanism for the pyrolysis of propylene alone,⁶⁾ a free radical chain mechanism may be proposed to explain the main reactions under the present conditions.

This mechanism is not intended to be comprehensive but only to indicate how the main products are probably formed.

At higher iodine concentrations, the contribution to hydrogen abstraction by the iodine atom or the allyl radical from the products and the addition of the allyl radical to the unsaturated products (especially, methylacetylene and allene) would increase remarkably.

Moreover, at higher conversions, secondary reactions (hydrogen abstraction, addition, *etc.*) of various radicals with the products become serious. However, these reactions are disregarded.

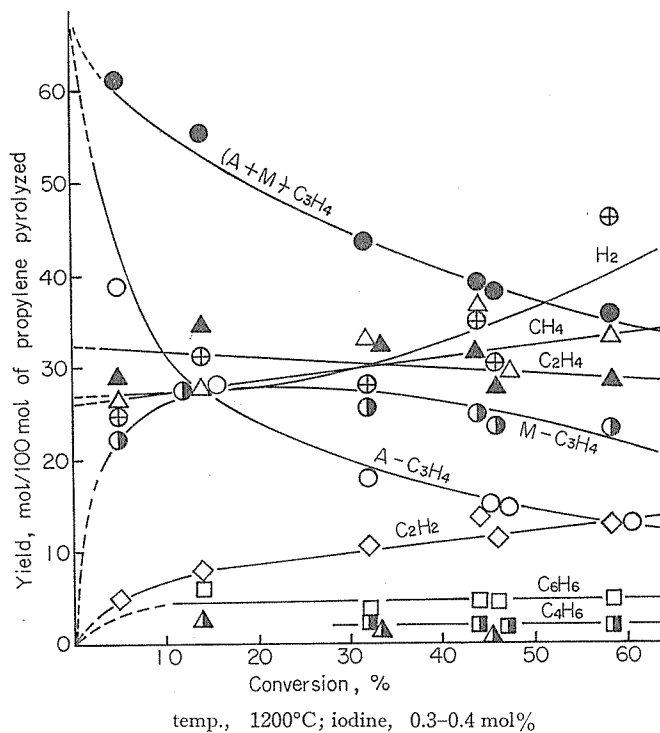


Fig. 1. Extrapolation of product yield to zero conversion.

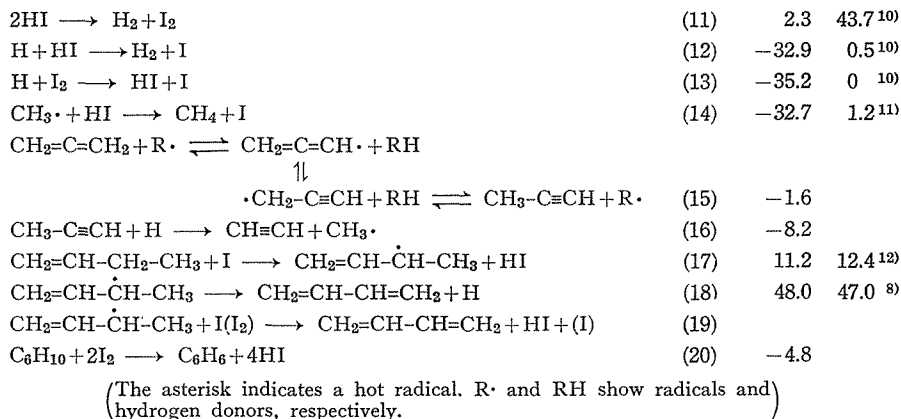
In Figs. 1 to 3

- ; (A+M)-C₃H₄, ○; A-C₃H₄, ⊙; M-C₃H₄, ⊕; H₂
 △; CH₄, ▲; C₂H₄, ▽; C₄H₈, ▲; C₃H₇I,
 ◇; C₂H₂, ◆; C₂H₆, □; C₆H₆, ■; C₄H₆

Primary Reactions

	ΔH	E
	kcal	kcal
$I_2 \longrightarrow 2I$	(1) 36.1	36.1
$CH_2=CH-CH_3 + I \longrightarrow CH_2=CH-CH_2\cdot + HI$	(2) 16.5	18.0 ⁷⁾
$CH_2=CH-CH_2\cdot \longrightarrow CH_2=C=CH_2 + H$	(3) 57.4	62.0 ²⁾
$CH_2=CH-CH_2\cdot + I \longrightarrow CH_2=C=CH_2 + HI$	(4) -13.9	
$CH_2=CH-CH_2\cdot + I_2 \longrightarrow CH_2=C=CH_2 + HI + I$	(5) 22.2	
$CH_2=CH-CH_3 + H \longrightarrow CH_2=CH-CH_2\cdot + H_2$	(6) -16.4	1.1 ⁸⁾
$CH_2=CH-CH_3 + H \longrightarrow [\cdot CH_2CH_2CH_3^*] \longrightarrow CH_2=CH_2 + CH_3\cdot$	(7) -10.5	3.6 ⁸⁾
$CH_2=CH-CH_3 + CH_3\cdot \longrightarrow CH_2=CH-CH_2\cdot + CH_4$	(8) -16.2	7.2 ⁸⁾
$CH_2=CH-CH_2\cdot + CH_2=CH-CH_3 \longrightarrow C_6 \text{ hydrocarbons} + H$	(9)	15.0 ⁹⁾
$CH_2=CH-CH_2\cdot + CH_3\cdot \longrightarrow CH_2=CH-CH_2-CH_3$	(10) -74.6	0

Secondary Reactions



With the above restrictions in mind, this mechanism was developed. The kinetic data for each reaction in the mechanism are also given when available. The values of the heats of formation of the related materials used in their computation are shown in Table 3.

Table 3. Heats of Formation for Some Gas Phase Species

at 298°K and 1 atm, kcal

CH_4 ^{13a)}	-17.9	C_6H_{10} ^{13c)}	20.0	H ^{13a)}	52.1
C_2H_2 ^{13a)}	54.2	C_6H_6 ^{13b)}	19.8	I ^{13a)}	25.5
C_2H_4 ^{13a)}	12.5	H_2 ^{13a)}	0	$\text{CH}_3\cdot$ ^{13a)}	34.0
C_3H_6 ^{13a)}	4.9	I_2 ^{13a)}	14.9	$\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}_2\cdot$ ^{13a)}	40.6
$\text{A}-\text{C}_3\text{H}_4$ ^{13a)}	45.9	HI ^{13a)}	6.3	$n-\text{C}_3\text{H}_7\cdot$ ^{13a)}	21.0
$\text{M}-\text{C}_3\text{H}_4$ ^{13b)}	44.3	O_2 ^{13a)}	0	$\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}-\text{CH}_3$ ¹²⁾	30.4
$1-\text{C}_4\text{H}_8$ ^{13b)}	0.0	H_2O ^{13a)}	-57.8		
C_4H_6 ^{13d)}	26.3				

A-C₃H₄; allene, M-C₃H₄; methylacetylene, C₆H₁₀; 1,5-hexadiene

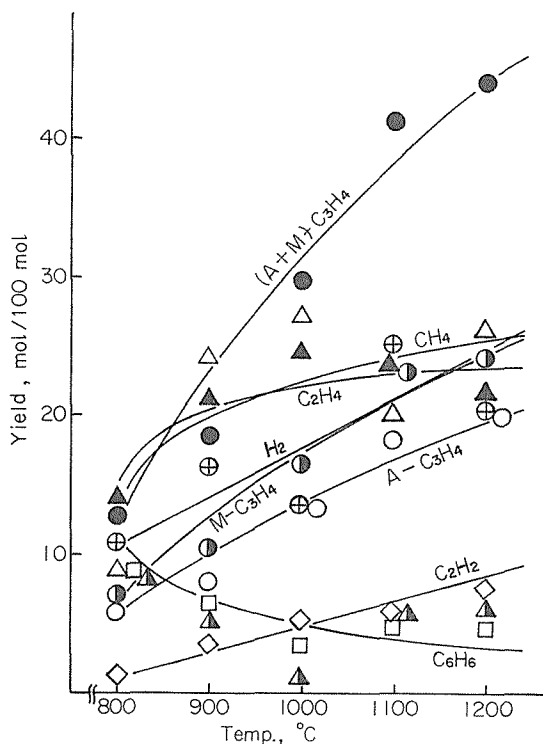
Reactions 1 to 20 seem to be the main reactions in the pyrolysis. Of these reactions, reactions 1 to 10 may be considered to be the main primary reactions, while the other reactions 11 to 20 may be estimated to be the chief secondary reactions. All the main products, allene, hydrogen, ethylene, methane, methylacetylene, acetylene, butadiene, and benzene are formed by reactions 3-4-5, 6, 7, 8, 15, 16, 18-19, and 20, respectively. Being not observed experimentally, butene-1 is considered to be a primary product from a consideration of the mechanism for the pyrolysis of propylene alone.⁶⁾ The probable explanation for the absence of butene-1 is that its formation (reaction 10) is suppressed by the other competitive reactions 8 and 14 and that, in addition, it is rapidly dehydrogenated to butadiene.^{5,14)}

Generally, the initiation reaction in the pyrolysis of propylene is considered to be the splitting of the $\alpha(\text{C}-\text{H})$ bond leading to the formation of the hydrogen atom and the allyl

Mechanism of the Iodine-catalyzed Pyrolysis of Propylene

radical. This requires a high activation energy, 87.5 kcal/mol.¹⁵⁾ Therefore, if iodine whose dissociation energy is 36 kcal/mol is present in the pyrolysis system, the pyrolysis would be initiated by the dissociation of molecular iodine into atomic iodine (reaction 1). The iodine atom would abstract the allylic hydrogen atom from propylene to form hydrogen iodide and the allyl radical (reaction 2). Thus, the pyrolysis would proceed. When the pyrolysis proceeds to a certain extent, the concentrations of iodine decrease and the regeneration of iodine by the decomposition of hydrogen iodide would become remarkable.¹⁾ In addition, the iodine atom itself would be recycled by the reactions 12 and 14. Therefore, the pyrolysis would always proceed by the dissociation of the iodine reformed and the recycled iodine atom.

Concerning the formation of allene from the allyl radical, reactions 3, 4 and 5 are expected to be important courses under the present conditions. At very low iodine concentrations, the unimolecular decomposition of the allyl radical to allene (reaction 3)⁶⁾ may prevail. As the iodine concentrations increase, two possible alternatives, reactions 4 and 5 may become important in addition to reaction 3.^{1,16)} As a result, the higher yields of methylacetylene and allene would be obtained in the presence of iodine. The experimental data seem to confirm this (Runs 73, 15, and 20 in Table 1). The concentration ratio of atomic iodine to molecular iodine increases with the increasing temperature, and reaches 1 : 1 around 1100°C.¹⁷⁾ Thus, as temperature increases, reaction 4 would



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

Fig. 2. Effect of temperature on product yields.

become more predominant than reaction 5. Moreover, reaction 3 is the unimolecular reaction and its ΔH value is the largest in the reactions 3, 4, and 5. Thus, the rate of reaction 3 increases rapidly with an increase in the temperature,⁶⁾ compared with the other two reactions 4 and 5. Therefore, reactions 3 and 4 are presumed to be predominant at high temperatures around 1200°C. In comparison between the rate of the formation of C₆ hydrocarbons by reaction 9 and that of allene by reaction 3, the former decreased fairly rapidly with the increasing temperature compared with the latter.⁶⁾ This is supported by the experimental results that methylacetylene and allene increased with an increase in the temperature and that C₆ hydrocarbons (benzene) decreased, notwithstanding an increase of the carbon and hydrogen balance (Fig. 2 and Table 1). In addition, since the supply of the hydrogen atom by secondary decompositions of products increases remarkably with the increasing temperature, reactions 6, 7, 8, and 16 would become predominant at high temperatures. The tendency for the formation of hydrogen, ethylene, methane and acetylene with temperature seems to confirm this (Fig. 2).

As the concentrations of iodine increased, the yields of both methylacetylene and allene showed maximum values at ca. 0.3 mol% of the iodine concentration (Fig. 3). The bond dissociation energies for $\text{CH}\equiv\text{C}-\text{CH}_2-\text{H}$ and for $\text{CH}_2=\text{C}=\text{CH}-\text{H}$ are reported to be 82.8 kcal/mol and 81.2 kcal/mol,¹⁸⁾ respectively. Therefore, the activation energies for hydrogen abstraction from methylacetylene and allene by the iodine atom are calculated to be 13.4 kcal/mol and 11.8 kcal/mol, respectively, by using Polanyi relation.¹⁹⁾ These values are considerably low as compared with that for propylene (18.0 kcal/mol).⁷⁾ Thus, at higher iodine concentrations, although the formation of allene would be accelerated by reactions 4 and 5, the decompositions of methylacetylene and allene also would be promoted mainly by hydrogen abstraction from them by the iodine atom. Therefore, the addition of allyl, allenyl, and propargyl radicals to propylene, allene, and methylacetylene would become important. The rapid decrease in the yields of both methylacetylene and allene at higher iodine concentrations may be mainly discussed in connection with this (Fig. 3). In addition, at higher iodine concentrations, reactions 2, 4, and 5 may proceed to give large amounts of hydrogen iodide and the hydrogen iodide and iodine may act to consume the hydrogen atom by reactions 12 and 13. Thus, reactions 6, 7, 8, and 16, which are competitive reactions with the above reactions 12 and 13, would be suppressed. The tendency for the formation of hydrogen, ethylene, methane, and acetylene with iodine concentration seems to confirm this (Fig. 3). In brief, at lower iodine concentrations, the formation of allene by reactions 4 and 5 is accelerated and the decomposition of propylene by reaction 7 is suppressed. These enable the higher yields of methylacetylene and allene to be obtained. However, at higher iodine concentrations, the decompositions of methylacetylene and allene as described above is presumed to be very serious. Consequently, it is considered that the yields of both methylacetylene and allene show maximum values at any iodine concentration. In the presence of iodine, the formation of ethane, butene-1, and butadiene was suppressed extremely (Fig. 3 and Runs 73 and 15 in Table 1). This may be because the rate of reaction 14 is very rapid as compared with that of reaction 10.

A rapid decrease in the total yield of methylacetylene and allene with the increasing conversion (Fig. 1) 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

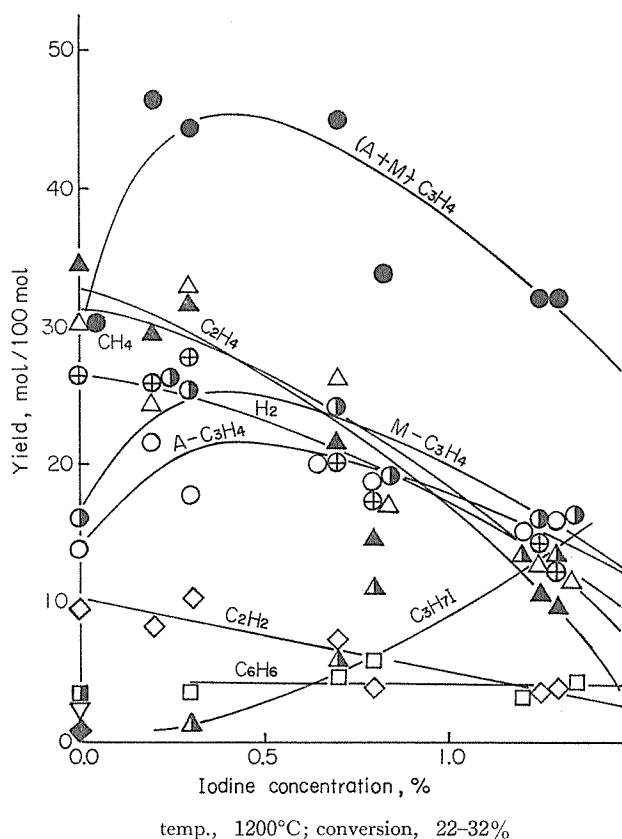
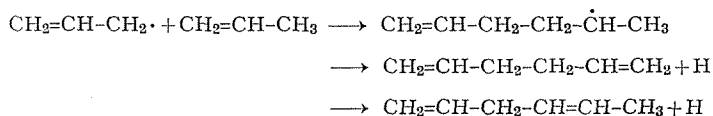


Fig. 3. Effect of iodine concentration on yields.

various secondary reactions including the isomerization reaction 15, while the approximate constancy in methylacetylene may be considered to be a result of the rapid isomerization of allene to methylacetylene (reaction 15) under the conditions used.^{1,6,16)} According to this mechanism, whenever an ethylene molecule is produced by reaction 7, a methyl radical is formed; this radical may give rise to methane by reactions 8 and 14. In the pyrolysis with iodine, small amounts of butadiene only were identified (Table 1). Therefore, the ethylene/methane ratio must be 1 : 1. The experimental data seem to confirm this 1 : 1 ratio roughly (Figs. 1 to 3). In addition, although the yield of ethylene was almost the same over the conversion range, the tendency for the yield of methane with conversion was in parallel with that of acetylene (Fig. 1). From this fact, it may be concluded that acetylene is formed mainly by reaction 16.⁶⁾ Since secondary decompositions of the products increase gradually with the increasing conversion, the pyrolysis would become extremely complex. Consequently, it seems difficult to account for the experimental results at high conversions.

Although hexadiene was not detected in the products, it may be reasonable to presume that reaction 9 would play an important role for the formation of hexadiene under the conditions used, since the formation of 1,5-hexadiene by the addition of the allyl radical to allyl iodide is considered to be very rapid at high temperatures.¹⁶⁾

M. TANIUCHI



In order to examine the behaviors of hexadiene under the present conditions, the pyrolyses of allyl iodide and 1,5-hexadiene were carried out (Table 2). From the relation between the amounts of benzene formed and the material balances of the products to the amounts of 1,5-hexadiene consumed, it may possibly be presumed that hexadiene would be for the most part converted into polymer and in part into benzene under the conditions used.

ACKNOWLEDGMENT

The author is very grateful to Emeritus Professor Sango Kunichika, to Professor Kazuhiro Maruyama, and to Dr. Yasumasa Sakakibara for their helpful advice and kind encouragement throughout this work.

REFERENCES

- (1) M. Taniuchi, *This Bulletin*, **50**, 383, (1972).
- (2) S. Kunichika, Y. Sakakibara, and M. Taniuchi, *Bull. Chem. Soc., Japan*, **42**, 1082 (1969).
- (3) R. L. Letsinger and J. G. Traynham, *J. Amer. Chem. Soc.*, **70**, 2818 (1948).
- (4) A. Turk and H. Chanan, "Organic Syntheses," Coll. Vol. III, p. 121.
- (5) J. H. Raley, R. D. Mullineaux, and C. W. Bittner, *J. Amer. Chem. Soc.*, **85**, 3174 (1963).
- (6) Y. Sakakibara, *Bull. Chem. Soc., Japan*, **37**, 1268 (1964).
- (7) D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966).
- (8) T. Kunugi, K. Soma, and T. Sakai, *Ind. Eng. Chem. Fundam.*, **9**, 319 (1970).
- (9) K. J. Laidler and B. W. Wojciechowski, *Proc. Roy. Soc.*, **A259**, 257 (1960).
- (10) J. H. Sullivan, *J. Chem. Phys.*, **30**, 1292 (1959).
- (11) M. C. Flowers and S. W. Benson, *ibid.*, **38**, 882 (1963).
- (12) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).
- (13) a) S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., (1968), p. 195; b) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Company, Inc., (1960), p. 662; c) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); d) J. G. Calvert and J. N. Pitts Jr., "Photochemistry," John Wiley & Sons, Inc., (1966), p. 815.
- (14) R. W. King, *Hydrocarbon Process. Petrol. Refiner*, **45**, (11), 189 (1966).
- (15) See Ref. 13a, p. 215.
- (16) S. Kunichika, Y. Sakakibara, and M. Taniuchi, *Bull. Chem. Soc., Japan*, **44**, 1383 (1971).
- (17) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Voll. II, Longmans, Green and Co. Ltd., (1927), p. 49.
- (18) J. Collin and F. P. Lossing, *Can. J. Chem.*, **35**, 778 (1957).
- (19) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).