The Synthesis of Methylacetylene by the Pyrolysis of Propylene. II. The Mechanism of the Pyrolysis*[1]

By Yasumasa SAKAKIBARA

(Received March 23, 1964)

Previously,⁽¹⁾ when the present author investigated the pyrolysis of propylene with the object of finding suitable conditions for the production of methylacetylene-allene,*[2] he found that high temperatures (1200~1300°C), low pressures (below 100 mmHg), and short contact times (conversion below 30%) were required for good results. In this paper the mechanism for the pyrolysis will be reported on.

The distribution of the products of the pyrolysis varies considerably with pyrolysis conditions, and on the basis of observed results several mechanisms have been suggested in recent years. Ingold and Stubbs,⁽²⁾ investigating the pyrolysis at temperatures from 570 to 650°C and at pressures from 50 to 500 mmHg, proposed a series of molecular

---

*[1] Presented at the 15th Annual meeting of the Chemical Society of Japan, Kyoto, Apil, 1962.

1) Y. Sakakibara, This Bulletin, 37, 1262 (1964).

*[2] Both materials are isomeric and are equilibrated over catalysts at 250 to 300°C.

2) K. U. Ingold and F. J. Stubbs, *J. Chem. Soc.*, **1951**, 1749.

rearrangement reactions. At higher temperatures, however, it is quite possible that a radical mechanism may predominate. Szwarc,[3] who used higher temperatures (680∼870°C), lower pressures (2∼15 mmHg), and very low conversions (0.01∼2%), found that allene, methane, ethylene, and hydrogen were the main products; he suggested a free-radical chain mechanism for the primary decomposition reaction. Another radical mechanism was proposed by Laidler and Wojciechowski,[4] who reinvestigated the pyrolysis under conditions similar to those used by Ingold and Stubbs and found a considerable amount of higher hydrocarbons but did not detect any allene. The mechanism was partly different from the Szwarc mechanism; namely, a step in the Szwarc method, $CH_2{=}CH{-}CH_2\cdot \rightarrow CH_2{=}C{=}CH_2 + H$, was replaced by the reaction, $CH_2{=}CH{-}CH_3 + CH_2{=}CH{-}CH_2\cdot \rightarrow$ higher hydrocarbons + H.

In the present investigation, an effort was made to clarify the mechanism for the pyrolysis at higher temperatures (800∼1400°C). Special attention was given to the development of mechanisms for the formation of allene and methylacetylene and for their subsequent decomposition, mechanisms by which we can account for the experimental results. In order to obtain information about secondary reactions involving allene, the pyrolysis of allene itself also was investigated under conditions similar to those of propylene.

Experimental

The Pyrolysis of Propylene. — A large number of experimental results have already been described.[1] The present additional experiments were carried out similarly.

The Pyrolysis of Allene. — The experimental methods were the same as those for propylene.

Allene was prepared by the debromination of 2,3-dibromopropene with zinc.[5] The crude allene was passed through two wash bottles, containing a 10% sodium hydroxide solution and a 3 M silver nitrate solution, and a cooled trap at −20°C, and was then condensed in an ethanol-dry ice trap. It was distilled roughly and stored over a saturated sodium chloride solution in a 25 l. gas holder. Gas chromatographic analysis showed that the purity was about 93 mol. %, the remainder being almost all propylene.

Results and Discussion

The Pyrolysis Products of Propylene. — The primary gaseous products were determined by extrapolating the products to zero conversion (the zero conversion method). With low conversion data obtained at 1100°C and 80 mmHg pressure, the extrapolation was easily treated (Fig. 1). From the figure it may be concluded that hydrogen, methane, ethylene, allene, and 1-butene are the primary products, and that methylacetylene, acetylene, and butadiene are the secondary products. Of the primary products, allene and 1-butene, which are less stable to heat than the original material, would undergo considerable subsequent decomposition, even at low conversion levels, to produce such secondary products as methylacetylene and butadiene respectively.

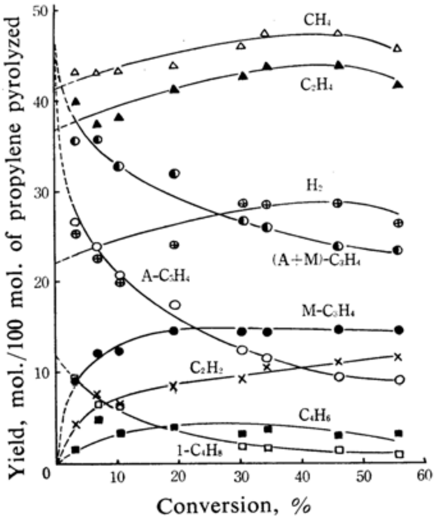


Fig. 1. Extrapolation of gaseous products from propylene to zero conversion (1100°C): A-C_3H_4, allene; M-C_3H_4, methylacetylene.

The formation of acetylene appears to be due to the decomposition of methylacetylene rather than to that of ethylene and methane, particularly at low conversion levels, in view of the results of the pyrolysis of allene described below. The effects of temperature (800∼1400°C) and pressure (40∼160 mmHg) on the product yield are shown in Tables I and II respectively.

Some higher hydrocarbons (C_5 and higher) and carbonaceous matter appeared to be formed, though they were not identified. Their amounts formed under the present conditions had previously been[1] estimated on the basis of the deficiencies of the percentage of hydrogen and carbon accounted for in the gaseous products (Table I). Laidler and Wojciechowski[4] obtained such liquid products as benzene, cyclopentadiene, cyclohexadiene, etc.

The Pyrolysis of Allene.—The data of the

---

[3] M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949).

[4] K. J. Laidler and B. W. Wojciechowski, *Proc. Roy. Soc.*, **A259**, 257 (1960).

[5] A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **78**, 109 (1956).

TABLE I. EFFECT OF TEMPERATURE ON YIELD OF PRODUCTS FROM PROPYLENE PYROLYSIS
Composition of reactant gas, propylene 80%+nitrogen 20%; pressure, 100 mmHg

Run No.	97	95	92	31	36	70	73
Temp., °C	800	900	1000	1100	1200	1300	1400
Contact time, 10^{-3} sec.	1100	92	11	2.5	1.4	0.83	0.46
Conversion, %	10.7	11.2	13.1	10.3	10.4	11.4	8.8
Yield, mol./100 mol. of propylene pyrolyzed							
Hydrogen	15.6	16.4	17.8	20.0	24.9	22.3	26.3
Methane	48.5	45.4	42.1	43.3	41.2	41.5	40.5
Ethylene	48.5	43.9	38.8	38.1	39.2	39.8	37.4
Acetylene	3.6	5.6	6.5	6.5	7.4	8.7	10.7
Allene	6.0	14.0	19.4	20.5	22.2	21.9	21.7
Methylacetylene	4.7	10.9	12.8	12.3	13.5	14.8	15.0
1-Butene	5.6	5.5	5.1	6.1	5.0	5.1	4.6
Butadiene	8.4	5.7	4.0	3.3	3.3	3.1	2.8
Total yield of allene and methylacetylene	10.7	24.9	32.2	32.8	35.7	36.7	36.7
Percentage of hydrogen and carbon accounted for in gaseous products through C_4 hydrocarbons							
Hydrogen	93.7	96.5	94.3	96.4	98.1	98.9	97.7
Carbon	79.9	88.0	88.6	89.5	91.6	93.8	92.1

TABLE II. EFFECT OF PRESSURE ON YIELD OF PRODUCTS FROM PROPYLENE PYROLYSIS
Composition of reactant gas, propylene 80%+nitrogen 20%; temp., 1200°C

Run No.	87	89	36	38	80	84
Press., mmHg	50	50	100	100	200	200
Contact time, 10^{-3} sec.	1.1	2.2	1.4	2.7	2.6	4.4
Conversion, %	9.0	31.2	10.4	39.0	8.4	31.8
Yield, mol./100 mol. of propylene pyrolyzed						
Hydrogen	21.0	24.5	24.9	29.6	23.4	28.3
Methane	39.6	40.2	41.2	44.1	44.5	46.4
Ethylene	39.1	38.2	39.2	40.9	43.0	44.0
Acetylene	6.9	10.6	7.4	10.6	9.0	9.7
Allene	26.1	18.7	22.2	13.3	20.1	11.2
Methylacetylene	13.5	17.0	13.5	15.5	14.3	13.2
1-Butene	6.7	2.6	5.0	1.6	5.0	2.5
Butadiene	3.0	3.5	3.3	3.2	3.9	3.5
Total yield of allene and methylacetylene	39.6	35.7	35.7	28.8	34.4	24.4
Percentage of hydrogen and carbon accounted for in gaseous products through C_4 hydrocarbons						
Hydrogen	100.1	94.7	98.1	94.6	102.6	96.0
Carbon	96.4	89.8	91.6	84.2	95.8	83.7

pyrolysis of allene,[*3] particularly at high temperatures and low pressures, were necessary for clarifying the mechanisms for the secondary reactions involving allene, in the pyrolysis of propylene. The results of the pyrolysis at temperatures of 800 to 1200°C and at a pressure of about 80 mmHg are shown in Table III. Allene was much less stable than propylene, as is shown by the relative stability of propylene and allene (Table V). At high temperatures, the isomerization to methylacetylene occurred predominantly, though lower temperatures favor polymerization rather than isomerization or decomposition (see footnote *3). Methylacetylene was a main gaseous product; much smaller amounts of hydrogen, methane, ethylene, and acetylene were found, together with a trace of C_4 hydrocarbons. At 800°C, the isomerization of allene

---

[*3] Although a few investigations have been reported, none of them was applied to the conditions under which the pyrolysis of propylene was studied by the present author. Cf. R. N. Meinert and C. D. Hurd, *J. Am. Chem. Soc.*, 52, 4540 (1930); A. T. Blomquist and J. A. Verdol, ibid., 78, 109 (1956).

TABLE III. PYROLYSIS OF ALLENE AT VARIOUS TEMPERATURES*

Pressure, 100 mmHg

Run No.	7	5	8	9	2	13	14	10	11	17	16	19	18
Temp., °C	800	800	800	800	800	1000	1000	1000	1000	1200	1200	1200	1200
Contact time, 10^{-3} sec.	88	120	200	320	930	3.3	4.4	8.0	16	0.40	0.53	0.81	1.3
Composition of reactant gas, vol. %													
Nitrogen	19.5	20.9	19.6	19.6	19.9	19.9	19.1	19.7	19.7	20.5	20.5	20.5	20.5
Allene	74.0	74.3	73.9	73.9	75.5	73.5	74.4	73.8	73.8	74.0	74.0	74.0	74.0
Propylene	6.5	4.8	6.5	6.5	4.6	6.6	6.5	6.5	6.5	5.5	5.5	5.5	5.5
Composition of pyrolyzed gas, vol. %													
Nitrogen	20.1	23.2	22.5	22.9	23.4	20.2	19.6	20.4	21.1	20.6	20.8	20.8	20.5
Hydrogen	0.4	1.6	4.8	6.3	13.1	0.2	0.7	1.8	4.9	0.3	1.1	3.7	6.3
Methane	0.3	1.7	6.4	9.1	20.4	0.2	0.6	2.0	6.6	0.2	0.8	3.8	6.6
Ethylene	1.0	2.4	4.5	5.5	8.0	0.4	0.7	1.5	2.8	0.4	0.6	1.3	2.0
Acetylene	0.1	0.7	2.6	3.9	8.1	0.1	0.3	1.3	4.7	0.1	0.6	3.6	6.9
Propylene	7.2	6.0	7.6	7.6	3.4	6.9	7.1	6.5	5.7	5.5	5.4	4.6	3.7
Allene	61.7	45.0	21.3	14.4	2.6	64.5	54.6	33.7	15.7	63.3	47.7	24.1	16.0
Methylacetylene	6.9	14.4	20.9	20.3	7.1	7.3	15.7	28.1	30.0	9.3	22.2	35.3	31.1
1-Butene (+Isobutene)	0.0	0.2	0.4	0.4	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Butadiene (+2-Butene)	0.0	0.0	0.3	0.3	0.4	0.0	0.0	0.1	0.4	0.0	0.0	0.3	0.6
Volume ratio of methylacetylene/allene	0.11	0.32	0.98	1.41	2.73	0.11	0.29	0.84	1.91	0.15	0.47	1.47	1.94
Rate of expansion	0.970	0.903	0.871	0.856	0.851	0.984	0.975	0.970	0.935	0.996	0.989	0.985	1.002
Conversion, %	19.1	45.4	75.0	83.4	97.1	13.7	28.4	55.9	80.2	14.5	36.4	68.0	78.2
Yield, mol./100 mol. of allene pyrolyzed													
Hydrogen	2.6	4.3	7.5	8.8	15.2	2.0	3.0	4.3	7.7	2.7	4.1	7.3	10.9
Methane	2.2	4.5	10.1	12.7	23.7	1.9	2.6	4.8	10.4	1.9	3.1	7.5	11.4
Ethylene	7.2	6.4	7.1	7.6	9.3	3.5	3.3	3.5	4.5	3.3	2.4	2.6	3.4
Acetylene	1.0	1.9	4.1	5.4	9.4	0.6	1.5	3.0	7.5	1.0	2.3	7.0	11.9
Propylene**	3.2	1.8	0.2	0.0	(−2.3)	2.0	1.9	(−0.5)	(−2.0)	0.0	(−0.7)	(−2.0)	(−3.1)
Methylacetylene	47.1	38.4	32.9	28.2	8.3	71.5	72.4	66.2	47.3	86.6	81.6	69.0	53.8
1-Butene (+Isobutene)	0.0	0.5	0.6	0.6	0.1	0.0	0.0	0.3	0.1	0.0	0.0	0.0	0.0
Butadiene (+2-Butene)	0.0	0.0	0.4	0.4	0.4	0.0	0.0	0.2	0.6	0.0	0.0	0.5	1.0
Percentage of hydrogen and carbon accounted for in gaseous products through C_4 hydrocarbons													
Hydrogen	63.1	56.1	58.0	57.4	52.6	81.2	83.4	78.5	68.9	93.7	89.5	84.5	78.0
Carbon	56.5	47.9	45.3	42.4	28.6	76.9	78.4	72.5	58.6	90.1	85.3	77.0	67.1

* Furnace I was used for Run Nos. 2—9 and furnace II for the others (See Ref. 1).

** The values were calculated in taking account of the amount of propylene contained in the reactant gas. The minus values shown in parentheses mean that propylene was pyrolyzed in the ratio of these values to 100 mol. of allene pyrolyzed.

to methylacetylene was incomplete. Judging from the low percentages of hydrogen and carbon accounted for in the gaseous products, considerable amounts of polymerized products appeared to be formed. On the other hand, at 1200°C and low conversion levels, other reactions than isomerization were considerably suppressed and the isomerization was performed efficiently. With increasing contact time (conversion), the yields of methylacetylene decreased rapidly. The methylacetylene/allene ratio, however, slowly approached the value of a theoretically calculated equilibrium constant for the allene $\rightleftarrows$ methylacetylene isomerization as was to be expected from the equilibrium relation (Table IV).

TABLE IV. EQUILIBRIUM CONSTANT FOR THE ISOMERIZATION OF ALLENE*
($CH_2=C=CH_2 \rightleftarrows CH_3-C\equiv CH$)

Temp., °K	800	1000	1200	1400	1500
$K_p=\frac{[CH_3-C\equiv CH]}{[CH_2=C=CH_2]}$	4.53	3.75	3.15	2.94	2.77

* The values were calculated on the basis of the $\Delta G°/T$ given in "Landolt-Börnstein Zahlenwerte und Funktionen" (6 Aufl. II Bd. 4 Teil, 453 (1961)); see also J. F. Cordes and H. Günzler, *Chem. Ber.*, **92**, 1055 (1959).

The main gaseous products other than methylacetylene, though they were found in much smaller quantities than those of methylacetylene, varied remarkably with the temperature and the rate of conversion. Figures 2 and 3 show the distribution of main gaseous products, exclusive of methylacetylene, and the methylacetylene/allene ratio at 800 and 1200°C. The conversion and yield described in these figures were those calculated by regarding both allene and its isomerization product, methylacetylene, as unreacted allene. The results of the zero conversion method suggest that ethylene is the primary product (Figs. 2 and 3).

This is supported also by the fact that, at both 800 and 1200°C, the yield of ethylene decreased with the increase in the methylacetylene/allene ratio which resulted from the isomerization of allene. Furthermore, it is reasonable that the decrease was rapid in the case of 1200°C, at which temperature the ratio increased rapidly with the increasing conversion. Hydrogen also appears to be a primary product. On the other hand, methane and acetylene are the secondary products, as determined by the zero conversion method. In the case of 1200°C, it should be noted that the yields of methane and acetylene were about the same, and that they increased rapidly with the increase in the methylacetylene/allene ratio. From these facts, it may be concluded that methane and acetylene are the decomposition products of methylacetylene, which is itself the isomerization product of allene.

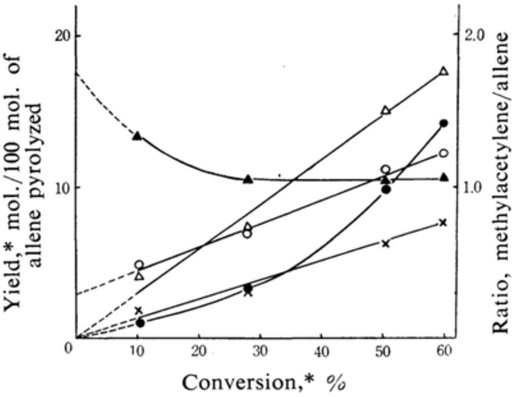


Fig. 2. Yields of main gaseous products (exclusive of methylacetylene) from allene pyrolysis at 800°C: ○, hydrogen; △, methane; ×, acetylene; ▲, ethylene; ●, methylacetylene/allene ratio.

* These values were calculated by regarding both allene and its isomerization product, methylacetylene, as unreacted allene.

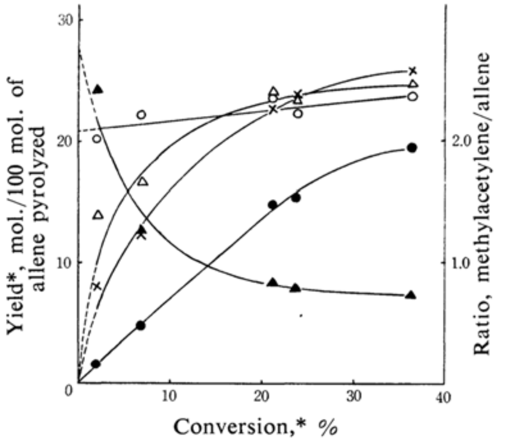


Fig. 3. Yields of main gaseous products (exclusive of methylacetylene) from allene pyrolysis at 1200°C: ○, hydrogen; △, methane; ×, acetylene; ▲, ethylene; ●, methylacetylene/allene ratio.

* See footnote* to Fig. 2.

Mechanism.—On the basis of the experimental results, a mechanism for the pyrolysis of propylene may be proposed. This mechanism may be developed by observing the following restrictions. Even at low conversions, secondary reactions involving such unstable products as allene and methylacetylene are considered to be important and are thus included. However, secondary reactions involving stable

TABLE V. RELATIVE STABILITY OF PROPYLENE AND ALLENE

Temp., °C	800	1000	1200	1200
Conversion, %	20	20	20	40
Contact time,* sec.				
Propylene	2.1	1.3×10^{-2}	1.9×10^{-3}	3.0×10^{-3}
Allene**	8.9×10^{-2} (0.10)	3.7×10^{-3} (8.2×10^{-3})	4.4×10^{-4} (8.1×10^{-4})	5.5×10^{-4} (1.5×10^{-3})
Ratio of contact time, propylene/allene	24 (21)	3.5 (1.6)	4.3 (2.4)	5.5 (2.0)

* Contact times for fixed conversions were obtained from the curves of the contact time vs. the conversion.

** The values shown in parentheses are those of cases in which conversion was calculated by regarding both allene and its isomerization product, methylacetylene, as unreacted allene.

pyrolysis products are disregarded. The order of the decreasing stability of methane and light olefins is as follows: methane>ethylene >propylene>2-butene>1-butene>isobutene.⁶⁾ Judging from the relative stability of propylene and allene, it may be said that allene is much less stable than propylene, especially at the lower temperatures investigated (Table V).

Although higher hydrocarbons (C_5 and higher) formed in the pyrolysis would readily undergo subsequent decomposition, these reactions are disregarded.

With the above restrictions in mind, the following mechanism was developed:

Primary reactions

$$\mathrm{CH_2{=}CH{-}CH_3 \rightarrow CH_2{=}CH{-}CH_2\cdot + H} \tag{1}$$

$$\mathrm{CH_2{=}CH{-}CH_3 + H \rightarrow CH_2{=}CH{-}CH_2\cdot + H_2} \tag{2}$$

$$\mathrm{CH_2{=}CH{-}CH_3 + H \rightarrow CH_3{-}CH_2{-}CH_2{}^{*}\cdot} \tag{3}$$

$$\mathrm{CH_3{-}CH_2{-}CH_2{}^{*}\cdot \rightarrow C_2H_4 + CH_3\cdot} \tag{4}$$

$$\mathrm{CH_2{=}CH{-}CH_3 + CH_3\cdot \rightarrow CH_2{=}CH{-}CH_2\cdot + CH_4} \tag{5}$$

$$\mathrm{CH_2{=}CH{-}CH_3 + CH_2{=}CH{-}CH_2\cdot \rightarrow higher\ hydrocarbons(HHC)\,(A) + H\,(CH_3\cdot)} \tag{6}$$

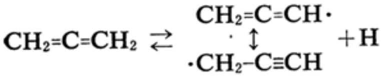
$$\mathrm{CH_2{=}CH{-}CH_2\cdot \rightarrow CH_2{=}C{=}CH_2 + H} \tag{7}$$

$$\mathrm{CH_2{=}CH{-}CH_2\cdot + H \rightarrow CH_2{=}CH{-}CH_3} \tag{8}$$

$$\mathrm{CH_2{=}CH{-}CH_2\cdot + CH_3\cdot \rightarrow CH_2{=}CH{-}CH_2{-}CH_3} \tag{9}$$

Secondary reactions

involving allene and methylacetylene



$$\mathrm{CH_2{=}C{=}CH_2 \rightleftarrows \begin{array}{c} CH_2{=}C{=}CH\cdot \\ \updownarrow \\ \cdot CH_2{-}C{\equiv}CH \end{array} + H \rightleftarrows CH_3{-}C{\equiv}CH} \tag{10}$$

$$\mathrm{CH_2{=}C{=}CH_2 + CH_2{=}CH{-}CH_2\cdot \rightarrow HHC(B) + H} \tag{11}$$

$$\mathrm{CH_2{=}C{=}CH\cdot \leftrightarrow \cdot CH_2{-}C{\equiv}CH + CH_2{=}CH{-}CH_3 \rightarrow HHC(C) + H} \tag{12}$$

$$\mathrm{CH{\equiv}C{-}CH_3 + CH_2{=}CH{-}CH_2\cdot \rightarrow HHC(D) + H} \tag{13}$$

$$\mathrm{CH{\equiv}C{-}CH_3 + H \rightarrow C_2H_2 + CH_3\cdot} \tag{14}$$

involving 1-butene

$$\mathrm{CH_2{=}CH{-}CH_2{-}CH_3 \xrightarrow{(or\ by\ radicals\ R)} CH_2{=}CH{-}\underset{\cdot}{C}H{-}CH_3 + H(RH)} \tag{15}$$

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

(The asterisks indicate a hot radical which decomposes easily into C_2H_4 and $CH_3\cdot$.)

The known frequency factors and activation energies for the elementary reactions 1 to 9 are shown in Table VI. Those shown in parentheses are less certain values assumed by Laidler and Wojciechowski,⁴⁾ and by Amano and Uchiyama.⁷⁾

In this mechanism, part of the primary decomposition reaction (reacitons 1–9) is a

TABLE VI. KINETIC PARAMETERS (AT 1000°K) FOR ELEMENTARY REACTIONS*

Reaction	Frequency factor sec⁻¹ or l./mol. sec.	Activation energy kcal./mol.
(1)	(10^{15})	79
(2)	$10^{10.1}$	1.5
(3)	$10^{10.5}$	1.5
(4)	$10^{13.4}$	30.4
(5)	$10^{7.8}$	7.7
(6)	(10^{6})	(15)
(7)	($10^{13.6}$)	(70)
(8)	(10^{9})	(0)
(9)	(10^{8})	(0)

* For the source of these values, see Ref. 7.

---

6) a) H. Tropsch, C. I. Parrish and G. Egloff, *Ind. Eng. Chem.*, **28**, 581 (1936); b) H. Tropsch and G. Egloff, ibid., **27**, 1063 (1935).

7) A. Amano and M. Uchiyama, *J. Phys. Chem.*, **67**, 1242 (1963).

chain process. Reaction 1 is the chain initiation, reactions 2–6, 2–7, 3–4–5–6, and 3–4–5–7 are four chain propagation processes, and, finally, reactions 8 and 9 are the chain termination. Reactions 10 to 16 are the main secondary reactions, chiefly involving allene and methylacetylene.

The compatibility of the proposed mechanism with the observed experimental data can now be examined.

Products and Processes of Formation.—All the primary gaseous products, hydrogen, ethylene, methane, allene, and 1-butene, are formed by reactions 2, 4, 5, 7, and 9 respectively. Reaction 6, proposed by Laidler and Wojciechowski⁴⁾ for the formation of higher hydrocarbons, is also included in this mechanism, because considerable amounts of higher hydrocarbons appeared to be formed at the lower part of the temperature range investigated. In reaction 6, instead of hydrogen atoms, the splitting of methyl radicals would also be possible in view of the fact that C_5 olefins, such as cyclopentene,⁸⁾ cyclopentadiene,⁴⁾ and pentadiene,⁹⁾ were formed in the early stage of the pyrolysis of propylene or in that of the reaction of allyl radicals with propylene. Reaction 9 is included as a termination reaction in addition to reaction 8, though Szwarc,³⁾ and Laidler and Wojciechowski⁴⁾ adopted only reaction 8. This is a result of the fact that 1-butene was obtained as the primary product and the observation by Dominey and Danby⁹⁾ that the formation of butyl radicals by the addition of methyl radicals to propylene occurred only at temperatures below 400°C. In addition, it has been shown, most recently by Amano and Uchiyama,⁷⁾ that in the reaction $CH_3\cdot + C_3H_6 \rightarrow$ butyl, the equilibrium ratio of [methyl] / [butyl] is 10^3 at 1000°K by calculation from thermodynamic data; therefore, the reverse reaction is faster.

Of secondary reactions, those involving allene and methylacetylene may be presumed to be predominant in view of the relative stability of propylene and allene (Table V). Allene isomerizes to methylacetylene according to reaction 10, and the allene/methylacetylene ratio approaches the equilibrium constant. It has been shown by Collin and Lossing¹⁰⁾ that the loss of a H atom from allene results in the formation of a C_3H_3 radical which has a propagyl rather than an allenyl configuration and that the $CH{\equiv}C{-}CH_2\cdot$ and $\cdot CH{=}C{=}CH_2$ forms are probably resonance hybrids. Furthermore, they have presented the bond dissociation energies of 82.8 kcal./mol. for $CH{\equiv}C{-}CH_2{-}H$ and 81.2 kcal./mol. for $CH_2{=}C{=}CH{-}H$. The formation of higher hydrocarbons from allene and methylacetylene, which would clearly be responsible for the loss of allene—methylacetylene, may be ascribed to the reactions with allyl radicals (reactions 11 and 13) as in the case of propylene and to the reaction of propagyl radicals, produced from allene and methylacetylene, with propylene (reaction 12). Acetylene is probably produced by the reaction of methylacetylene with hydrogen atoms (reaction 14), in view of the experimental data of the pyrolysis of allene (Fig. 2 and 3). Considering the relative stability of ethylene and propylene,⁶ᵃ⁾ another process for the production of acetylene, the dehydrogenation of ethylene, appears to be less important in the early stage of the pyrolysis of propylene. Butadiene is probably produced by the dehydrogenation of 1-(and 2-)butene (reactions 15 and 16).

The Rates of the Formation of Products and Yields. — According to this mechanism, whenever an ethylene molecule is produced by reaction 4 a methyl radical is formed; this radical may give rise to a methane molecule by reaction 5 or, in a lesser degree, a 1-butene molecule by reaction 9. Therefore, the ethylene/(methane + 1-butene) ratio must be 1 : 1. The experimental data seem to confirm this 1 : 1 ratio, considering that some amounts of methane are produced also from the methyl radicals formed by reaction 6 and by secondary reaction 14 (Fig. 1 and Table I).

The hydrogen/ethylene ratio should be independent of the pressure of propylene, since reactions 2 and 3, the latter followed by reaction 4 leading to the formation of ethylene, are the same reaction of propylene with hydrogen atoms. This is consistent with the experimental data (Table II). On the other hand, since the activation energies for both reaction processes are small (both 1.5 kcal./mol.), the hydrogen/ethylene ratio should be nearly independent of the temperature. The experimental data seem to confirm this requirement, and the experimental ratios are in fairly good agreement with the values (about 0.4) calculated from kinetic parameters (Table I).

Inspections were also made of allene and methylacetylene, whose production is an important object of this series of investigations. According to this mechanism, allyl radicals, which give allene by the elimination of a hydrogen atom, are produced by reactions 2

---

8) W. A. Bryce and D. J. Ruzicka, *Can. J. Chem.*, 38, 835 (1960).

9) D. A. Dominey and C. J. Danby, *J. Chem. Soc.*, 1962, 4656.

10) J. Collin and F. P. Lossing, *Can. J. Chem.*, 35, 778 (1957).

and 5, together with reaction 1. The allyl radicals disappear in any one of four reaction processes, 6, 7, 8, and 9. Of these processes, the last two, which are the chain-terminating reactions, are disregarded if the chain is long. In fact, however, it appears to be very short in view of the amount of 1-butene and the chain length estimated by Szwarc.[3)]

First, the rates of the formation of higher hydrocarbons by reaction 6 (v_6) and of allene by reaction 7 (v_7) will be compared. Table VII shows the v_6/v_7 ratio, at various temperatures and at a 80 mmHg pressure, as calculated on the basis of the kinetic parameters shown in Table VI. From the calculated values, it follows that at 900°C the rate of reaction 7 is more rapid than that of reaction 6 and that reaction 6 may be practically disregarded above 1000°C.

TABLE VII. RATIO OF THE RATES OF REACTIONS 6 AND 7

$$\frac{v_6}{v_7}=\frac{k_6}{k_7}[C_3H_6]=10^{-7.6}e^{-\frac{55000}{RT}}\times\frac{1.28}{T}$$

Temp., °C	800	900	1000	1100
v_6/v_7	5.0	0.40	0.062	0.013

Next, assuming that the chain reaction is terminated only by reaction 9, it can be shown via the steady-state approximation method, that the yield (in moles per 100 mol. of propylene pyrolyzed) of allene is calculated by the following equation:

Yield of allene

$$=\frac{L(1+C_1)}{(L+1)(2+C_1)(1+C_2)+LC_2(1+C_1)}\times 100$$

where L=chain length
C_1=ratio of rates of reactions 2 and 3, v_2/v_3
C_2=ratio of rates of reactions 6 and 7, v_6/v_7

Figure 4 compares the experimental yields of allene-methylacetylene (in 9∼13% conversion) and the calculated yields of allene at various temperatures. The calculated values are those obtained by assuming that $L=5$, $C_1=0.50$, and $C_2=$ the values shown in Table VII. The results of the calculation (calculated yields I) show that the temperature has a remarkable effect on the yield of allene, as was observed in the experiments (Table I), and that high temperatures are suitable for the production of allene. Furthermore, considering that the values of kinetic parameters for elementary reactions 6 and 7 are uncertain and that allene undergoes secondary reactions readily, the experimental yields are in fair agreement with the calculated ones. The experimental yields however, can reasonably be accounted for on the basis of the yields of allene calculated by assuming $E_7-E_6=50$ kcal./mol., which is lower by 5 kcal./mol. than the value estimated by Laidler-Wojciechowski.[4)] The second calculated yields (calculated yields II) are shown in Fig. 4 to be comparable with the experimental yields of allene-methylacetylene. The experimental values are considerably lower than the calculated ones. This may be supposed to be due to the loss of allene-methylacetylene by secondary reactions, probably by reactions 10 to 14, which proceed considerably even at low conversion levels. Furthermore, judging from the fact that the stability of allene-methylacetylene approaches that of propylene fairly rapidly with the increase in the temperature (Table V), it may be concluded that the degree of the loss by secondary reactions decreases with the increasing temperature and that, therefore, at high temperatures, for example, at 1100°C, allene-methylacetylene is obtained in yields comparatively close to the calculated yields.

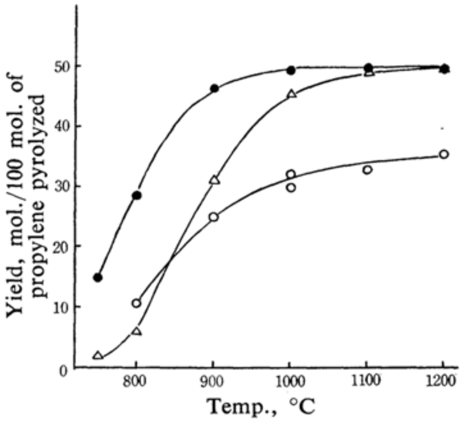


Fig. 4. A comparison of the experimental yields of allene-methylacetylene and the calculated yields of allene: ○, experimental yields; △, calculated yields I; ●, calculated yields II.

The rapid decrease in the yield of allene-methylacetylene with the increase in conversion may be supposed to be due to the loss of allene, methylacetylene, and propylene, probably by various secondary reactions involving reactions 10 to 14. The variation in the methylacetylene/allene ratio with conversion can be accounted for by the equilibrium relation between the two. Namely, the experimental ratio (1.6 at 56% conversion) approached the calculated equilibrium constant (3.0 at 1100°C) with the increasing conversion (Fig. 1).

The decrease in the pressure of propylene suppresses secondary reactions 11 to 14, by which means allene, methylacetylene, and propylene are lost; moreover, reaction 6 leads to the formation of higher hydrocarbons. Therefore, it may be expected that low pressures give better yields of allene-methylacetylene. The experimental data seem to confirm this (Table II).

Summary

A study has been made of the mechanism of the pyrolysis of propylene at high temperatures (800~1400°C). Of the gaseous products, hydrogen, methane, ethylene, allene, and 1-butene, obtained in the yields of 25, 43, 40, 27, and 9 mol. per 100 mol. of propylene pyrolyzed (3% conversion) respectively, have been found to be the primary products, while methylacetylene, acetylene, and butadiene, obtained in the yields of 9, 4, and 2 mol. respectively, have been found to be the secondary products. In view of the results of the pyrolysis of allene itself, even at a low conversion of 3%, allene appears to undergo considerable secondary reactions, such as isomerization to methylacetylene, addition to propylene and allyl radicals, and decomposition, for example, to acetylene and methane via methylacetylene. On the basis of the observed results, free-radical mechanisms have been proposed for the primary reactions and main secondary reactions. The mechanism for the primary decomposition reaction is a chain process in which the chain is initiated by the reaction $C_3H_6 \to C_3H_5\cdot$ (allyl radical) + H, and is, via the chain-propagating step, terminated by two types of reactions, $C_3H_5\cdot + H \to C_3H_6$ and $C_3H_5\cdot + CH_3\cdot \to 1\text{-}C_4H_8$. The formation of allene-methylacetylene has been satisfactorily explained by considering secondary reactions.

The author wishes to express his thanks to Professor Sango Kunichika of Kyoto University for his helpful advice and kind encouragement throughout this work.

Institute for Chemical Research
Kyoto University
Daigaku-cho, Takatsuki