*The Synthesis of Methylacetylene by the Pyrolysis of Propylene. I. The Effect of Pyrolysis Conditions on Product Yields**

By Yasumasa SAKAKIBARA

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Methylacetylene would be a valuable material in the field of synthetic chemistry. For example, it is known that methylacetylene is carbonylated with carbon monoxide to give methacrylate,[1] just as acetylene gives acrylate. Although various methods have been reported for the synthesis of methylacetylene, however, there is no economically attractive one. The present author was interested in obtaining methylacetylene by the pyrolysis of light hydrocarbons, especially by the direct dehydrogenation of propylene.

Rice et al.[2] were the first to report the synthesis of methylacetylene and allene, both being isomeric and equilibrated thermo-catalytically,[3] by the pyrolysis of isobutylene. In many investigations[4-14] of the pyrolysis of propylene, methylacetylene has not been detected in the products, while Szwarc[15] alone has found allene as a main product. He pyrolyzed propylene at temperatures ranging from 680 to 870°C and at pressures from 2 to 15 mmHg; there was a low conversion of 0.01 to 2 per cent. Recently, in the course of this study, it has been announced (U. S. Pat.[16]) that allene and methylacetylene were produced by contacting propylene with a metal filament heated over 900°C, at low pressure and with a short contact time. The purpose of the present investigation is to determine suitable conditions for the production of methylacetylene and allene by the pyrolysis of propylene and to obtain data on the distribution of the pyrolysis products.

Experimental

Materials.—Propylene was prepared by the vapor phase dehydration of isopropyl alcohol, using activated clay as a catalyst. After it had been washed with about a 15% solution of sodium hydroxide, it was stored in a 25 l. water-gas holder. Gas chromatographic analysis showed that the purity was better than 99.0 mol. % and that the principal impurities were hydrogen, methane, ethylene, and propane. Cylinder nitrogen of 99.9 mol.% purity was used as a reference gas, a known amount (about one-fourth of the propylene volume) being added to the propylene. The change in the volume (rate of expansion) of the reactant gas upon pyrolysis was calculated from the change in the concentration (mol.%) of the nitrogen.

Apparatus and Procedure. — The apparatus is shown in Fig. 1. The reactant gas, consisting of about 80 vol.% propylene and 20 vol.% nitrogen, was introduced into a silica (or porcelain) reaction tube from the gas holder through a water bubbler, a drying tower containing calcium chloride, and a needle valve. The gas pressure in the gas holder was always kept at atmospheric pressure by allowing water to run into it. To carry out experiments over a wide temperature range, various silica reaction tubes, from 2.9 to 11.0 mm. in inside diameter, and two different types of electric furnaces, one 30 cm. long (furnace I) and the other 10 cm. long (furnace II), were employed. Furnace II, having been constructed from a spiral "Siliconit" heating element,* was used mainly for heating to 1100°C and above. The reaction tube was suspended in the center of another silica tube, which extended through the furnace. The exhausted gas from the reaction tube was rapidly cooled with running water at the exit of the tube; it then passed through a trap immersed in ice-water to remove any liquid products and then through a 300-ml. glass gas-sampling flask, which was attached to a

* Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

1) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York (1949), p. 299.

2) F. O. Rice and W. S. Haynes, *J. Am. Chem. Soc.*, **70**, 964 (1948); F. O. Rice and L. A. Wall, ibid., **72**, 3967 (1950).

3) J. F. Cordes and H. Günzler, *Chem. Ber.*, **92**, 1055 (1959); *Z. Naturforsch.*, **15b**, 682 (1960); German Pat. 1093350 (1960).

4) E. F. Frey and D. F. Smith, *Ind. Eng. Chem.*, **20**, 948 (1928).

5) R. H. Wheeler and W. L. Wood, *J. Chem. Soc.*, **1930**, 1819.

6) C. D. Hurd and R. N. Meinert, *J. Am. Chem. Soc.*, **52**, 4978 (1930).

7) V. Schneider and P. K. Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).

8) C. D. Hurd and L. K. Eilers, ibid., **26**, 776 (1934).

9) H. Tropsch, C. I. Parrish and G. Egloff, ibid., **28**, 581 (1936).

10) V. G. Moor, N. V. Strigaleva and A. V. Frost, *J. Gen. Chem. U. S. S. R.*, **7**, 860 (1937); *Chem. Abstr.*, **31**, 5662 (1937).

11) H. D. Burnham and R. N. Pease, *J. Am. Chem. Soc.*, **64**, 1404 (1942).

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

13) R. E. Kinney and D. J. Crowley, *Ind. Eng. Chem.*, **46**, 258 (1954).

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

15) M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949).

16) M. J. Hogsed, U. S. Pat. 2925451 (1960).

* Manufactured by the Siliconit Kōnetsu Kōgyo Co., Ltd.

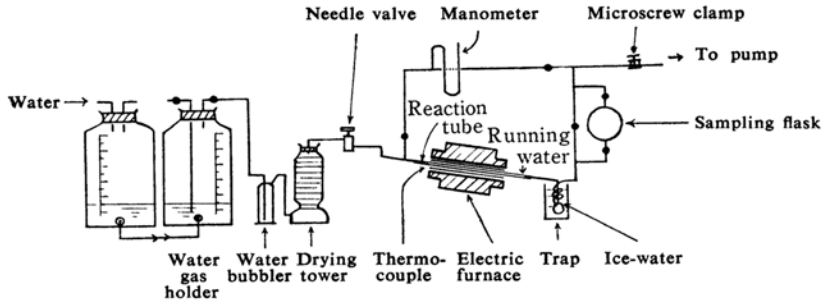

Fig. 1. Apparatus for pyrolysis.

bypass. The gas leaving the flask passed through a microscrew clamp and was continuously pumped out by an oil pump. The reactant-gas feed and the pressure, measured at the entrance of the reaction tube and at the exit of the sampling flask, were regulated to the desired grades by means of the needle valve before the reaction tube and the microscrew clamp.

The temperature was measured by a Pt-Pt·Rh thermocouple tied to the external wall of the reaction tube. The total volume of the reaction tube was measured, and a section, 20 cm. long in furnace I and 7 cm. long in furnace II, was assumed to be heated to the recorded temperature. The volume of the reaction zone, calculated on the basis of the above assumption, was used in the calculation of the contact time by means of the formula:

$$\text{Contact time (sec.)} = V_R/F$$

where V_R = the volume of the reaction zone (ml.)
F = the flow rate of the reactant gas corrected to the temperature and pressure of the reaction zone (ml./sec.)

The pyrolysis was performed under conditions varying over the following wide range: temperature, 800~1400°C; contact time, 4.4×10^{-4}~2.3 sec.; pressure, 50~200 mmHg (partial pressure of propylene, about 40~160 mmHg).

Analysis.—All hydrocarbon products through C_4 were analyzed, using mainly an 11.0-wt.% β,β'-oxydipropionitrile on silica gel column (1.0 or 2.4 m.) at 60°C and a 30-wt.% dioctyl phthalate column (2.4 m.) at room temperature and with hydrogen as the carrier gas. Although the β,β'-oxydipropionitrile-modified silica gel column was found by the present author to give a good separation of air and most of hydrocarbons through C_4 at temperatures below 70°C, the dioctyl phthalate column appeared to be more suitable for the rapid analysis of small quantities of methylacetylene and allene in the pyrolyzed gas. In practice, the latter column was used for the analysis of allene, methylacetylene, the isobutene-1-butene pair, and the 2-butenes-butadiene pair. For the sake of convenience, the overlapped peaks of isobutene-1-butene and 2-butenes-butadiene were adopted as those of 1-butene and butadiene respectively, because in most cases, the amounts of isobutene and 2-butenes formed were negligible (particularly of the former) or, at most, slight. For the quantitative analysis, relative gas volume response factors which had been measured for a series of hydrocarbons for hydrogen were used. The factors (per unit chromatographic peak area, propylene=1.00) used for methylacetylene and allene were 1.07 and 1.10 respectively. Hydrogen was analyzed using the above β,β'-oxydipropionitrile-modified silica gel column and using nitrogen as the carrier gas. In a gas-sampling procedure for gas chromatography, the gas sample of reduced pressure in the sampling flask was introduced into one to five milliliters glass sample tubes using a vacuum system.

In several cases, acetylenic hydrogen of methylacetylene and acetylene was determined chemically by a concentrated silver nitrate solution.[17] The results were in full accord with those of gas chromatography.

Results and Discussion

The conversion of propylene (per cent of propylene pyrolyzed) and the yield of each product (moles per 100 mol. of propylene pyrolyzed) to be given below were obtained by the formulas:

$$\text{Conversion} = \{(a-b\cdot f)/a\}\times 100$$

$$\text{Yield} = \{p\cdot f/(a-b\cdot f)\}\times 100$$

where a, the volume percentage of propylene in the reactant gas; b, the volume percentage of propylene in the pyrolyzed gas; f, the rate of the expansion of the reactant gas by pyrolysis; the ratio of the volume percentage of nitrogen before to that after pyrolysis; and p, the volume percentage of the product.

In the composition of the pyrolyzed gas, the volume percentage was calculated on the basis of gases from hydrogen through C_4 hydrocarbons, though C_5 and higher hydrocarbons were present to a slight degree. Such treatment is possible without distorting the conversion and yield, because they are determined only on the basis of the ratio of each component to nitrogen. Furthermore, since methylacetylene and allene are equilibrated rapidly over catalysts,[3] the total yield was used to evaluate conditions for the synthesis of methylacetylene. In order to examine the hydrogen and carbon balance,

17) L. Barnes, Jr. and L. J. Molinini, *Anal. Chem.*, 27, 1025 (1955).

TABLE I. PYROLYSIS OF PROPYLENE AT VARIOUS TEMPERATURES

	Pressure, 100 mmHg								
Run No.	17*	97*	95*	22	92*	31	36	70	73
Temp., °C	800	800	900	1000	1000	1100	1200	1300	1400
Contact time, 10^{-3} sec.	1100	1100	92	9.4	11	2.5	1.4	0.83	0.46
Nitrogen content in reactant gas, vol. %	19.9	20.6	20.2	22.4	20.0	20.2	20.2	20.0	20.0
Composition of pyrolyzed gas, vol. %									
Nitrogen	19.2	19.9	19.4	21.6	19.1	19.4	19.3	19.0	19.2
Hydrogen	1.3	1.3	1.4	1.2	1.8	1.6	2.0	1.9	1.8
Methane	4.0	4.0	3.9	3.1	4.2	3.4	3.3	3.6	2.7
Ethylene	3.9	3.9	3.7	2.8	3.9	3.0	3.1	3.4	2.5
Acetylene	0.3	0.3	0.5	0.4	0.7	0.5	0.6	0.8	0.7
Propylene	69.5	68.5	68.0	67.9	66.2	68.7	68.3	67.4	70.1
Allene	0.4	0.5	1.2	1.3	1.9	1.6	1.8	1.9	1.5
Methylacetylene	0.4	0.4	0.9	0.8	1.3	1.0	1.1	1.3	1.0
1-Butene	0.3	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.3
Butadiene	0.7	0.7	0.5	0.4	0.4	0.3	0.3	0.3	0.2
Rate of expansion	1.039	1.034	1.041	1.039	1.049	1.042	1.047	1.051	1.040
Conversion, %	9.9	10.7	11.2	9.1	13.1	10.3	10.4	11.4	8.8
Yield, mol./100 mol. of propylene pyrolyzed									
Hydrogen	17.1	15.6	16.4	18.0	17.8	20.0	24.9	22.3	26.3
Methane	52.8	48.5	45.4	46.0	42.1	43.3	41.2	41.5	40.5
Ethylene	51.3	48.0	43.9	40.7	38.8	38.1	39.2	39.8	37.4
Acetylene	3.3	3.6	5.6	6.3	6.5	6.5	7.4	8.7	10.7
Allene	5.8	6.0	14.0	18.3	19.4	20.5	22.2	21.9	21.7
Methylacetylene	4.7	4.7	10.9	11.6	12.8	12.3	13.5	14.8	15.0
1-Butene	4.6	5.6	5.5	7.0	5.1	6.1	5.0	5.1	4.6
Butadiene	8.6	8.4	5.7	5.7	4.0	3.3	3.3	3.1	2.8
Total yield of methylacetylene and allene	10.5	10.7	24.9	29.9	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	97.9	93.7	96.5	100.9	94.3	96.4	98.1	98.9	97.7
Carbon	82.1	79.9	88.0	93.5	88.6	89.5	91.6	93.8	92.1

* Furnace I was used.

the percentages of hydrogen and carbon accounted for in gaseous products through C_4 hydrocarbons were calculated from their yields.

Concerning pyrolysis products, no ethane was detected in any experiment, except in those at 200 mmHg pressure, in which a trace of ethane was found. Propane was disregarded, because the reactant gas was contaminated with a small amount (0.4%) of propane and its amount decreased with increasing conversion until it showed only a trace at conversion levels above about 20%. Also, the total of butadiene and 2-butenes, the latter being much smaller than the former, was given as butadiene, as was described in the analytical procedure section.

The Effect of Temperature on Product Yields. —The results obtained in the conversion range from 8 to 14% are shown in Table I 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 in the range investigated, from 800 to 1400°C; the total yield [(M+A)-C_3H_4] ranged from 10 mol. at 800°C up to 37 mol. at 1300°C. Although the total yield increased rapidly in the lower part of the temperature range, it was almost constant (36 to 37 mol.) at high temperatures, ranging from 1200 to 1400°C. Thus, a high temperature of 1200 to 1300°C was found to be suitable for the synthesis.

The main products through C_4 hydrocarbons, except for methylacetylene and allene, were methane, ethylene, hydrogen, acetylene, 1-butene, and butadiene. The approximate decreasing order of yield is as just listed. The yields of methane and ethylene, formed in the ratio of about 1 to 1, decreased with an increase in the temperature from about 50 mol. to 40 mol. Contrarily, the yields of hydrogen and acetylene increased regularly with an increase in the temperature, reaching 26 mol. and

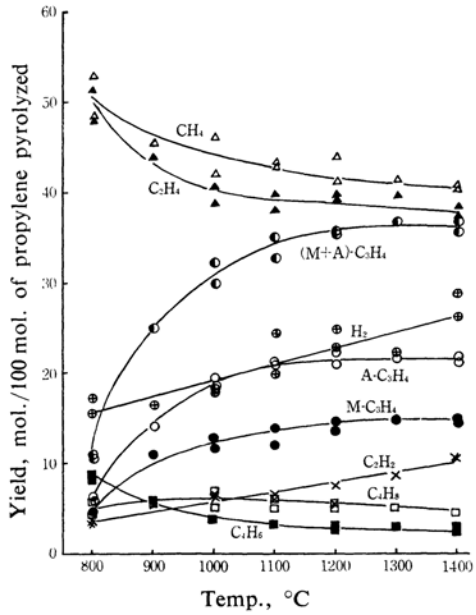

Fig. 2. Effect of temperature on product yields. Conversion, 9 to 14%

10 mol. respectively at 1400°C. The amount of 1-butene was nearly constant at about 5 mol., while that of butadiene fell from 8 mol. at 800°C to 3 mol. at 1400°C.

Some amounts of higher hydrocarbons (C_5 and higher) and coke appeared to be formed. In Table I, the deficiencies of the hydrogen and carbon accounted for in the gaseous products (in hydrogen and in hydrocarbons through C_4) must be explained in terms of the formation of higher hydrocarbons, and of them and coke respectively, when these deficiencies are not due to experimental error. Thus, the

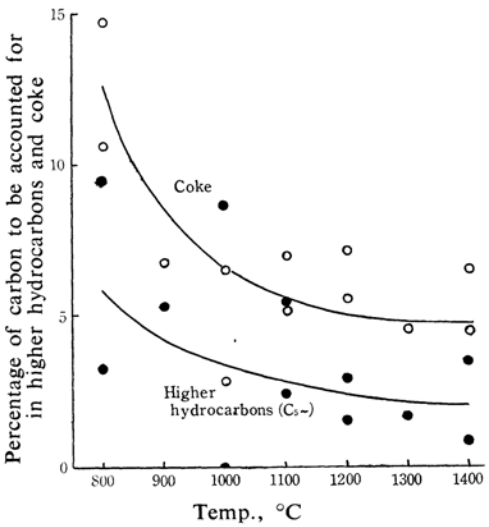

Fig. 3. Estimated amounts of higher hydrocarbons and coke.

percentage of carbon to be accounted for in the higher hydrocarbons and coke (Fig. 3) was derived from the deficiencies of the hydrogen and carbon, on the assumption of an average ratio of carbon to hydrogen of 3:4 in the higher hydrocarbons (probably olefins, cycloolefins, aromatics etc.[14]) formed. On the whole, the estimated amounts (in percentages of carbon) of both higher hydrocarbons and coke, though a part of their values are scattered, fall at a considerable rate with an increase in the temperature.

The Effect of Contact Time (Conversion) on Yields. — The results of the pyrolysis at 100 mmHg pressure and 1200°C, which was a suitable temperature for the synthesis, are shown in Table II (Run No. 36—52) and Fig. 4. The

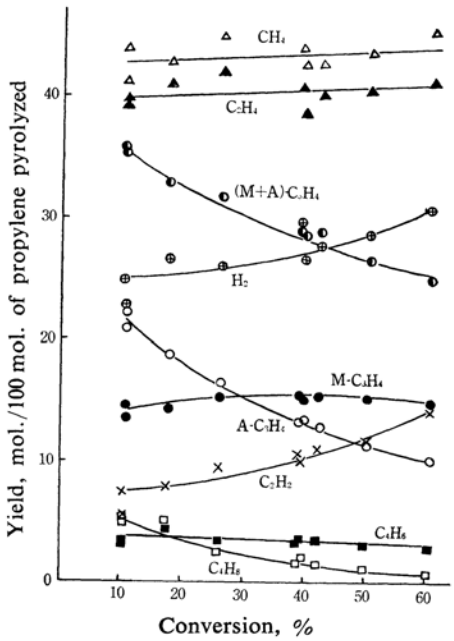

Fig. 4. Effect of contact time (conversion) on product yields. Temp., 1200°C

total yield of methylacetylene and allene decreased with the increasing conversion, ranging from 36 mol. at 10% conversion down to 25 mol. at 60% conversion. In this connection, the yield of allene fell at a considerable rate as the conversion was increased, while that of methylacetylene was fairly constant at 13 to 15 mol. over the wide conversion range studied. Thus, taking account of an equilibrium relation between methylacetylene and allene, it seems probable that methylacetylene is not a primary but a secondary product of the isomerization of allene. On the other hand, the yields (in moles per 100 mol. of entering propylene) of methylacetylene and allene increased with the increasing conversion, being 9 mol.

TABLE II. PYROLYSIS OF PROPYLENE AT VARIOUS CONTACT TIMES AND PRESSURES*

	Temp., 1200°C														
Run No.	87	88	89	81	36	40	47	38	51	52	80	83	82	84	90
Press., mmHg	50	50	50	50	100	100	100	100	100	100	200	200	200	200	200
Contact time, 10^{-3} sec.	1.1	1.7	2.2	2.9	1.4	1.8	2.4	2.7	3.5	4.5	2.6	3.0	3.4	4.4	4.8
Nitrogen content in reactant gas, vol. %	19.8	19.8	19.8	20.0	20.2	19.4	21.0	19.9	21.1	21.1	20.1	20.1	20.1	20.0	19.8
Composition of pyrolyzed gas, vol. %															
Nitrogen	19.0	17.9	17.4	16.1	19.3	17.9	18.7	16.8	17.3	16.4	19.3	18.9	18.5	17.4	17.2
Hydrogen	1.4	4.1	5.4	9.1	2.0	3.4	4.7	7.8	9.3	11.4	1.5	2.5	3.6	6.2	7.6
Methane	2.7	6.9	8.8	13.7	3.3	5.5	8.2	11.6	14.2	16.8	2.9	4.6	6.7	10.2	11.9
Ethylene	2.7	6.8	8.4	12.7	3.1	5.3	7.7	10.8	13.2	15.3	2.8	4.4	6.4	9.7	10.9
Acetylene	0.5	1.5	2.3	4.3	0.6	1.0	1.7	2.8	3.8	5.2	0.6	0.9	1.3	2.1	2.7
Propylene	70.2	55.0	48.5	32.2	68.3	61.4	52.0	41.3	32.2	24.3	70.3	64.7	58.2	47.5	42.9
Allene	1.8	3.7	4.1	4.5	1.8	2.4	3.0	3.5	3.7	3.8	1.3	1.6	2.0	2.5	2.8
Methylacetylene	0.9	2.9	3.7	5.8	1.1	1.9	2.8	4.1	4.9	5.5	0.9	1.5	2.1	2.9	2.6
1-Butene	0.5	0.5	0.6	0.5	0.4	0.6	0.5	0.4	0.4	0.2	0.3	0.4	0.5	0.6	0.5
Butadiene	0.2	0.6	0.8	1.2	0.3	0.6	0.6	0.8	1.0	1.1	0.2	0.5	0.6	0.8	0.9
Rate of expansion	1.040	1.106	1.138	1.242	1.047	1.085	1.124	1.182	1.220	1.288	1.042	1.063	1.089	1.150	1.149
Conversion, %	9.0	24.1	31.2	50.0	10.4	17.4	26.0	39.0	50.2	60.4	8.4	14.0	20.7	31.8	44.2
Yield, mol./100 mol. of propylene pyrolyzed															
Hydrogen	21.0	23.7	24.5	28.2	24.9	26.6	26.0	29.6	28.6	30.8	23.4	23.5	23.9	28.3	28.3
Methane	39.6	39.8	40.2	42.5	41.2	42.9	45.0	44.1	43.7	45.4	44.5	43.5	44.4	46.4	44.3
Ethylene	39.1	39.0	38.2	39.5	39.2	41.1	42.2	40.9	40.6	41.3	43.0	42.1	42.5	44.0	40.5
Acetylene	6.9	8.8	10.6	13.2	7.4	7.9	9.5	10.6	11.7	14.1	9.0	8.6	8.5	9.7	10.0
Allene	26.1	21.1	18.7	14.0	22.2	18.7	16.6	13.3	11.4	10.2	20.1	15.6	13.3	11.2	10.4
Methylacetylene	13.5	16.6	17.0	18.0	13.5	14.3	15.3	15.5	15.2	14.9	14.3	13.9	13.9	13.2	9.6
1-Butene	6.7	3.0	2.6	1.4	5.0	5.0	2.5	1.6	1.1	0.7	5.0	4.0	3.2	2.5	1.7
Butadiene	3.0	3.4	3.5	3.6	3.3	4.3	3.3	3.2	3.1	2.9	3.9	4.5	4.2	3.5	3.5
Total yield of methylacetylene and allene	39.6	37.7	35.7	32.0	35.7	33.0	31.9	28.8	26.6	25.1	34.4	29.4	27.2	24.4	20.0
Percentage of hydrogen and carbon accounted for in gaseous products through C_4 hydrocarbons															
Hydrogen	100.1	95.9	94.7	95.3	98.1	100.5	97.9	94.6	91.9	93.3	102.6	97.6	95.3	96.0	88.4
Carbon	96.4	91.4	89.8	88.0	91.6	92.3	89.1	84.2	81.6	82.0	95.8	89.8	85.9	83.7	75.4

* Furnace II was used.

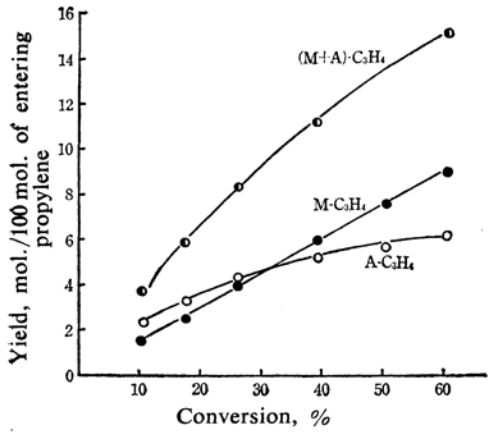

Fig. 5. Variation of yields (in moles per 100 mol. of entering propylene) of methylacetylene and allene with conversion. Temp., 1200°C

and 6 mol. respectively (total 15 mol.) at the highest conversion, 60% (Fig. 5).

The yields of both methane (42~44 mol.) and ethylene (39~41 mol.) hardly varied over the conversion range investigated. The yields of hydrogen and acetylene, however, increased fairly rapidly with the increasing conversion, being 31 mol. and 14 mol. at 60% conversion respectively. In the conversion range, butadiene, formed probably by the secondary decomposition of 1-butene, was obtained in a constant yield of about 3 mol., while the yield of 1-butene decreased with the increasing conversion from 5 mol. to 1 mol. The percentage of hydrogen and carbon accounted for in the gaseous products decreased with an increase in the contact time (conversion). Admittedly, the decrease of hydrogen means that the formation of higher hydrocarbons becomes striking. Furthermore, in view of the results that the yield of methylacetylene-allene, because it is unstable as compared with propylene, decreased fairly rapidly with the increasing contact time, it may be supposed that they react easily with propylene or various radicals, e.g., allyl, to form higher hydrocarbons.

The variations in the yields of methylacetylene and allene, and in the total yield with conversion at 1100°C and 1300°C, in addition to that at 1200°C, are shown in Fig. 6. In the cases of 1100°C and 1300°C, the variation in their yields with conversion was almost the same as that at 1200°C, except that it was somewhat lower at 1100°C.

The Effect of Pressure on Yields.—In addition to the experiments made at 100 mmHg pressure (partial pressure of propylene, about 80 mmHg), a number of experiments were carried out at 50 and 200 mmHg pressure (partial pressure of propylene, about 40 and 160 mmHg respectively). The results are shown in Table II. Also, Fig. 7 shows the effect of pressure on the yields of methylacetylene and allene, as well as the total yields. When yields at fixed conversions are compared, the total yields and also each yields are found to increase with a decrease in the pressure. The differences in the total yields between different pressures were larger at higher conversions. The highest

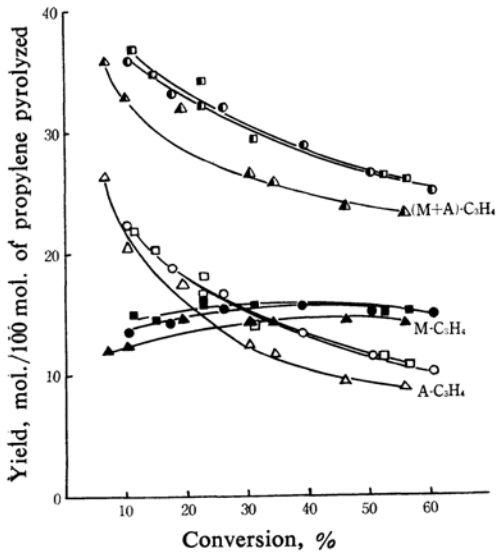

Fig. 6. Variation of yields of methylacetylene and allene with conversion at various temperatures.
Triangles, 1100°C; Circles, 1200°C; Squares, 1300°C

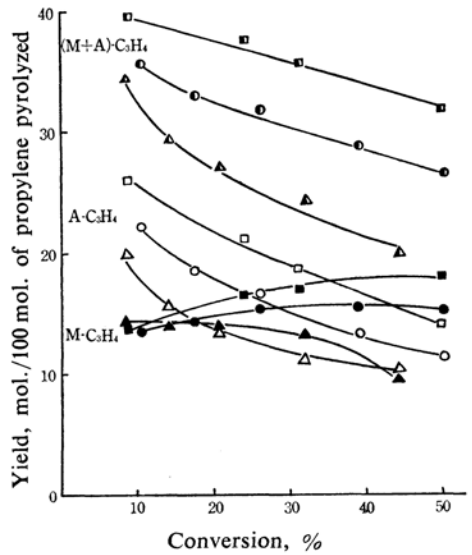

Fig. 7. Effect of pressure on yields of methylacetylene and allene.
Triangles, 200 mmHg; Circles, 100 mmHg; Squares, 50 mmHg.

total yield of 40 mol. was obtained when the pressure (50 mmHg) and the conversion (9.0%) were the lowest studied. It is noticeable that, with 100 mmHg pressure, the yield of methylacetylene is fairly constant over the conversion range, while with 50 mmHg pressure the yield increases with the increasing conversion.

The yields of other gaseous products varied slightly with pressure over the range investigated. Namely, with a decrease in the pressure the yields of methane and ethylene decreased slowly, while reversely, that of acetylene increased. On the other hand, the yields of 1-butene and butadiene almost did not vary at all with the pressure. The percentage of hydrogen and carbon accounted for in the gaseous products increased with the decrease in the pressure from 88% and 75% at 200 mmHg pressure (44% conversion) to 95% and 88% at 50 mmHg pressuse (50% conversion) respectively. On the basis of the above variation in the distribution of pyrolysis products with pressure, it is assumed that the formation of higher hydrocarbons by the additions to propylene of propylene, allene, and methylacetylene (as molecules or radicals derived from them) is diminished as the pyrolysis pressure is decreased, and that, consequently, the yield of methylacetylene-allene is increased.

Summary

Propylene has been pyrolyzed in a flow system over a wide range of conditions (temperature, 800～1400°C; contact time, 4.4×10^{-4} ～2.3 sec.; pressure, 40～160 mmHg) to find suitable conditions for producing methylacetylene (and allene) and for obtaining data concerning the distribution of pyrolysis products. Under proper conditions, the pyrolysis occurred without any appreciable production of tarry and carbonaceous materials. High temperatures (1200～1300°C), short contact times (millisecond order; conversions below 30%), and low pressures (below 100 mmHg) were found to required for the good production of methylacetylene-allene. A methylacetylene-allene yield of 38 mol. per 100 mol. of propylene pyrolyzed was realized at 1200°C, 50 mmHg pressure (partial pressure of propylene, 40 mmHg), and 24% conversion (contact time, 1.7 msec.). The other gaseous products were found to be methane, ethylene, hydrogen, acetylene, 1-butene and butadiene, in decreasing order.

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Institute for Chemical Research
Kyoto University
Daigaku-cho, Takatsuki