[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF ALLENE AND METHYLACETYLENE[1]

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Prior to this work, no record exists concerning the behavior of methylacetylene, $CH_3—C\equiv CH$, at high temperatures. Except for Lebedev's work, the same may be said for allene, $CH_2=C=CH_2$. Lebedev[4] heated allene at 140° under pressure for several days and obtained a series of polymers. He also subjected trimethylallene, *sym-* and *unsym*-dimethylallene to the same conditions of warmth, pressure and time and found that they also gave rise to polymers.

General Results with Allene

The present experiments were made over a temperature range of 400 to 600° and the hot contact time was made a matter of seconds rather than a matter of hours and days as in Lebedev's experiments. Here, also, it was found that polymerization was the predominant reaction of allene. At a temperature of 500° and with a contact time of eighty-six seconds, four-fifths of the allene entering the reaction tube was consumed and 90% of the product appeared as liquids. These liquid products were distilled repeatedly so as to obtain pure fractions. The properties of the lower-boiling fractions were found to be very nearly identical in physical constants and general appearance with two of Lebedev's polymers, namely, the dimer and the alpha tetramer. The higher-boiling fractions differed from Lebedev's polymers but were high-boiling tarry substances. Lebedev stated that several of the polymers, in particular the trimer and the beta tetramer, were unstable at elevated temperatures, so it is not surprising that they were not encountered in the present experiments.

A temperature of 500° seems to be the best for the formation of these liquids by the flow method. At lower temperatures, the reaction proceeds too slowly, while at higher temperatures less polymeric liquids and more gaseous products are formed although the percentage of allene pyrolyzed is greater. Thus, at 600°, with a hot contact time of fifty seconds, only 43%

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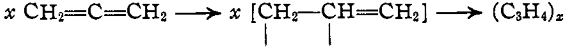
[4] Lebedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1249–1388 (1913); *J. Chem. Soc.* (abst.), **104**, 1285 (1913).

of the non-recoverable allene appeared as liquids. Concurrently, each 10 cc. (gaseous) of this allene gave rise to about four cc. of gas. At 500°, with a hot contact time of eighty-six seconds, nine-tenths of the non-recoverable allene was changed into liquids and only 1 cc. of gas was formed from each 10 cc. of allene. Carbon and tar formation played a major role in the 600° experiments, whereas at 500° almost no tar or carbon was formed.

The gases formed in the pyrolysis of allene were methane, hydrogen, ethane, ethylene and small amounts of acetylenes. Methane represented the larger part at 500°, but at 600° the volumes of methane and hydrogen were almost equal. In all cases, however, the gases represented but a small part of the reaction products.

Mechanism of the Pyrolysis.—Earlier studies on the behavior of butane, isobutane[5] and isobutylene[6] at high temperatures furnish a basis with which to predict something of the mechanism of allene pyrolysis. The butanes, having no double bonds in their structure, change exclusively into compounds of simpler structure, evidently by complete rupture of C–C or C–H bonds. Isobutylene, with one double bond and one single bond, gives rise not only to simpler compounds but also to more complex ones. The simpler compounds appear to be formed by single bond C–C scission, whereas the complex liquid hydrocarbons are formed because of double bond C═C activation which is followed by a polymerization process. Allene presents no opportunity to break into simpler compounds by scission of single bonds since only double bonds are present in the allene chain. Therefore, it would be logical to assume that only complex liquid polymerization products should be formed on pyrolysis. As has been shown, this is indeed the major, and nearly the exclusive, primary effect. It may be symbolized as follows



$$x\,\mathrm{CH_2{=}C{=}CH_2} \longrightarrow x\,[\underset{|}{\mathrm{C}}\mathrm{H_2}\text{—}\underset{|}{\mathrm{C}}\mathrm{H{=}CH_2}] \longrightarrow (\mathrm{C_3H_4})_x$$

Probably, as Lebedev suggested, these polymers are cyclobutane derivatives, the dimer being dimethenylcyclobutane. This dimer, with two double bonds still in its structure, may undergo further polymerization reactions.

General Results with Methylacetylene.—Methylacetylene which contained about 5% of allene as an impurity was prepared by the action of alcoholic potassium hydroxide on propylene bromide. This was used in the first experiments. As in the case of allene, liquids were by far the most abundant product of the pyrolytic reaction. With a hot contact time of one hundred seconds at 500° the liquids accounted for 78% of the methylacetylene pyrolyzed, while at 575° and forty-eight seconds the percentage

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[5] Hurd and Spence, This Journal, **51**, 3353 (1929).

[6] Hurd and Spence, *ibid.*, **51**, 3561 (1929).

of liquids rose to 88. At 650° there was a great increase in the amount of ethylene, hydrogen and methane formed, while the yield of liquids dropped to 61%. This behavior paralleled that of allene under similar conditions. Furthermore, when these liquid products were fractionally distilled as carefully as the small amounts available would permit, the fractions were found to be very nearly identical with the lower-boiling allene polymers. There was no trace of the formation of any aromatic hydrocarbons.

When the off-gas which resulted from the pyrolysis of methylacetylene was analyzed, there was always a considerable portion which was gradually absorbed in 82.4% sulfuric acid. This portion might represent either allene or propylene. Aside from the fact that some allene was a contaminant in the original methylacetylene, the reasons for thinking that it was allene are as follows: (1) because of its slow rate of solution; (2) because propylene could not have been formed except by hydrogenation, an improbability in view of the small concentration of hydrogen in the off-gas; (3) because the liquid products were so very similar to those obtained from pure allene. To settle the point definitely, however, it was decided to pyrolyze an allene-free specimen of methylacetylene and to identify the off-gas in question as bromides. Propylene would give its dibromide, whereas allene would give rise to its di- and tetrabromides, the latter of which would be recognized by its lachrymatory properties, its high boiling point and its comparatively high melting point.

Accordingly, some pure methylacetylene was prepared by the interaction of sodium acetylide and either methyl iodide or dimethyl sulfate. The use of dimethyl sulfate, which is a new method, is preferable. This methylacetylene was pyrolyzed at 500°. The off-gas was carefully collected and all acetylenes were extracted from it by alkaline potassium iodomercurate reagent. The gas which remained was passed several times through a solution of bromine in carbon tetrachloride so as to form bromides of all unsaturated hydrocarbons still remaining. On fractionation these bromides were found to consist principally of allene dibromide and allene tetrabromide. This proves that allene was formed during the pyrolysis of methylacetylene. The similarity of the liquids obtained from methylacetylene to those obtained from allene suggests that these liquids are formed from allene, rather than directly from methylacetylene.

Theoretical Considerations

Acetylene, when heated, undergoes pyrolysis to a large extent into benzene[7] and other aromatic hydrocarbons. Analogously, one might assume that methylacetylene should change into mesitylene and other aromatics. Such, however, is not the case. The fundamental change in methylacetylene is one of isomerism into allene, a change which is predictable on the

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[7] Pease, THIS JOURNAL, 51, 3470 (1929).

basis of the "three carbon system."[8] If E represents any such element as C, N or O, the expression: $\mathrm{H-E-E=E'} \rightleftarrows \mathrm{E=E-E'-H}$ represents a general formulation of this type of rearrangement. Familiar cases of this type are keto–enol, nitroso to oxime, and the three-carbon system.

With a triple bond in the chain rather than a double bond, similar mobility of hydrogen exists: $\mathrm{H-E-E\equiv E} \rightleftarrows \mathrm{E=E=E-H}$. Because of its similarity to the keto–enol isomerism, the name "keteno-ynol" is suggested for this type of change. Some well-known illustrative cases are HOCN and HNCO, $C_6H_5CH_2—CN$ and $C_6H_5CH=C=NH$, $H_2N—CN$ and $HN=C=NH$, ketene and hydroxyacetylene. Methylacetylene and allene also fit into this scheme: $\mathrm{H_3C-C\equiv CH} \rightleftarrows \mathrm{H_2C=C=CH_2}$. Allene may be converted into its isomer by the action of sodium. The reverse reaction is the pyrolysis of methylacetylene. It is interesting to point out that all the "keteno" structures mentioned above are the forms into which the "ynol" isomers change at high temperatures. No doubt this is associated with the fact that the former represent more symmetrical structures.

Experimental Part

Apparatus.—The flow method was used. The gaseous hydrocarbon was stored in a gasometer of 57-liter capacity, in an 8-liter bottle, or in a closed steel cylinder under pressure. The gas was passed from its container through a wet test meter, thence through two drying towers, a flowmeter of the capillary type, a calcium chloride tube, and then it was conducted into the reaction tube. The tube was of pyrex glass 2.5 cm. in diameter and was heated over 76 cm. of its length by an electric tube furnace. The volume of the tube within the furnace limits, after deduction of the volume of the thermocouple sheath, was 290 cc. The furnace was supported in a vertical position so that any liquids formed in the reaction could be removed from the tube by gravity. The effluent gases were passed through a trap at 0° which was placed directly beneath the furnace. This trap served to collect the liquid products.

The temperature of the furnace was measured and automatically controlled by a Leeds–Northrup potentiometer type recorder-controller. A chromel–alumel thermocouple was used, and it was protected by a thin pyrex sheath which was placed directly within the reaction tube.

The gases were analyzed in the manner previously outlined by Hurd and Spence.[9]

Preparation of Allene and Methylacetylene.—Allene was prepared from dibromo-2,3-propene-1, as outlined by Hurd, Meinert and Spence.[10] The gas was washed and stored in a gasometer over saturated sodium chloride solution.

Methylacetylene, contaminated with about 5% of allene, was prepared from propylene bromide and hot alcoholic potassium hydroxide solution. This preparation, and also the preparation of pure methylacetylene from methyl iodide and sodium acetylide, is given in detail in the same reference.[11] The methylacetylene, after purification, was liquefied and stored in a small steel gas cylinder.

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[8] For a discussion of recent work on this subject, see "Annual Reports on the Progress of Chemistry," **25**, 119–130 (1929).

[9] Hurd and Spence, This Journal, **51**, 3356–3357 (1929).

[10] Hurd, Meinert and Spence, *ibid.*, **52**, 1143 (1930).

[11] Ref. 10, p. 1141.

Methylacetylene from Dimethyl Sulfate.—A one-liter, 3-necked flask was fitted with a mercury-sealed stirrer, an exit tube, and a wide-mouthed inlet tube which reached nearly to the bottom of the flask. After replacing air in the flask with dry hydrogen, 36 g. of sodium was inserted, the flask cooled to −60° with a bath of acetone and solid carbon dioxide, and then dry ammonia was condensed in the flask. The stirrer was started as soon as a little ammonia had condensed. In all, about 500 cc. of liquid ammonia was required. When the sodium had dissolved, the stream of ammonia was detached and a current of acetylene was passed into the well-stirred mixture. When all of the sodium-blue color had disappeared due to the formation of colorless sodium acetylide, the current of acetylene was stopped, and a dropping funnel was inserted to replace the stirrer. The top of the funnel was connected with a tube to the reaction flask, the tube serving as a pressure equalizer.

The exit tube was connected to a gas washing train consisting of a Wolff bottle with water, another with 10% sulfuric acid, and a calcium chloride drying tower. Bunsen valves were inserted between the two wash bottles and between the reaction flask and the first wash bottle. From the drying tower a connection led to a spiral glass condenser with receiver attached, which was immersed in a Dewar flask and maintained at −78°. The methylacetylene condensed therein.

Two hundred grams of dimethyl sulfate was added very slowly into the reaction flask from the dropping funnel, keeping the flask at −60°. As each drop fell there was a rush of gas from the exit tube. This necessitated careful control during the addition of the reagent. Most of the methylacetylene had passed over into the condenser by the time the last of the dimethyl sulfate was added. Then the reaction flask was allowed to warm up to drive over the remainder of the product. The methylacetylene was distilled from a large test-tube, using the Davis spiral, vacuum-jacketed column. The yield and the ease of manipulation were about the same with dimethyl sulfate as with methyl iodide. The relative cheapness of the former, however, is greatly in its favor.

The boiling point of the methylacetylene was found[12] to be −23°. Since this differs from the literature value of −27.5°, the accurate vapor pressure of methylacetylene has been studied in considerable detail by Professor G. B. Heisig of the University of Minnesota. This will be published separately.

Products Obtained from the Pyrolysis of Allene.—The data for the pyrolysis of allene are given in Table I.

These data show clearly that when allene was pyrolyzed, most of it was converted into liquids. As would be expected, the conversion was more

TABLE I

PRODUCTS OBTAINED FROM THE PYROLYSIS OF ALLENE

Run number	1	2	3	4	5
Temperature, °C.	500	400	450	600	500
Contact time, seconds	54.7	60.8	52.0	50	86
Entering flow, cc./min.	111	115	126	108	69
Exit flow, cc./min.	45	102	93	62	23
Pressure in tube, mm.	754	754	754	753	730
Vol. entering gas, liters	4.79	3.34	3.59	2.37	13.05
Vol. exit gas, liters	1.96	2.97	2.64	1.35	4.30
Allene in entering gas, %	96.0	92.9	92.9	95.8	93.0

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[12] For assistance in the purification of the methylacetylene we are indebted to Mr. Forrest Pilgrim.

Table I (*Concluded*)

Composition of exit gas, percentage by volume					
Acetylenes	2.5	0.9	0.7	1.0	5.0
Allene	79.7	89.8	89.5	28.0	52.7
Ethylene	2.3	....	....	10.6	4.3
Hydrogen	1.4	....	....	21.3	6.2
Paraffins, C_nH_{2n+2}	4.9	....	....	23.8	14.2
n equivalent to	1.82	....	....	1.10	1.47
CO and CO_2	1.1	....	....	0.7	1.1
Nitrogen	7.2	....	....	13.4	13.2
Extent of pyrolysis, %	66.2	13.8	28.8	83.5	80.5
Gaseous products formed per liter of allene entering, cc.					
Acetylenes	11.9	....	....	0	18.5
Ethylene	11.9	....	....	65	15.3
Hydrogen	5.9	....	....	130	21.8
Paraffins	20.2	....	....	146	50.9
Gaseous products formed per liter of allene pyrolyzed, cc.					
Acetylenes	18	....	....	0	23
Ethylene	18	....	....	78	19
Hydrogen	9	....	....	156	27
Paraffins	32	....	....	175	63
Liquid products, wt. in g.	....	0.24	1.29	1.41	15.8
Percentage yield of liquids, on basis of allene pyrolyzed	....	32	75	43	90

nearly complete when the gas was heated for a longer time and when the temperature was between 500 and 600°. A comparison of Runs 2, 3, 1 and 4, all of which had similar contact times, shows the increasing percentage of decomposition of allene with the increase in temperature. A comparison of Runs 1 and 4 shows that at 600° about five times the volume of gases was formed as was noticed at 500°, while the percentage of liquids was considerably less. It should be stated that the deposit of carbon and viscous tarry matter in the tube was quite considerable at 600° and almost negligible at 500°. Comparison of Runs 1 and 5 shows that if the allene was heated for a longer time, the amount of gaseous products increased. This suggests that a large part of the gases is formed by the decomposition of the allene polymers if the reaction is carried out at 600°, or for too long a time at 500°.

The Liquid Products from Allene.—The 15.8 g. of liquids formed in Run 5 was fractionally distilled, taking care to obtain cuts as nearly pure as possible. The refractive index of each fraction was determined. In Table II the physical properties of these liquids are compared with similar data as given by Lebedev.[4] The properties in question are boiling point, odor, refractive index and general appearance.

A comparison of Fraction I with Lebedev's dimer and Fractions II and III with his α-tetramer shows that they possess similar properties. Lebe-

TABLE II

PROPERTIES OF ALLENE POLYMERS

	Fractions from allene at 500°	Lebedev's polymers
I	B. p. 63–66°; n_D^{20} 1.4358 Sharp, irritating odor; 1.2 g.	Dimer, b. p. 63–65°; n_D^{20} 1.42317 Sharp odor
II	B. p. 35–50° (10 mm.); n_D^{20} 1.5002 Turpentine odor; 2.9 g.	Trimer, b. p. 135°; n_D^{20} 1.49064
III	B. p. 71–80° (10 mm.); n_D^{20} 1.5142 Turpentine odor; 0.8 g.	α-Tetramer, b. p. 72–74° (9 mm.) Turpentine odor; n_D^{20} 1.50501
IV	B. p. 80–105° (10 mm.); n_D^{20} 1.5617 Kerosene odor; 1.2 g.	β-Tetramer, b. p. 101° (10 mm.) Kerosene odor; n_D^{20} 1.52624
V	B. p. 105–155° (8 mm.); 1.3 g.; n_D^{20} 1.596	
VI	B. p. 160–190° (10 mm.); 1.5 g.; n_D^{20} 1.63; very viscous; odor of burnt rubber	

dev stated that only the dimer and the α-tetramer were stable at elevated temperatures. Therefore, in our polymerization at 500°, one would not expect to find much of the other polymers as they tend to form tarry material. The first four fractions all gave a test for unsaturation with bromine.

Pyrolysis of Methylacetylene.—The data for the pyrolysis of methylacetylene which contained 5% of allene as impurity are given in Table III.

TABLE III

PRODUCTS OF THE PYROLYSIS OF METHYLACETYLENE

Run number	1	3	5	2	4
Temperature, °C.	500	500	550	575	650
Contact time, seconds	100	42	76	48	30
Entering flow, cc./min.	59	141	72.6	112	164
Exit flow, cc./min.	45	128	44.2	63	136
Pressure in tube, mm.	750	750	750	750	750
Vol. entering gas, liters	4.84	3.97	13.05	6.73	2.13
Volume exit gas, liters	3.69	3.60	7.92	3.77	1.76
Composition of entering gas					
Methylacetylene, %	95.9	95.0	95.6	95.0	95.0
Allene, %	4.1	5.0	4.4	5.0	5.0
Composition of exit gases, percentage by volume					
Acetylenes	83.7	88.0	52.0	48.0	14.0
Allene[a]	4.4	4.6	18.6	16.8	11.8
Ethylene	1.5	....	3.6	3.0	23.1
Hydrogen	0.2	....	6.8	5.9	18.9
Paraffins, C_nH_{2n+2}	....	....	11.6	....	27.6
n equivalent to	....	....	1.34	....	1.17
Extent of pyrolysis, %	27.4	10.6	64.5	67	87
Gaseous products formed per liter of methylacetylene entering, cc.					
Allene[a]	....	....	124	107	109
Ethylene	....	....	24.6	19	214
Hydrogen	....	....	46.4	38	175
Paraffins	....	....	79.1	...	255

Table III (*Concluded*)

Gaseous products formed per liter of methylacetylene pyrolyzed, cc.					
Allene[a]	....	....	192	159	125
Ethylene	....	....	37.1	28.5	246
Hydrogen	....	....	72.0	57.0	201
Paraffins	....	....	123.0	....	294
Liquid products, wt. in g.	1.8	....	12.6	6.3	8.1
Percentage yield of liquids, on basis of methylacetylene pyrolyzed	78.0	....	58.8	88.0	61.0

[a] "Allene" represents the gases dissolved in 82.5% sulfuric acid; it may contain propylene, but later work has shown that allene is the chief if not the exclusive product.

In Runs 1 and 3 the gaseous products formed were of such a small volume that a complete analysis was not made. In making the calculations it was assumed that the small amount of allene present in the entering gas was polymerized for the most part, inasmuch as the work on allene showed this to be the case at temperatures above 500°. In addition to the gaseous and liquid products, there was a considerable amount of carbon and some very viscid tarry material which was deposited on the walls of the reaction tube. At the higher temperatures, this deposit became so great as to nearly clog the exit of the reaction tube.

Liquid Products from Methylacetylene.—The comparatively small volume of liquids which were obtained from methylacetylene made it impossible to carry the fractionation as far as was done in the case of the allene polymers. However, they were fractionated and the boiling points and refractive indices taken. These data are listed in Table IV.

Table IV

Properties of the Liquid Products from Methylacetylene

Run number	2			5		
Temperature	575°			550°		
Contact time	48 sec.			76.3 sec.		
Fraction	B. p., °C.	n^{20}_{D}	Odor	B. p., °C.	n^{20}_{D}	Odor
I	60–90	1.4780	Sharp	30–70	1.4602	Sharp
II	90–150	1.4990	Turpentine	35–60 (10 mm.)	1.4995	Turpentine
III	150–215	1.5320	......	60–85 (10 mm.)	1.537	Burnt rubber

The properties of the lower-boiling fractions greatly resembled the properties of the low-boiling allene polymers. The liquid fractions were distinctly not aromatic in type. They all decolorized bromine in carbon tetrachloride. Nor did they form any nitro derivatives when they were treated with a nitrating mixture of nitric and sulfuric acids. There was no evidence of any pure compound in quantity since the boiling point ascended steadily during the distillation. An examination of the boiling point and refractive index data shows that they lie outside of the range of the aromatic compounds. Considering the evident impurity of the methylacetylene liquid fractions, it is apparent that they lie within the range of the corresponding data from allene liquid fractions (compare Tables II and IV). This, together with the very strong resemblance which they have to the allene liquids in odor and general appearance, indicates that these liquids also consisted mostly of polymers of the same nature as those obtained from allene. The presence of considerable amounts of allene in the off gas shows that these liquids were probably formed from allene, which in turn was formed by an isomerization of the methylacetylene.

The Pyrolysis of Pure Methylacetylene.—Table V gives the data for this experiment, and includes the analysis of the entering gas and the exit gases.

Table V

Pyrolysis of Pure Methylacetylene

Temperature, °C.	555°	Exit volume, cc.	3380
Contact time, seconds	74.5	Pressure in tube	740 mm.
Entrance flow	95.7 cc./min.	Extent of pyrolysis	71%
Entrance volume, cc.	6320	Liquids formed	3 g.

Gas analysis, % by volume

	Entrance gas	Exit gas
Carbon dioxide	0.0	0.6
Methylacetylene	95.7	46.1
Gas absorbed by 62.5% H_2SO_4	0.0	1.5
Gas absorbed by 82.4% H_2SO_4	.0	24.3
Ethylene	.0	2.2
Hydrogen	.0	2.2
Carbon monoxide	.0	1.0
Oxygen	.6	1.5
Paraffins, C_nH_{2n+2}	.0	9.7
n equivalent to	..	1.67
Nitrogen	3.4	10.9

Since 82.4% sulfuric acid dissolves both allene and propylene, it was decided to remove the acetylenes from the gas and to convert the remaining unsaturated hydrocarbons into their bromide derivatives. Differentiation between olefin dibromides and diene tetrabromides would then be fairly simple.

The off gas from the run (Table V) was passed from its storage bottle into a bottle filled with potassium iodomercurate solution in order to remove all of the unchanged methylacetylene. The bottle was shaken from time to time and finally allowed to stand overnight. The volume became constant, indicating complete removal of all acetylenes. The original volume of gas was 3300 cc., and the volume after removal of acetylenes was 1700 cc. The volume of acetylenes in the original gas, based on the gas analysis was 1518 cc., so it was certain that all acetylenes were taken out. The residual gas was then dried and passed into a solution of bromine in carbon tetrachloride. The unbrominated gas was collected and passed again through the bromine solution, and the apparatus was flushed out with a liter of air.

The bromides in the brominating bottle were then worked up. Their volume was 2 cc.; refractive index 1.533; initial boiling point, 140°. The liquid did not solidify at −75°. This 2 cc. of bromides was separated into two very small fractions by distillation at 9 mm. The boiling points could not be determined accurately due to the small amount of material distilled, but that of the first fraction was between 60 and 90°. Its refractive index was 1.523 and it did not solidify at −75°. The higher-boiling fraction which remained in the distilling flask had a refractive index of 1.582. It solidified at −20° in an ice–salt mixture. It began to melt at −5° and melted over a considerable range, indicating that it was not pure. This fraction of the bromides had an odor like that of allene tetrabromide and it had the powerful lachrymatory properties which are characteristic of allene tetrabromide.

The results provide satisfactory evidence that the portion of unsaturated hydrocarbons which were removed in the 82.4% sulfuric acid during the gas analysis consisted of allene. The bromides were evidently a mixture of allene dibromide and allene tetrabromide. Previous experience in brominating allene has shown that there is always some allene dibromide formed which is difficult to convert to the tetrabromide. The fact that highly purified allene tetrabromide solidifies in a salt–ice mixture[13] and melts at 10.7°, while the impure bromide obtained in this experiment also solidified and melted in the range of −5 to 0°, is a satisfactory proof of the identity of the latter. That the refractive index, 1.582, is lower than that of pure allene tetrabromide, 1.6206, is not surprising in view of the evident impurity of the former. Some of the dibromide undoubtedly remained in the tetrabromide residue. To obtain allene tetrabromide of high purity, it has been shown[13] that fairly large quantities, enabling several crystallizations, are essential.

Summary

In the pyrolysis of allene, it has been shown that the predominant reaction is a polymerization to form a dimer, a tetramer and higher polymers. There is no evidence of the formation of aromatic hydrocarbons.

The pyrolysis of methylacetylene has also been investigated. Evidence is offered to show that it first isomerizes to allene, which then polymerizes in its customary manner. The relationship of methylacetylene to the "three-carbon system" has been developed, and the classification of allene and methylacetylene as of the keteno-ynol type has been suggested.

A method for the preparation of methylacetylene from dimethyl sulfate and sodium acetylide has been given.

EVANSTON, ILLINOIS

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[13] Hurd, Meinert and Spence, THIS JOURNAL, **52**, 1145 (1930).