the extent of the reduction is due to its promoting basic dissociation and thereby limiting acidic dissociation. On the other hand, the effect of pyridine in increasing the extent of reduction is due to its basic properties, which promote acidic dissociation of sodium hydroxide.[9]

CINCINNATI, OHIO

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THE POLYMERIZATION OF THE AMYLENES[1]

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The object of this work was to study in detail the conditions under which the amylenes are polymerized by sulfuric acid, the mechanism of the reaction, and the structure of the resulting compounds. The investigation seemed of importance because our knowledge of the mechanism of polymerization and of the properties of the higher olefins is limited, and because of the fact that these hydrocarbons are formed in the cracking of oils and are present in commercial products. Brooks and Humphrey[2] have studied the behavior of certain olefins with sulfuric acid and have shown that the process of treating crude cracked oils with the acid does not free them from unsaturated compounds. Since the preparation of olefins can be effected from petroleum, it is possible that they may become a source of compounds of industrial importance.

The polymerization of the butylenes has been studied in some detail, but the statements in regard to the amylenes are conflicting and incomplete.

The five isomeric amylenes were prepared in pure condition and their behavior was studied with varying concentrations of sulfuric acid. The effect of the structure of the hydrocarbon was marked. There were great variations in the strength of the acid required to dissolve the hydrocarbons, in the times required for solution and for the precipitation of the polymer, and in the extent to which polymerization took place.

The isomers which have two radicals in combination with an unsaturated carbon atom reacted most readily. They did not appear to form a sulfuric acid ester when they dissolved because the tertiary alcohol was precipi-

[9] An investigation of the effects of other basic substances upon the reducing action of sodium methylate is in progress. A preliminary note should also be made of the observation that certain carbon compounds *in aqueous solution* of sodium hydroxide are partially oxidized, in the presence of a catalyst, with concomitant liberation of hydrogen. This is evidence of acidic dissociation of sodium hydroxide in aqueous solution.

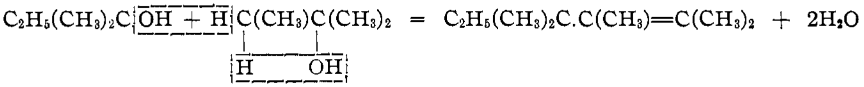
[1] From the thesis of J. M. Joubert presented, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1922.

[2] Brooks and Humphrey, THIS JOURNAL, **40**, 822 (1918).

tated in the two cases when the solution was saturated with ammonium sulfate. *iso*Propylethylene was the only isomer which did not appreciably dissolve in sulfuric acid; it was polymerized slowly and only by the acids of the higher concentrations. Pentene-2 and pentene-1 dissolved slowly and formed sulfuric acid esters, which yielded the corresponding alcohols after hydrolysis. The solutions of these hydrocarbons slowly deposited polymers.

The mechanism of the reaction was investigated and evidence was obtained which showed that polymerization takes place more readily when the acid ester is not produced. It appears that the reaction in these cases consists in the withdrawal of water from the alcohol first formed. The accepted explanation of the polymerization, namely, that it consists of the condensation of the alkyl sulfuric acid and the unsaturated hydrocarbon, does not appear to be correct in the case of at least four of the five isomers, because these hydrocarbons can be made to pass completely into solution as the alcohol or acid ester before polymerization begins.

In the case of trimethylethylene the evidence indicates that the condensation takes place between two molecules of *tert.*-amyl alcohol as indicated by the following formulas.



$$C_2H_5(CH_3)_2C\,\boxed{OH + H}\,\underset{\boxed{H\qquad OH}}{C(CH_3)C(CH_3)_2} = C_2H_5(CH_3)_2C.C(CH_3){=}C(CH_3)_2 + 2H_2O$$

One molecule of the alcohol condenses with the second as the result of the elimination of an hydroxyl group from the former and a hydrogen atom from the latter; the tertiary alcohol formed in this way loses a second molecule of water. The hydrogen atoms involved in the two cases are those in a CH_2 group, the carbon of which is linked to the tertiary carbon atom in combination with an hydroxyl group. This explanation is in accord with our knowledge of the reactivity of hydrogen atoms and hydroxyl groups in organic compounds, and with the facts reported later. The removal of an hydroxyl group takes place most readily in the case of a tertiary alcohol, and hydrogen atoms joined as indicated above are, in general, the most reactive in such compounds. Other methods of condensation than that just described would lead to compounds containing a hydrogen atom in combination with an unsaturated carbon atom. Compounds of this structure would yield aldehydes on oxidation. The diamylene from trimethylethylene, however, yielded no aldehyde, but ketones were formed.

The results given below show that polymerization takes place easily with relatively dilute acid when it is possible to form a tertiary alcohol from the unsaturated hydrocarbon. If a secondary alcohol is formed, a much higher concentration of sulfuric acid is required to effect the condensation. This explanation is in accord with the results obtained with the different amylenes and with the study of the properties of the diamylenes.

An attempt was made to determine the structure of the dimers formed from trimethylethylene and *iso*propylethylene. The products were studied which were formed as the result of the decomposition by water of ozonides of the hydrocarbons. The results are in accord with the view that the compounds formed are olefins which contain one double bond. There was no evidence of ring structure.

The work has led to improved methods of preparation of a number of the compounds used.

The Action of Sulfuric Acid on the Amylenes

Previous Work.—No systematic investigation of the polymerization of the amylenes has been reported. Butlerow[3] mixed amylene prepared from *tert.*-amyl alcohol, with sulfuric acid (2 volumes of concd. sulfuric acid to one volume of water); the hydrocarbon dissolved and after some time diamylene separated. Wischnegradsky[4] states that amylene (b. p., 35°) when shaken with sulfuric acid (d., 1.64) dissolves after a time, and on standing two days gives diamylene. He states also[5] that trimethylethylene dissolves readily in sulfuric acid, and gives on dilution *tert.*-amyl alcohol. He found[6] that the amylene (b. p., 25–45°) prepared by the action of zinc chloride on fermentation amyl alcohol was only partially soluble in acid diluted with one-half its volume of water. Schneider[7] described the preparation of diamylene from amylene (b. p., 35–37°) by mixing it with twice its volume of sulfuric acid (2 volumes to 1 of water). Wischnegradsky[8] found that *iso*propylethylene did not dissolve at 0° in acid diluted with one-half its volume of water. Michael and Brunel[9] showed that tetramethylethylene reacted readily and completely with 77% sulfuric acid at room temperature, but less readily than trimethylethylene. They state that unsymmetrical methylethylethylene dissolves more readily than *iso*propylethylene. Michael and Zeidler[10] have reported the behavior of *iso*propylethylene, trimethylethylene and unsymmetrical methylethylethylene with certain strengths of sulfuric acid. Some of the above statements are contradictory and most are indefinite. No statements were found in regard to the behavior of either symmetrical methylethylethylene or pentene-1 with sulfuric acid.

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[3] Butlerow, *Ann.*, **189,** 75 (1878).

[4] Wischnegradsky, *Ber.*, **8,** 434 (1875).

[5] Wischnegradsky, *Ber.*, **9,** 1028 (1876).

[6] Wischnegradsky, *Ann.*, **190,** 328 (1878).

[7] Schneider, *Ann.*, **157,** 207 (1871).

[8] Ref. 6, p. 354.

[9] Michael and Brunel, *Am. Chem. J.*, **41,** 118 (1909).

[10] Michael and Zeidler, *Ann.*, **385,** 252 (1911).

In order to obtain comparable results with the several isomers, it was necessary to study all of them under the same conditions. In previous work attention had been paid largely to the conditions under which solution in sulfuric acid took place, and not to the phenomena of polymerization.

General Procedure.—The sulfuric acid which had been previously cooled was added to the amylene contained in a glass tube placed in ice water. The tube was sealed and the volumes of the substances noted. It was then placed in a horizontal position in a shaking machine, which was run for eight to nine hours during the day. All experiments, unless otherwise stated, were carried out at room temperature and with equal molecular quantities of the acid and the hydrocarbon. The concentrations of sulfuric acid are stated in parts of the concentrated acid to parts of water by volume, the first number indicating the parts of acid. From 5 to 10 cc. of amylene was used in each experiment.

The progress of the reactions was noted by observing the changes in the volumes of the contents of the tubes. When polymerization was complete, the volume of the hydrocarbon was in each case about six-sevenths of that of the amylene used.

The Relative Reactivity of the Amylenes toward Sulfuric Acid

The results of the experiments which can be used to compare the relative reactivities of the double bond in the amylenes toward sulfuric acid are given in Table I. It is seen that the amylenes which have two radicals linked to an unsaturated carbon atom react much more rapidly and with acids of lower concentrations than do their isomers. At room temperature trimethylethylene and unsymmetrical methylethylethylene dissolve in an equal molecular quantity of 61% sulfuric acid in approximately one-twentieth of the time required to effect the solution of either pentene-1 or pentene-2. This strength of acid does not affect *iso*propylethylene; it does not polymerize the straight-chain amylenes, but slowly converts the two more reactive amylenes into dimers.

The tabulated results show that with the various concentrations of acid used by us, and when equal molecular quantities of the hydrocarbons and acid were used, trimethylethylene dissolved slightly more rapidly than unsymmetrical ethylene. Michael and Zander,[10] however, found that with a large excess (10 volumes) of either 38 or 47% acid solution of unsymmetrical methylethylethylene took place in approximately seven-tenths the time required by its isomer. The procedure used in this investigation was not designed to test small differences in reactivity. Since the reactions are very susceptible to changes in temperature, special precautions would have to be observed to note such small differences.

The amylenes can be arranged in the following order based on the de-

TABLE I

ACTION OF SULFURIC ACID ON THE AMYLENES[a]
Equal Molecular Quantities

Concn. of acid Vol. concn.	Approx., %	Trimethyl-ethylene	*iso*Propyl-ethylene	*unsym.*-Methyl-ethylethylene	*sym.*-Methyl-ethylethylene	Pentene-1
$H_2SO_4 + H_2O$	H_2SO_4					
1:2	48	Nearly S. 8 h.; S. overnight; no P. 14 d.	No effect 14 d.	Slightly slower than trimethylethylene; no P. 14 d.		
4:5	57	S. 8 h.; small amt. P. 3 d; 25% P. 14 d.	No effect 14 d.			
1:1	61	S. 3 h.; Pz. complete 6 d.; D. only	No effect 10 d.	S. 4 h.; Pz. not quite complete 6 d.; D. only	S $^1/_3$ 7 d.; not complete 21 d.	S. $^1/_2$ 7 d.
3:2	70	S. 1 h.; Pz. complete 2 d.	Did not dissolve; Pz. complete 25 d.; mostly D.			
2:1	75	Heated; Pz. complete 20 min.; mostly D.	Did not dissolve; Pz. complete 6 d.; $^2/_3$ D., $^1/_3$ higher P.	Heated; Pz. complete 25 min.; mostly D.	S. 8.5 h.; no P. 14 d.	S. 10 h.; in 3 d. few drops P.; no change 7 d.
3:1	81	Heated; immediate Pz.; inc. in trimer.				S. 4 h.; small amt. P. in several d.
4:1	84				S. 1.4 h.; trace P. 14 d.; no D.	S. 2 h.; trace P.; no D.
5:1	86				Heated; S. rapidly; small amt. P.; 14 d.; no D.	S.; Pz. began 2 h.; no D.
1:0	96	S. at once; Pz. complete; no D.			S. at once; Pz. began 1 h.; no D.	

[a] The abbreviations used in the table signify the following: D = dimer; d. = days; h. = hours; P. = polymer as measured by volume of upper layer formed after the solution of the amylene; Pz. = polymerization; S. = dissolved.

creasing rate at which they react with sulfuric acid: (1) trimethylethylethylene, (2) unsymmetrical methylethylethylene, (3) symmetrical methylethylethylene, (4) pentene-1, (5) *iso*propylethylene. The difference in reactivity between 1 and 2 is slight. These hydrocarbons are much more reactive than 3 and 4, which are very similar in reactivity.

It is a striking fact that *iso*propylethylene is so inactive toward sulfuric acid. It is not clear why the *iso*propyl radical differs so markedly from the *n*-propyl radical (in pentene-1) in its effect on the double bond.

*iso*Propylethylene appears to be affected only by acids of such strength that polymerization takes place at once. It was impossible to obtain an alcohol from the sulfuric acid used in the reaction. When pentene-1 dissolved in acid the solution yielded an alcohol.

The Conversion of the Amylenes into Alcohols

All of the amylenes except *iso*propylethylene dissolved in sulfuric acid, and from the solutions so obtained alcohols were separated. The mechanism by which an olefin is converted into an alcohol under the influence of sulfuric acid has not been definitely established. The prevailing explanation that the acid first adds to the olefin to form an alkyl sulfuric acid, which subsequently yields an alcohol on hydrolysis, may be correct in the case of those amylenes which are converted into secondary alcohols. Brooks[2] has given another explanation of this reaction. No one has established the fact that an alkyl sulfuric acid is formed from the two amylenes containing two radicals linked to an unsaturated carbon atom—that is, those yielding a tertiary alcohol. An acid sulfate of such an alcohol, if it existed, would be so rapidly hydrolyzed that the isolation of the ester or its salt would probably be difficult or impossible.

In order to determine if such acid esters were present in the solutions obtained by dissolving the different amylenes in sulfuric acid, the solutions were treated directly, without the addition of water, with solid ammonium sulfate. The salt reacted with the sulfuric acid and formed primary ammonium sulfate without the production of water. In the case of the hydrocarbons which yielded *tert.*-amyl alcohol, the latter immediately separated out in the free condition. With pentene-1 and pentene-2 an alcohol was not precipitated, but was obtained only after water was added to permit hydrolysis.

These results make possible the view that the formation of an alcohol from an olefin may be due to the direct addition of water to the double bond under the activating influence of the sulfuric acid upon the water. If this view is correct, in the case of secondary alcohols an acid alkyl sulfate is subsequently formed.

Experiments with trimethylethylene gave results in accord with this hypothesis. It was found that by shaking successive amounts of the hydrocarbon with 46% sulfuric acid, about five equivalents of the former could be converted into *tert.*-amyl alcohol. The alcohol could be obtained by extraction with ether or by adding ammonium sulfate to the solution.

When a solution of *tert.*-amyl alcohol in 46% sulfuric acid (1:2) was placed in warm water, it separated into two layers; when the mixture was shaken and slowly cooled it became homogeneous. At a slightly elevated temperature the alcohol is dehydrated and trimethylethylene is formed; when the temperature falls, the hydrocarbon is hydrated in the presence of the acid. The reaction is reversible and appears to be quantitative. It furnishes a much improved method of preparing the hydrocarbon from the alcohol or the alcohol from the hydrocarbon. No polymerization takes place in either process.

Pentene-1 and pentene-2 can be readily converted into alcohols by shaking the hydrocarbon with an equal volume of 4:1 sulfuric acid, diluting the solution formed with 8 volumes of water and distilling the mixture. The part of the alcohol soluble in the aqueous distillate can be precipitated by adding salt or sodium hydroxide. The time required for solution can be shortened by using 5:1 sulfuric acid if the mixture is kept cool during the reaction.

The Formation of the Polymers of the Amylene

The methods of polymerizing the amylene previously described consisted in treating the hydrocarbons with large amounts of sulfuric acid. Experiments showed that relatively small quantities of the acid will effect the change.

When 5 cc. of trimethylethylene was shaken with 0.65 cc. of concd. sulfuric acid (10 moles to 1), polymerization took place at once and the product was mostly the dimer. Five cc. of the hydrocarbon was completely polymerized in eight days by 0.4 cc. of sulfuric acid (2:1). When 0.5 cc. of acid (1:1) was used, about one-half of the hydrocarbon had been polymerized at the end of eight days.

When 10 moles of *iso*propylethylene was shaken with 1 mole of concd. sulfuric acid, the temperature rose and polymerization was complete in a few minutes. The product boiled above 200°, showing that no dimer was formed. Under the same conditions trimethylethylene yielded mostly the dimer. When 10 moles of *iso*propylethylene was left in contact with 1 mole of 2:1 acid for seven days the product boiled at 153–158° and consisted almost entirely of the dimer.

None of the conditions under which pentene-1 and pentene-2 have been studied with sulfuric acid has led to the formation of the dimers of these hydrocarbons. The strong acid needed for polymerization yields higher polymers.

The Mechanism of the Polymerization of the Amylenes

Berthelot was the first to put forward an explanation of the polymerization of olefins by sulfuric acid. According to this view, a molecule of the hydrocarbon first adds sulfuric acid, and the alkyl sulfuric acid thus formed condenses with a second molecule of the hydrocarbon as the result of the loss of a molecule of the acid. Butlerow,[11] after studying the action of sulfuric acid on *iso*butylene, accepted this view but made no attempt to verify it experimentally.

Lermontoff,[12] in order to test further the view that polymerization was the result of this type of condensation, attempted to condense *iso*butylene with *tert.*-butyl iodide by heating a mixture of the two with lime for 24

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[11] Ref. 3, p. 44.

[12] Lermontoff, *Ann.*, **196**, 116 (1879).

hours. He obtained polymers of butylene and assumed that he had effected a condensation as the result of the loss of hydrogen iodide. Since Dobbin[13] had shown that *tert.*-butyl iodide is readily converted by zinc oxide into polymers of *iso*butylene, we heated the iodide alone with lime at 100° for several hours. It was completely changed to a mixture of polymers of the hydrocarbon. The result indicates that Lermontoff's experiment does not explain the mechanism of the condensation.

Kondakow[14] obtained diamylene by allowing equivalent quantities of *tert.*-amyl chloride and trimethylethylene to come in contact in the presence of zinc chloride. The experiment was not conclusive as he had previously shown that the hydrocarbon alone was converted into polymers by zinc chloride. In the work referred to above details of the experiments are lacking and it is impossible to decide whether or not a real condensation had been effected.

The Condensation of the Amylenes with Alkyl Halides

In order to get more definite evidence in regard to the condensation of the amylenes with alkyl halides, and thus have information on which to base an explanation of polymerization, the condensation of trimethylethylene and *iso*propylethylene with primary, secondary and tertiary halides was studied. These amylenes were selected because the former undergoes polymerization more readily and the latter less readily than the other amylenes.

The results showed that condensation took place only when trimethylethylene and a tertiary halide were used.

The fact that *iso*propylethylene did not condense with an alkyl halide indicates that trimethylethylene contains a more active hydrogen than its isomer. This atom is, no doubt, the one linked to the unsaturated carbon atom. The fact that condensation took place only when a tertiary halide was used is in accord with the difference in ease of polymerization of the two hydrocarbons by means of sulfuric acid. Trimethylethylene in the presence of water and sulfuric acid forms a tertiary alcohol. The final conclusion from these experiments is that the condensation, which yields a diamylene from trimethylethylene and *tert.*-amyl chloride, is brought about as the result of the elimination of chlorine from the halide and of the hydrogen linked to the unsaturated carbon atom in the hydrocarbon. This structure is identical with that arrived at as the result of the study of the condensation of *tert.*-amyl alcohol by sulfuric acid.

The experimental conditions were as follows.

*iso*Propylethylene was heated in sealed tubes for 24 hours at 100° with methyl iodide and *iso*propyl iodide, respectively, and with twice the

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[13] Dobbin, *J. Chem. Soc.*, **37**, 242 (1880).

[14] Kondakow, *J. prakt. Chem.*, **54**, 454 (1896).

quantity of lime required to react with the iodine. The three substances were also heated separately with lime under the same conditions. No reaction took place in any case.

When *iso*propylethylene and *tert.*-butyl iodide were used, the hydrocarbon remained unchanged and the halide was converted in polymers of butylene.

No condensation was effected when trimethylethylene was heated with lime and methyl or *iso*-amyl iodide. With a tertiary halide, however, the result was different. When a mixture of the hydrocarbon and *tert.*-amyl iodide was heated with lime in a sealed tube, a reaction apparently took place at a slightly elevated temperature; the lime lost its granular appearance. The material obtained after 24 hours' heating at 100° contained no trimethylethylene and boiled from 150° to over 200°. Since lime at 100° will not polymerize the hydrocarbon, the experiment shows that a true condensation had been effected.

The Chemical Reactions of the Diamylenes

With Bromine.—All of the diamylenes prepared as described above decolorized a solution of bromine in carbon tetrachloride, a fact which showed that they were unsaturated compounds. The products formed were very unstable and distilled with decomposition.

With Sulfuric Acid.—The polymers were much more stable than the parent substances when treated with sulfuric acid. It was found, however, that if the diamylene prepared from either trimethylethylene or *iso*propylethylene were shaken with sulfuric acid (3:1) for two days, a part of the hydrocarbon was converted into higher-boiling products, although solution in the acid did not appear to take place. This result explains the fact that the diamylenes are formed from the amylene only with the more dilute acids, and the fact that the dimers are not produced when a high concentration of acid is required to effect the first polymerization. It is evident that the more dilute acid should be used if it is desired to dissolve unsaturated hydrocarbons from commercial mixtures of these hydrocarbons and paraffins. The practice of using the concentrated acid converts the lower-boiling, unsaturated hydrocarbons into high-boiling compounds which are insoluble in the acid.

With Halogen Acids.—The diamylenes did not react with the constant-boiling solution of hydrochloric or hydriodic acid after contact for two days. With the latter acid, saturated at 0°, a very small amount of iodide was obtained.

The diamylene from trimethylethylene was heated with saturated hydriodic acid at 90–100° for 12 hours. When the product was distilled at 15 mm. pressure, the main portion boiled at 45–50°, and proved to be diamylene. A very small amount of a heavy oil was obtained; b. p., 106–109°. In a second experiment the oil which contained iodine boiled at 104–106° at 10 mm.

In a similar way a very small percentage of the iodide from the diamylene from *iso*propylethylene was prepared; b. p., 106–108°, at 15 mm. The iodide prepared from the dimer of trimethylethylene was very unstable and decomposed slowly on distillation. Attempts were made to convert the iodide into the corresponding alcohol by shaking it with a suspension of silver oxide in water. The chief product of the reactions was the original diamylenes. A small part of the iodide was converted into an oil which had an odor resembling camphor and boiled at 190–200°. It was evident that an alcohol had been formed, but the quantity obtained after the two reactions made further study inadvisable. The iodide from the dimer of *iso*propylethylene gave similar results.

The diamylene from *iso*propylethylene, when heated with saturated hydrochloric acid at 90–100° for nine hours gave, besides the unchanged olefin, a small percentage of liquid that boiled at 86–91°, at 19 mm. Kondakow gives the boiling point of the chloride prepared from the diamylene from trimethylethylene as 87–89°, at 19 mm.

With Oxidizing Agents.—The diamylenes were subjected to oxidation to determine their constitution and to obtain, if possible, further information as to the mechanism of polymerization.

With an aqueous solution of potassium permanganate the oxidation was very slow and incomplete; with the diamylene from trimethylethylene but a small percentage of the compound was oxidized at the end of ten days. Potassium dichromate and sulfuric acid, hot or cold, gave similar results. The study of the products formed by oxidation led to results similar to those obtained by decomposing the ozonides, which are described below.

Ozonized air, prepared by a small apparatus made by the Ozone Pure Airifier Company, after passing through concd. sulfuric acid and a solution of sodium hydroxide was led through the diamylene contained in a tube surrounded by ice. The treatment was continued until the product formed smelled strongly of ozone, and did not decolorize bromine. The percentage of ozone formed by the apparatus was small, as it took five hours to saturate 1 g. of diamylene.

The ozonide from the dimer of trimethylethylene was a light yellow, viscous liquid which had a piercing odor. It decomposed with the evolution of a large amount of gas when heated, and finally exploded. It decomposed more slowly when an attempt was made to distil it under diminished pressure. When treated with boiling water, the latter gave at once a marked test for hydrogen peroxide. The cooled solution gave the iodoform test, and a red coloration with sodium nitroprusside and alkali which turned purple on the addition of acetic acid.

The ozonide was decomposed by shaking with cold water and yielded an oil, the volume of which was three-fourths that of the original compound. No further change took place when the oil was heated for eight hours with boiling water. The aqueous layer, which was strongly acidic, was neutralized and about one-half of it was distilled. The distillate was redistilled twice, the first portions that distilled being used in each case. The final distillate gave a marked test for acetone with sodium nitroprusside; the cold solution gave the iodoform test and an immediate turbidity with phenylhydrazine acetate. The sodium salt obtained from the original solution gave all the characteristic tests for acetic acid.

A portion of the original aqueous solution reduced silver nitrate, precipitated mercurous chloride from mercuric chloride and reduced potassium permanganate. These tests proved the presence of acetone, acetic acid and formic acid.

The insoluble oil was shaken with a solution of sodium hydroxide until it became neutral. The mixture was then distilled with steam. The volume of the oil that passed over was four-fifths of that used. A resinous material was left in the flask. The aqueous solution remaining in the flask was filtered, acidified and again distilled with steam; a small amount of an insoluble acid, which was lighter than water and possessed an offensive odor, passed over. The silver salt of this acid was prepared and found to contain 47.8% of silver. The silver salt of the acid of the composition $C_5H_{11}COOH$ contains 48.2% of silver.

The insoluble neutral oil was dried and distilled. It proved to be a mixture and yielded three equal fractions: 130–150°, 150–160° and 160° to over 200°. The products had a camphoric, turpentine-like odor and decolorized a solution of bromine, the higher-boiling oil showing the latter reaction to a slight degree only. They gave a turbidity with phenylhydrazine acetate and an orange color with sodium nitroprusside which turned pink on the addition of acetic acid. With metallic sodium there was a slow reaction and after a few days most of the liquid had formed a jelly-like mass. Neither in the case of the aqueous solution nor in that of the aqueous distillate were any tests for an aldehyde obtained.

These results are in accord with the view that the diamylene from trimethylethylene has the structure $CH_3CH_2C(CH_3)_2C(CH_3)=C(CH_3)_2$. The decomposition of the ozonide of a hydrocarbon of this structure would lead to the primary formation of acetone and the ketone, $CH_3CH_2C(CH_3)_2CO.CH_3$. The latter on further oxidation would yield among other products formic acid, acetic acid and dimethylethylacetic acid. The experimental results showed the presence of these acids and of ketones of high molecular weight. It was impossible to isolate the ketones in pure condition for analysis.

The ozonide prepared from the diamylene made from *iso*propylethylene was studied in the way described above. In this case the aqueous solution contained no ketone, but gave a definite test for an aldehyde with Schiff's reagent, Fehling's solution and ammoniacal silver nitrate. No acetic acid was formed, but from the solution an acid was obtained in small quantity which appeared to be a butyric acid from the qualitative test applied.

No ketone tests were obtained with the neutral oil, which proved to be a mixture. In the case of this diamylene it is evident that the condensation does not take place in such a way as to lead to the formation of a compound containing two carbon atoms linked to an unsaturated carbon atom. The study of the structure of the diamylenes will be continued as it is now possible to prepare large quantities of the hydrocarbons from material made industrially.

Preparation of Compounds

The methods of making amylenes and the compounds required in their preparation were studied carefully, and as a result improved or new methods were devised. The more important results are given below.

Preparation of Trimethylethylene.—At first a method based on a German patent[15] was used. Ten g. of crystalline oxalic acid was placed in a 200cc. distilling flask, placed in water at about 90° and connected with a well cooled condenser. From a separatory funnel fitted to the flask, 100 g. of pure *tert.*-amyl alcohol was allowed to drop on the acid. The amylene formed was collected in a receiver cooled by ice. The distillate was washed with water, dried over calcium chloride and distilled. It was next refluxed for about four hours with metallic sodium until the latter was not affected. When it was finally distilled with a column of beads, the hydrocarbon boiled constantly at 38°. The yield of purified compound was 63.6 g., which is 80% of that calculated.

This method was later replaced by a new one based on the fact discovered during the course of the work that sulfuric acid (1 vol. of concd. acid to 2 volumes of water) dehydrated the alcohol without causing any polymerization. A mixture of 60 g. of *tert.*-amyl alcohol and 146 g. of the acid (1 : 2) in a distilling flask connected with a condenser was placed in hot water (60–80°). The distillate was purified as described above. The product boiled at 38°. The yield was 84% of that calculated.

Preparation of *iso*Propylethylene.—An electrically heated silica tube 60 cm. long and 2 cm. in internal diameter was used. The temperature was controlled by a rheostat and observed by means of a pyrometer placed in the center of the tube, which was filled with aluminum oxide that had previously been heated at 600° in a stream of air. During the preparation the temperature was kept at 350–380°. *iso*-Amyl alcohol from fermentation was dropped at the rate of 50 g. per hour into a silica test-tube placed in a heated oil-bath, and the vapor formed was led through the furnace. In one experiment 200 cc. of alcohol gave 160 cc. of product which boiled below 40°. This was cooled in ice and added to an equal volume of sulfuric acid (2:1)[16] which was kept at 0°. After shaking for one hour, the hydrocarbon was separated and a fresh portion of acid was added to it. The treatment was repeated until the volume of the hydrocarbon remained constant and its boiling point was not further lowered. The product was washed with water, dried over calcium chloride and distilled to separate the amylene from a small quantity of diamylene that was always formed. The amylene was refluxed with metallic sodium for five to six hours. The purified product boiled at 20.5–21.5°; yield, 130 cc., or 66%.

The amylene which passed into solution when the crude product was shaken with

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[15] Kahlbaum, Ger. pat. 66,866; *Z. angew. Chem.*, **7**, 202 (1893); *Friedländer*, **3**, 980 (1890–1894).

[16] Ref. 6, p. 354. Adams, Kamm and Marvel, THIS JOURNAL, **40**, 1950 (1918).

sulfuric acid (2:1) could be recovered as trimethylethylene by diluting the acid to 1:2 strength and warming it. When the acid solution was neutralized *tert.*-amyl alcohol separated.

Preparation of Symmetrical Methylethylethylene.—The diethylcarbinol used was prepared by the Grignard reaction from ethyl bromide and ethyl formate. The carbinol was slowly added to one-third its equivalent of phosphorus pentoxide and placed in a distilling flask surrounded by ice water. The mixture was then heated by means of hot water until the vapor reached 60°. The distillate was dried, distilled and the portion tertiary below 40° was refluxed with sodium for six hours. The amylene was redistilled with a fractionating column; it boiled at 36°, the temperature rising to 37.5° at the end of the distillation. It has recently been shown in this Laboratory that this amylene can be prepared conveniently from the *sec.*-amyl alcohol manufactured by the Standard Oil Company of New Jersey. Equal volumes of the alcohol and of a mixture of 1 volume of concd. sulfuric acid and 1 volume of water are distilled from a boiling water-bath. If the rectified alcohol is used, the yield of amylene obtained is about 90% of the calculated amount.

Preparation of Unsymmetrical Methylethylethylene.—This was prepared by dehydrating active amyl alcohol (b. p., 128°, Kahlbaum). When phosphorus pentoxide was used the chief product was diamylene. The dehydration was best accomplished by passing the vapor through the hot tube described above under the preparation of *iso*propylethylene. The temperature used in this case was 380–400°. The product was washed, dried, distilled and the product boiling below 40° was refluxed with sodium and on redistillation gave 80% of the calculated yield of amylene, which boiled at 31–33°.

Preparation of Pentene-1.—The Grignard compound was prepared from 54 g. of ethyl bromide and 12 g. of magnesium in 80 cc. of dry ether in a 700cc. flask. When reaction was complete the flask was immersed in ice water and 60 g. of allyl bromide was added very slowly. A very vigorous reaction took place. The mixture was left overnight and then distilled from a water-bath. Because of the fact that the boiling points of ethyl bromide, ether and the amylene are so close together, the product had to be treated with appropriate reagents to remove the ether and the halide. When the product was boiled with metallic sodium it turned blue as the result of the presence of halides. It was next boiled ten hours with magnesium turnings. The liquid which was left gave no test for halogen. To remove the ether present the hydrocarbon was shaken several times with a mixture of equal volumes of concd. and 6 N hydrochloric acid. It was then repeatedly washed with cold water until the odor of ether disappeared. After drying over sodium, 15 g. of the amylene, b. p. 39–41°, was obtained; a small amount of diallyl, b. p. 59–61°, was also obtained. The yield of the purified product was 43% of that calculated.[17]

Preparation of the Diamylenes.—The diamylene from trimethylethylene can be readily prepared by shaking equal molecular quantities of the latter and sulfuric acid (2:1) for half an hour. When 10 moles of the hydrocarbon and 1 mole of concd. sulfuric acid are shaken for a few minutes a good yield of the dimer is also obtained.

This diamylene can also be prepared directly from *tert.*-amyl alcohol. When the latter is shaken with a molecular quantity of sulfuric acid (2:1), diamylene only is obtained after three to four days.

The diamylene from *iso*propylethylene is best prepared by shaking 10 moles of the hydrocarbon with 1 mole of sulfuric acid (2:1). The product obtained at the end of seven days consists of two-thirds diamylene and one-third higher polymers.

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[17] Since this work was finished, the preparation of pentene-1 by this reaction has been described by Kirrman [*Bull. soc. chim.*, **39**, 988 (1926)]. He found that the hydrocarbon boils at 30.5–31°. The temperature recorded in the literature is 39–40°.

Summary

The action of various concentrations of sulfuric acid at room temperature on the five amylenes and the chemical properties of the resulting diamylenes were studied. In all cases equal molecular quantities of the hydrocarbon and acid were used. The principal conclusions are as follows.

1. The amylenes most readily polymerized are trimethylethylene and unsymmetrical methylethylene.
2. *iso*Propylethylene is the only amylene which is polymerized without first dissolving in the acid used.
3. The solutions in the acid obtained from the hydrocarbons mentioned in (1) yielded *tert.*-amyl alcohol when they were saturated with ammonium sulfate; consequently, they contained no alkyl sulfuric acid. The solutions obtained when pentene-2 and pentene-1 were used gave *sec.*-amyl alcohol only after dilution and hydrolysis.
4. The formation of the diamylenes appears to be the result of the dehydration of the amyl alcohol in solution or that formed as the result of hydrolysis of an alkyl sulfuric acid.
5. The amylenes did not condense with primary or secondary alkyl halides when heated at 100° with lime or zinc oxide. Trimethylethylene condensed with tertiary halides under these conditions, but *iso*propylethylene did not.
6. The diamylenes prepared were shown to be olefins, which are much less reactive than the amylenes.
7. The study of the decomposition of the ozonides of the diamylenes yielded results which throw some light on the structure of these hydrocarbons.
8. A number of improved methods for preparation of the compounds used were worked out.

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