This invention relates to an improved process for producing tri-alkyl benzene hydrocarbons from aliphatic ketones. More specifically, our invention is concerned with a method for manufacturing mesitylene from acetone.

An object of this invention is a process for condensing an alkylic ketone to form a substantial yield of poly-alkyl benzene hydrocarbons.

Another object of this invention is to provide an improved process for producing mesitylene from acetone.

One specific embodiment of this invention relates to a process which comprises treating an alkylic ketone at a temperature of from about 200° to about 450° C. in the presence of a heteropoly acid catalyst.

A further embodiment of this invention is concerned with a process for producing mesitylene which comprises treating acetone at a temperature of from about 200° to about 450° C. in the presence of a heteropoly acid catalyst in which one of the components is an element selected from the members of the left-hand columns of groups V and VI of the periodic table.

Alkylic ketones utilisable in our process for producing poly-alkyl benzene hydrocarbons comprise particularly the methyl ketones including acetone, methyl ethyl ketone, methyl propyl and methyl isopropyl ketones, etc. Aliphatic methyl ketones, when treated by our process, yield symmetrical tri-alkyl benzene hydrocarbons, the simplest of which is mesitylene which is also known as 1,3,5-trimethylbenzene. Aliphatic ketones other than the methyl ketones may also be treated by our process to form hexa-alkyl benzene hydrocarbons. Methyl aryl ketones are also convertible into tri-aryl benzene hydrocarbons while other aryl ketones yield tri-aryl tri-aryl benzene hydrocarbons.

The term 'heteropolyacid' used in this specification and in the claims should be regarded as having the same scope as indicated in the following material quoted from "Inorganic Chemistry," by Ephraim, English edition, Gurney and Jackson (1934), p. 434.

The term 'polyacid' is applied to acids which contain several acid radicals, such as pyrosulfuric acid, (O(SO_2)O)H; pyrophosphoric acid (O(PO_2)O)H; tetrachromic acid (O(CrO_3)O)H; and metatungstic acid, H_2W_18O_49. When polyacids contain only one kind of acid radical they are termed 'isopolyacids,' but if one of the radicals is derived from another negative element, the term 'heteropolyacid' is applied. The radicals of vanadic, tungstic, and molybdic acids unite with radicals of other fairly strong acids or with amphoteric metallic hydroxides, to form heteropolyacids. Examples of these are phosphotungstic, phosphomolybdic, and phosphovanadic acids, silico-tungstic or -molybdic acids, and boro tungstic acid. It is distinctive of heteropolyacids that a single radical of one of the acids is united with many, perhaps twelve, radicals derived from the second acid.

Also, the heteropolyacids which are used as catalysts for the process of our invention are regarded as compounds of the co-ordination type involving acid radicals such as phosphates, arsenates, borates, and silicates surrounded by molecular groupings composed of oxides of molybdenum, tungsten, or vanadium. While the structures of heteropolyacids are not known with certainty, recent investigators have concluded that phosphotungstic acid has a structure which may be represented as H_2[SiW_12O_40] or H_2[PO_4·12W(H_2O)_2].

Certain investigators have expressed the view that the water of crystallization of phosphotungstic acid is packed into interstices between the anions [SiW_12O_40]^4-. This structure has been considered present also in silicotungstic acid, boro tungstic acid, and metatungstic acid which become H_2[SiW_12O_40], H_2[BW_12O_40], and H_2[WO_12O_40] respectively; whereas other workers indicate that the same type of structure is present in phosphomolybdic acid, H_2[PMo_12O_40]; arsenomolybdic acid, H_2[AsMo_12O_40]; and silicomolybdic acid, H_2[SiMo_12O_40], respectively, and their salts. Also it has been considered probable that all compounds formerly regarded as H_2[SiMo_12O_40] should be written H_2[XMo_12O_40], where X represents cerium, zirconium, tin, and thorium. Many other complex substances as those containing vanadium and other elements may be of this type. The central tetrahedral group XO_4 is an essential feature of all the foregoing acids and salts. In heteropolyacids it is general that a single radical of one of the acids is combined with many radicals derived from the second acid.

The catalysts which we prefer to use in the process of this invention are the heteropolyacids as defined above and in which one component of the heteropolyacid is an element selected from the members of the left-hand columns of groups V and VI of the periodic table.

Although heteropolyacids may be used as such in our process, we prefer to so employ solid gran-
ular catalytic material formed by impregnating a carrier or supporting material with an aqueous solution of the heteropolyacid and then calcining the impregnated material to form a granular solid utilizable as a reactor filling material and from which the catalytically active substance is not removed readily by water.

The process of our invention is carried out using either batch or continuous types of treatment. In batch type treatment, a ketone or a ketone mixture and a heteropolyacid catalyst of the type herein described are charged to an autoclave and brought to a desired superatmospheric pressure, for example by the introduction of nitrogen to the autoclave. The charged autoclave is then rotated and heated at a temperature of from about 200° to about 450°C. This treatment is continued for a time sufficient that a substantial proportion of the charged ketone is converted into the desired poly-alkyl benzene hydrocarbon such as mesitylene.

It is preferable, however, to carry out the process in a continuous manner by passing a ketone or mixture of ketones through a reactor containing a calcined granular composite of a heteropolyacid and a carrier maintained at a temperature of from about 200° to about 450°C and at a superatmospheric pressure generally not greater than about 100 atmospheres. The reaction products obtained from either the batch or continuous types of treatment are separated into unconverted ketone, unsaturated by-products such as mesityl oxide and isophorone and the desired poly-alkyl benzene hydrocarbons, of which mesitylene is representative. Unconverted acetone and by-products, the latter including mesityl oxide and isophorone, are recycled to the process for producing higher yields of polyalkyl benzene hydrocarbons.

Sometimes it may also be desirable to carry out the process in a continuous manner by pumping an alkylated ketone and an aqueous solution of a water-soluble heteropolyacid through a reactor maintained at the desired temperature but at a pressure sufficient to maintain the reaction mixture in substantially liquid phase and thus reduce the amount of solid heteropolyacid from the aqueous catalyst solution. The reaction mixture obtained from such a process is then separated into an organic liquid layer and an aqueous catalyst layer, the latter being generally recycled to the process. The organic liquid layer is then separated by suitable means into unconverted ketone, by-products, and the desired poly-alkyl benzene hydrocarbon. The unconverted ketone and the by-products, the latter including for example mesityl oxide and isophorone, are recycled to the process.

The following examples are given to show results obtained in treating an alkyl ketone in the presence of a heteropolyacid catalyst at conditions adequate to convert a substantial proportion of said ketone into a tri-alkyl benzene hydrocarbon.

**Example I**

A phosphotungstic acid-alumina catalyst was prepared by dissolving 8 grams of phosphotungstic acid, 20WO3-2H2PO4-25H2O, in 46 grams of water and adding thereto 78 grams of 6-14 mesh activated alumina. The alumina so impregnated with the phosphotungstic acid solution was dried at 100° C. for 15 hours and then calcined at 370-425° C. for 1 hour.

42 grams of the catalyst prepared as described above was placed in a steel catalyst tube of 14 mm. diameter and heated at 350° C. while acetone was passed therethrough at a pressure of 70 atmospheres and at an hourly liquid feed rate of 1 velocity of 1 during a period of 20 hours. A total of 975 grams of acetone thus yielded 4 grams of non-condensable gas, 82 grams of condensable gas, and 845 grams of liquid product. The recovered liquid product was found to contain 478 grams of unconverted acetone, 139 grams of water, 23 grams of mesityl oxide boiling between 123° and 135°C., 18 grams of a fraction boiling from 135° to 153°C., 132 grams of a mesitylene fraction boiling from 153° to 170°C., 5 grams of material boiling from 170° to 200°C., 17 grams of isophorone boiling from 206° to 220°C., and 31 grams of higher boiling material. The condensable gas was found to contain 7.3 mole percent carbon dioxide, 3.5% ethylene and propylene, 0.4% ethane and propane, 58.5% isobutylene, 3.7% n-butylene, 3.6% butane, 0.5% pentane and pentenes, and 22.8% of higher boiling material consisting essentially of unconverted acetone.

Thus 50.8% of the acetone charged underwent reaction. The yield based upon the weight percent of acetone reacting were as follows: mesitylene, 27%; mesityl oxide, 4%; isophorone, 3%; and liquid products boiling above 220° C., 6%.

**Example II**

The catalyst employed in this run was similar to that described in Example I, but in addition it was calcined for 2 hours at 450° C. Following the procedure employed in Example I, a total of 1025 grams of acetone was passed during 20 hours through a reactor containing 40 grams of the above described catalyst maintained at 350° C. and at a pressure of 70 atmospheres. The resultant reaction products contained 4 grams of non-condensable gas, 124 grams of condensable gas and 870 grams of liquid product. This liquid product was found to contain 477 grams of unconverted acetone, 139 grams of water, 26 grams of mesityl oxide, 9 grams of liquid boiling from 135° to 155°C., 156 grams of a mesitylene fraction, 5 grams of material boiling from 170° to 200°C., 15 grams of isophorone, and 40 grams of liquid material boiling above 220°C. Analysis of the condensable gas gave the following results: 17.5% carbon dioxide; 2.5% ethylene and propylene; 50.5% isobutylene; 3.2% n-butylene; 6.8% of a mixture of ethane, propane and butane; 6.6% pentanes and pentenes, and 18.6% of higher boiling material consisting mainly of unconverted acetone.

In this run, 53.4% of the acetone charged underwent reaction. The yields of products based upon the weight of acetone reacting were as follows: mesitylene, 28%; mesityl oxide, 5%; isophorone, 3%; and liquid products boiling above 220° C., 7%.

**Example III**

The catalyst employed in this run was prepared by impregnating 98 grams of 6-14 mesh activated alumina with a solution formed by dissolving 10 grams of silico-tungstic acid,

\[ SiO_2·12WO_3·28H_2O \]

in 60 grams of water. The impregnated material was dried overnight at 100° C. and then calcined at 650° C. for 2 hours.

Following the procedure used in Examples I and II, a total of 935 grams of acetone was passed...
over 43 grams of the catalyst at 350° C. and at a pressure of 70 atmospheres during a period of 20 hours. The resultant reaction product contained 6 grams of non-condensable gas, 85 grams of condensable gas, and 621 grams of liquid product. The liquid product was found to contain 429 grams of acetone, 137 grams of water, 20 grams of mesityl oxide, 8 grams of liquid product boiling from 135° to 155° C., 154 grams of a mesitylene fraction, 6 grams of liquid boiling from 170° to 206° C., 21 grams of isophorone, and 42 grams of liquid material boiling above 220° C.

The condensable gas contained 13 mole % of carbon dioxide, 2.4% ethylene and propylene, 0.8% of ethane and propane, 46.5% isobutylene, 4.4% n-butylene, 1.7% of butane, 0.7% of pentanes and pentenes, and 28.5% of higher boiling material consisting essentially of unconverted acetone.

Of the acetone charged, 54.2% reacted. Upon the basis of the acetone reacting, the weight % yields of the different products were as follows: 30.9% of acetone; 4% isophorone; and 8% of liquid boiling above 220° C. The yield of mesitylene obtained was 44% of the theoretical based upon the reaction of 3 molecular proportions of acetone yielding 1 molecular proportion of mesitylene and 3 molecular proportions of water.

**Example IV**

The catalyst employed in this run was prepared by impregnating 95 grams of 6-14 mesh activated alumina with a solution formed by dissolving 10 grams of phosphomolybdic acid, 20MoO₃·2H₂PO₄·48H₂O, in 60 grams of water. The impregnated material was dried at 100° C. for 12 hours and then calcined at 650° C. for 3 hours.

Following the procedure employed in the preceding examples, 858 grams of acetone was passed over 41 grams of the phosphomolybdic acid-alumina catalyst at 350° C. and at a pressure of 70 atmospheres during a period of 20 hours. The reaction products so obtained contained 8 grams of non-condensable gas, 27 grams of condensable gas, and 822 grams of liquid product. The liquid product contained 475 grams of unconverted acetone, 101 grams of a mixture of water and acetic acid, 25 grams of mesityl oxide, 22 grams of liquid material boiling between 135° and 155° C., 105 grams of a mesitylene fraction, 4 grams of liquid boiling between 170° and 206° C., 24 grams of isophorone, and 64 grams of liquid material boiling above 230° C.

Of the acetone charged, 44.7% by weight reacted. The weight % yields of the different products based upon the acetone which reacted were as follows: mesitylene, 27.4%; mesityl oxide, 6.5%; isophorone, 6.3%; higher boiling liquids, 16.7%; non-condensable gas, 2.1%, and condensable gas, 7%.

The condensable gas fraction contained 9.6 mole % of carbon dioxide, 8.1% propylene, 0.9% propane, 41.2% isobutylene, 2.5% n-butylene, 2.5% butane, 1% pentane, and 43.3% of unconverted acetone.

**Example V**

Following the procedure of Example III and employing a fresh sample of the same catalyst, a total of 596 grams of acetone was passed over 44 grams of the catalyst at 300° C. and at a pressure of 70 atmospheres during a period of 20 hours. The resultant reaction product contained 1 gram of non-condensable gas, 11 grams of condensable gas, and 988 grams of liquid product. The liquid product was found to contain 777 grams of unconverted acetone, 54 grams of a mixture of water and acetic acid, 5 grams of liquid boiling from 60° to 120° C., 77 grams of a mesityl oxide fraction, 8 grams of liquid boiling from 135° to 155° C., 53 grams of a mesitylene fraction, 4 grams of liquid boiling from 170° to 206° C., 14 grams of isophorone, and 16 grams of higher boiling liquids.

Of the acetone charged, 24% reacted. Upon the basis of the acetone which reacted, the weight % yields of the different products were as follows: 32.2% mesityl oxide, 22.2% mesitylene, 5.5% isophorone, 6.7% of liquids boiling above 220° C., 0.4% of non-condensable gas, and 4.8% of condensable gas.

The character of the process of the present invention and its commercial value are evident from the preceding specification and examples, although neither section is intended to limit the broad scope of the invention.

We claim as our invention:

1. A process for the production of aromatics which comprises dehydrating and cyclizando a ketone in the presence of a catalyst comprising a heteropolyacid at a temperature above 200° C. but not greater than about 450° C.

2. A process for the production of aromatics which comprises dehydrating and cyclizando an alkyl ketone in the presence of a catalyst comprising a heteropolyacid at a temperature above 200° C. but not greater than about 450° C.

3. A process for the production of aromatics which comprises dehydrating and cyclizando an alkyl ketone at a temperature above 200° C. but not greater than about 450° C. In the presence of a catalyst comprising a heteropolyacid having phosphorus as one component.

4. A process for the production of aromatics which comprises dehydrating and cyclizando an alkyl ketone at a temperature above 200° C. but not greater than about 450° C. In the presence of a catalyst comprising a heteropolyacid having silicon as one component.

5. A process for producing a trialkyl benzene hydrocarbon which comprises dehydrating and cyclizando a methyl ketone at a temperature above 200° C. but not greater than about 450° C. In the presence of a catalyst comprising a heteropolyacid having phosphorus as one component.

6. A process for producing a trialkyl benzene hydrocarbon which comprises dehydrating and cyclizando a methyl ketone at a temperature above 200° C. but not greater than about 450° C. In the presence of a catalyst comprising a heteropolyacid having silicon as one component.

7. A process for producing a trialkyl benzene hydrocarbon which comprises dehydrating and cyclizando a methyl ketone at a temperature above 200° C. but not greater than about 450° C. In the presence of a catalyst comprising a heteropolyacid having phosphorus as one component.

8. A process for producing a trialkyl benzene hydrocarbon which comprises dehydrating and cyclizando acetone at a temperature above 200° C. but not greater than about 450° C. In the presence of a catalyst comprising a heteropolyacid having phosphorus as one component.
10. A process for producing mesitylene which comprises dehydrating and cyclizing acetone at a temperature above 200° C., but not greater than about 450° C., in the presence of a catalyst comprising its essential active ingredient a heteropolyacid having silicon as one component.

11. A process for producing mesitylene which comprises dehydrating and cyclizing acetone at a temperature above 200° C. but not greater than about 450° C. in the presence of a phosphotungstic acid catalyst.

12. A process for producing mesitylene which comprises dehydrating and cyclizing acetone at a temperature above 200° C. but not greater than about 450° C. in the presence of a phosphomolybdic acid catalyst.

13. A process for producing mesitylene which comprises dehydrating and cyclizing acetone at a temperature above 200° C. but not greater than about 450° C. in the presence of a silicotungstic acid catalyst.

14. A process for the production of aromatics which comprises dehydrating and cyclizing an alkyl ketone at a temperature above 200° C., but not greater than about 450° C., in the presence of an aqueous solution of a heteropolyacid.

15. A process for the production of aromatics which comprises dehydrating and cyclizing an alkyl ketone at a temperature above 200° C. but not greater than about 450° C. in the presence of a catalyst comprising essentially a composite of a heteropolyacid and a substantially inert carrier.

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