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CONDENSATION OF ALKYL KETONES IN PRESENCE OF AQUEOUS AMMONIUM HALIDE SOLUTIONS

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This invention relates to a process for treating an alkyl ketone with a particular catalytic material. More specifically, the invention is concerned with a process for manufacturing mesityl oxide and/or mesitylene from acetone.

An object of this invention is to provide an improved process for converting an alkyl ketone into a poly-alkyl benzene hydrocarbon.

Another object of this invention is the production of mesitylene from acetone.

A further object of this invention is the production of higher molecular weight unsaturated ketones and trialkyl benzene hydrocarbons by the treatment of alkyl ketones at an elevated temperature in the presence of an aqueous solution of an ammonium halide.

One specific embodiment of this invention relates to a process which comprises reacting an alkyl ketone at a temperature of from about 100° to about 450° C. in the presence of an ammonium halide.

A further embodiment of this invention relates to a process which comprises reacting acetone at a temperature of from about 100° to about 450° C. in the presence of an aqueous solution of an ammonium halide.

Alkyl ketones utilizable as starting materials for our process comprise dialkyl ketones and alkyl aryl ketones. We prefer to charge to our process methyl ketones including acetone, methyl ethyl ketone, methyl propyl and methyl isopropyl ketones, other methyl alkyl ketones, acetophenone, etc. These compounds yield mesitylene type hydrocarbons, that is, acetone yields mesitylene whereas the other methyl ketones yield substantial amounts of trialkyl and triaryl benzene hydrocarbons. However, aliphatic ketones other than the methyl ketones are converted by our process into unsaturated organic compounds including unsaturated ketones and olefins and also into hexa-alkyl benzene hydrocarbons. The benzene hydrocarbons formed in this process are also regarded as unsaturated organic compounds in that they will combine with hydrogen in the presence of a hydrogenation catalyst to produce saturated hydrocarbons.

Catalysts utilizable in our process comprise ammonium halides and particularly those in which the halogen has an atomic weight between about 35 and about 80, thus including ammonium chloride and ammonium bromide. The different catalysts may be used individually or in combination with one another or in the form of aqueous solutions.

The process of our invention is carried out using either batch type treatment or a continuous treatment of an alkyl ketone. Batch type conversion of an alkyl ketone to an alkylated aromatic hydrocarbon or to an unsaturated ketone is carried out by subjecting an alkyl ketone and a catalyst of the type herein described to contact in an autoclave or other suitable reactor at a temperature of from about 100° to about 450° C.

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After this treatment, this reaction product is separated into unconverted ketone, small amounts of unsaturated ketones, the desired poly-alkyl benzene hydrocarbon, and higher boiling condensation products. The unconverted ketone and unsaturated ketones formed in the process are then subjected to further conversion treatment in the presence of the catalyst to produce an additional quantity of poly-alkyl benzene hydrocarbons.

In order to obtain a relatively high yield of mesitylene from acetone, or of other poly-alkyl benzene hydrocarbons from other methyl ketones, we prefer to operate our process in a continuous manner. This is accomplished, for example, by commingling the alkyl ketone and an aqueous solution of an ammonium halide and passing the commingled mixture through a reactor maintained at a temperature of from about 100° C. to the critical temperature of the reaction mixture. When employing high proportions of catalyst solution relative to the amount of ketone charged, the maximum operating temperature will thus approach the critical temperature of water, namely about 374° C. with an operating pressure of 225 or more atmospheres. In general, the operating pressure employed is at least that needed to keep the reaction mixture in substantially liquid phase and thus prevent the deposition and accumulation of the catalyst in the heated reaction zone as would occur at lower pressures. While deposition of the catalyst in the reaction zone does not prevent the occurrence of the ketone condensation reaction, it does interfere with smooth, continuous operation of the process. In order to produce relatively high yields of mesitylene and its homologs, it is preferred to treat the alkyl ketone at a temperature of at least 250° C. as at lower temperatures production of mesityl oxide is the principal reaction of the process.

The catalyst solution so employed in the continuous treatment of an alkyl ketone is recovered from the reaction products and recycled for treating an additional quantity of the alkyl ketone. Not only the catalyst solution, but also the unsaturated carbonyl compounds including mesityl oxide and isophorone, which are by-prod-

ucts of the reaction, are recycled and commingled with the fresh alkyl ketone being charged to the process.

The following examples are given to indicate the type of results obtained in our process although not with the intention of limiting unduly the broad scope of the invention.

Example I

A rotatable steel autoclave of 850 cc. capacity was charged with 157 grams of acetone, 15 grams of water, and 13 grams of ammonium chloride. Hydrogen was then introduced to the charged autoclave to 100 atmospheres pressure and the autoclave and contents were then heated at 250° C. for 12 hours. The reaction product consisted of 155 grams of an upper layer and 2.7 grams of a lower layer, mostly water. Fractional distillation of the upper layer separated therefrom 118.6 grams of unconverted acetone, 17 grams of water, 8.3 grams of mesityl oxide, 2 grams of a mesitylene fraction boiling between 160° and 170° C., and 4.9 grams of higher boiling material.

Example II

The autoclave employed in Example I and charged with the same quantities of reactants was heated at 300° C. for 12 hours. The reaction product consisted of 60.7 grams of upper layer and 78 grams of lower layer. Fractional distillation of the upper layer separated therefrom 21.5 grams of acetone, 1.9 grams of water, 9.6 grams of mesityl oxide, 6.0 grams of mesitylene, and 16.9 grams of higher boiling products.

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 unduly the broad scope of the invention.

We claim as our invention:

1. A process for dehydrating ketones which comprises reacting an alkyl ketone at a temperature of from about 100° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of an ammonium halide in which the halogen has an atomic weight between about 35 and about 80.

2. A process for dehydrating ketones which comprises reacting an alkyl ketone at a temperature of from about 100° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of an ammonium halide.

3. A process for dehydrating ketones which comprises reacting a methyl ketone at a temperature of from about 100° to about 450° C. in the presence of an aqueous solution of an ammonium halide in which the halogen has an atomic weight between about 35 and about 80.

4. A process for dehydrating ketones which comprises reacting a methyl ketone at a temperature of from about 250° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of an ammonium halide in which the halogen has an atomic weight between about 35 and about 80 and separating a trialkyl benzene from the resultant dehydration products.

5. A process for dehydrating ketones which comprises reacting acetone at a temperature of from about 250° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of an ammonium halide in which the halogen has an atomic weight between about 35 and about 80 and separating mesitylene from the resultant dehydration products.

6. A process for dehydrating ketones which comprises reacting acetone at a temperature of from about 250° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of ammonium chloride and separating mesitylene from the resultant dehydration products.

7. A process for dehydrating ketones which comprises reacting acetone at a temperature of from about 100° to about 250° C. in the presence of a catalyst comprising essentially an aqueous solution of an ammonium halide in which the halogen has an atomic weight between about 35 and about 80.

8. A process for dehydrating ketones which comprises reacting acetone at a temperature of from about 100° to about 250° C. and at a superatmospheric pressure in the presence of an aqueous solution of ammonium chloride as a catalyst.

9. A process for dehydrating ketones which comprises reacting a methyl ketone at a temperature of from about 100° to about 450° C. in the presence of a catalyst comprising essentially an aqueous solution of an ammonium halide.

10. A process for dehydrating ketones which comprises reacting an alkyl ketone at a temperature of from about 100° C. to about 450° C. in the presence of an aqueous solution of ammonium chloride.

11. A process for dehydrating ketones which comprises reacting an alkyl ketone at a temperature of from about 250° C. to about 450° C. in the presence of an aqueous solution of an ammonium halide in which the halogen has an atomic weight between about 35 and about 80.

12. A process for dehydrating ketones which comprises reacting an alkyl ketone at a temperature of from about 100° C. to about 250° C. in the presence of an aqueous solution of an ammonium halide in which the halogen has an atomic weight between about 35 and about 80.

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