PREPARATION OF CYCLIC ALCOHOLS BY OXIDATION IN THE PRESENCE OF BORIC ACID

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No Drawing. Filed Dec. 17, 1962, Ser. No. 244,894


11 Claims. (Cl. 260—631)

The present invention relates to certain improvements in the preparation of cyclic alcohols by oxidizing saturated cyclic hydrocarbons with the aid of boric acid. It is known that a saturated cyclic hydrocarbon may be oxidized to a cyclic alcohol in the presence of boric acid. This oxidation is usually carried out in the liquid phase, oxidizing the hydrocarbon with a gas containing molecular oxygen, for example, air, at a temperature of 100-300° C. The formation of undesired by-products, such as acids, is partly counteracted by the reaction of the boric acid with the alcohols formed to yield esters which resist further oxidation. This favorable activity of the boric acid, which is rather hard to dissolve in the hydrocarbon to be oxidized, can be promoted by suspending the solid boric acid in the hydrocarbon in a finely divided state. To this end, the boric acid crystals may first be ground in a mill and screened, after which the resulting fine powder can be distributed in the hydrocarbon.

As will be appreciated, this pretreatment of the boric acid, including grinding and screening, is quite complicated and there are attendant losses of acid. Accordingly, the principal object of the present invention is to provide a novel way of preparing a finely divided suspension of boric acid in the hydrocarbon which is free from the indicated prior difficulties. Another object of the invention is to provide a simplified procedure for preparing the desired boric acid suspension in hydrocarbon. A more specific object is the provision of a process for oxidizing cyclic hydrocarbons to give high yields of cyclic alcohols. A further specific object is to avoid the complicated boric acid pre-treatment and attendant losses of acid encountered in prior procedures. Other objects will also be apparent from the following detailed description of the invention.

Briefly stated, the objects of the invention are realized by utilizing for the oxidation reaction herein involved, a suspension of boric acid in hydrocarbon which has been prepared by mixing the hydrocarbon with an aqueous solution of boric acid and then evaporating the water from this mixture.

The amount of boric acid utilized can be varied and should be related to the amount of alcohol formed so that the alcohol can be bound as an ester. Desirably an excess of the acid is used over that theoretically necessary to react with all of the alcohol which is formed. Thus, for example, if the hydrocarbon oxidation is to be terminated at an early stage where there is only a low degree of hydrocarbon conversion, for example, 5-25%, it is sufficient to use just a small amount of boric acid, typically, 10-15% excess over that theoretically required to react with all of the alcohol.

In preparing the boric acid suspension according to the present invention, it is preferred, because of the low solubility of boric acid in water, to use a hot, aqueous solution containing about 15 to 20% by weight of boric acid, the temperature of the solution usually being 40 to 60° C.

After the aqueous boric acid solution has been mixed with the hydrocarbon (which is also desirably at a temperature of 40-60° C. for the mixing operation) all or essentially all of the water is evaporated from the resulting mixture. Any hydrocarbon which may be evaporated along with the water can be recirculated after a phase separation. When the water is withdrawn from the mixture, the boric acid separates out in a very finely divided form and can be easily kept suspended in the hydrocarbon by stirring. The amount of boric acid in the suspension may be varied by adding further amounts of hydrocarbon. Preferably, the resulting suspension comprises from 5 to 15% by weight of boric acid although proportions outside this range may also be used.

The hydrocarbon is oxidized by bringing the suspension of boric acid in hydrocarbon at a temperature of 100-300° C. into contact with molecular oxygen, e.g., pure oxygen or a gas containing molecular oxygen, such as air or other mixtures of oxygen and inert gas, typically nitrogen. This can be accomplished very simply by passing the gas through the suspension. A catalyst is not necessary although one may be used if desired. Typical catalysts include cobalt naphthenate and cobalt oleate.

It is recommended that the boric acid be used together with a boric acid salt, preferably an alkali metal salt, such as potassium borate or borax. It has been found that during the oxidation the boric acid salts react with the acid by-products which are formed along with the alcohol to produce additional boric acid. The amount of boric acid salt used for this purpose may be varied considerably. For example, the salt may be used in amount equivalent to the amount of boric acid used. Less salt may also be used, typically, 10, 25, 40 or 75% of the amount of acid.

The oxidation should be carried out under sufficient pressure to keep the hydrocarbon in the liquid phase during the oxidation. The actual pressure utilized in any particular situation will, of course, depend on the oxidation temperature and the boiling point of the hydrocarbon. A temperature of from 100° C. to 300° C. is generally the customary range for this oxidation.

The water formed in the oxidation is readily removed by evaporation during the oxidation and any hydrocarbon evaporated along with the water can be recirculated after condensation and phase separation. When the oxidation is completed, the nonconverted hydrocarbon can be recovered by distillation and the desired alcohol can be recovered from the remaining reaction mixture by saponifying the resulting esters by treatment with water and/or alkali hydroxide.

The invention is illustrated but not limited by the following examples:

Example 1

A hot solution (temperature 50 to 55° C.) of 2 kg. of boric acid in 10 kg. of water is mixed with 25 kg. of cyclohexane at a temperature of 50 to 55° C. in an autoclave with a capacity of 50 litres and provided with a stirrer. After that, water and cyclohexane are evaporated from the autoclave at a temperature of 60 to 75° C. until a suspension of solid boric acid in cyclohexane is obtained. Following the evaporation and phase separation, the cyclohexane evaporated in this operation is returned to the autoclave.

The temperature of the suspension is then raised to 164-165° C., and a gas consisting of nitrogen and oxygen (5% by volume of oxygen) is passed through the autoclave at the rate of 5 m.3 per hour (measured at 0° C. and 1 atm.), the pressure being kept at 9 atm. The water formed during the oxidation is removed in the vapor state, while hydrocarbon evaporated along with the water is recirculated after condensation.

After 2 hours the oxidation is stopped, and the nonconverted cyclohexane is separated off by distillation.
kg. of cyclohexane are recovered, which corresponds to a degree of conversion of 8% by weight. The raw oxidation product is washed with a dilute, aqueous sodium hydroxide solution (0.5%) at a temperature of 60 to 90°C. This operation saponifies the esters which are present. After repeated washing with water and phase separation, an oil containing 1.62 kg. of cyclohexanol and 0.29 kg. of cyclohexanone (molar ratio about 5:1) is obtained. The boric acid and the resulting acid oxidation products are contained in the water phase.

The yield, calculated on the amount of converted cyclohexane, amounts to 68.3% of cyclohexanol and 13.7% of cyclohexanone.

Example 2

The oxidation described in Example 1 is repeated except that a solution of 3.5 kg. of boric acid in 20 kg. of water is used to prepare the suspension and the oxidation is continued for 4 hours.

The result is:

Recovered cyclohexane 21 kg.; degree of conversion 16%. Cyclohexanol, 3.06 kg.; yield 64.4%. Cyclohexanone, 0.50 kg.; yield 10.7%. Molar ratio cyclohexanol:cyclohexanone = 6:1.

Example 3

The oxidation described in Example 1 is repeated except that a solution of 2 kg. of boric acid and 4 kg. of borax in 30 kg. of water is used in preparing the suspension. After the oxidation has been continued for 2 hours, the result is:

Recovered cyclohexane 22.74 kg.; degree of conversion 9%. Cyclohexanol, 2.02 kg.; yield 74.3%. Cyclohexanone, 0.28 kg.; yield 10.6%. Molar ratio cyclohexanol:cyclohexanone = 7:1.

Example 4

The oxidation described in Example 1 is repeated except that the oxidation pressure is maintained at 30 atm. The stirrer in the autoclave is a propeller stirrer rotating in a tube which produces intensive agitation. The oxidation is continued for 4 hours.

The result is:

Recovered cyclohexane 21.3 kg.; degree of conversion 15%. Cyclohexanol, 2.94 kg.; yield 78%. Cyclohexanone, 0.36 kg.; yield 9.6%. Molar ratio cyclohexanol:cyclohexanone = 8:2:1.

As will be apparent from the foregoing examples, the oxidation reaction gives esters which are saponified or hydrolyzed by heating with water, aqueous sodium hydroxide or the like to give the desired alcohols. This gives a two phase system, i.e., an oil phase containing the alcohol and a water phase which has boric acid dissolved therein. These two phases can be readily separated from each other by phase separation.

The aqueous boric acid solution which is obtained by the phase separation referred to in the preceding paragraph may be used to prepare boric acid suspension subjected to oxidation. However, this aqueous solution also contains acid by-products formed in the oxidation and these by-products should preferably be removed before the solution is used, not only to prevent by-products from accumulating in the oxidation reactor, but also to prevent any unfavorable influence on the oxidation, including the formation of undesired decomposition products.

Examination of the acid by-products present in the aqueous solution resulting from hydrolysis of the oxidation mixture has shown that these products consist substantially of alkane-carboxylic acids. Quite surprisingly, these include such valuable alkane-dicarboxylic acids as succinic acid, glutaric acid, adipic acid and higher alkane-dicarboxylic acids. According to another aspect of the invention, it has also been found that these acid by-products can be effectively removed from the aqueous boric acid solution by means of a basic anion exchanger so as to leave an aequous solution of boric acid which is suitable for reuse. The ion exchanger may be any anion exchanger containing active amine groups or quaternary ammonium groups such as the so-called amelite exchangers and permelt exchangers.

After removing the acid by-products, the aqueous boric acid solution is mixed with hydrocarbon as aforesaid for the purpose of preparing a boric acid suspension in hydrocarbon suitable for oxidation. To this end, it is usually preferred, in order to minimize hydrocarbon evaporation and to avoid evaporating large amounts of water after the solution has been mixed with hydrocarbon, to first evaporate the aqueous solution of boric acid to a smaller volume, preferably until a boric acid solution is obtained which is saturated at a temperature of 40 to 85°C, and then mix this concentrated solution with the hydrocarbon. This has the additional advantage that any volatile by-products generated in the aqueous solution, such as monocarboxylic acids, can be removed in a simple way by the concentrating step. The volatile by-products may also be removed by evaporating the aqueous solution before it is brought into contact with the ion exchanger so as to minimize the load on the ion exchanger.

As indicated above, the oxidation reaction product can be conveniently saponified or hydrolyzed by heating it with water at, for example, a temperature of 60 to 90°C, with simultaneous stirring. Substances giving an alkaline reaction, such as the alkali metal carbonates as well as the alkali metal hydroxides as previously mentioned, may also be used.

If the resulting oil phase contains esters that have not yet been hydrolyzed, this phase may be re-subjected to a hydrolysis treatment and the resulting alcohol can be recovered if necessary after distillation. In addition to the cyclic alcohol, the oxidation reaction product usually contains the corresponding cyclic ketones, in amounts of approx. 1/10 to 1/4 of the amount by weight of cyclic alcohol. If alkaline substances are used in the hydrolysis, it will be recognized that metal ions will be present in the aqueous phase which is separated from the alcohol oil phase. These metal ions can be removed by means of an acid cation exchanger but if the boric acid is used together with a boric acid salt, at least some of these metal ions may be retained in the aqueous phase.

The additional features of the invention as discussed above are further illustrated by the following:

Example 5

A hot solution (temperature 80 to 85°C) of 2 kg. of boric acid in 7 kg. of water is mixed with 25 kg. of cyclohexane in an autoclave, having a capacity of 50 liters and provided with a stirrer, at a temperature of 80 to 85°C and a pressure of 25 atm. After that, water and cyclohexane are evaporated from the autoclave at a temperature of 100 to 110°C until a suspension of solid boric acid in cyclohexane results. The evaporated cyclohexane is returned to the autoclave after condensation and phase separation.

The temperature is then raised to 164–165°C, and a gas consisting of nitrogen and oxygen (5% by volume of oxygen) is passed through the autoclave at a rate of 3 m³ per hour (measured at 0°C and 1 atm.), the pressure being kept at 25 atm. The water formed during oxidation is removed in the vapor state, while hydrocarbon evaporated along with the water is recondensed after condensation.

After 2 hours the oxidation is stopped, and the nonconverted cyclohexane separated off by distillation.
3,287,423 kg. of cyclohexane are recovered, which corresponds to a degree of conversion of 8% by weight. The raw oxidation product is mixed with 20 kg. of water and hydrolyzed at a temperature of 80 to 90° C. with simultaneous stirring, after which the oil is separated from the aqueous phase. From the oil obtained 1.62 kg. of cyclohexanol (yield 68.3%) and 0.29 kg. of cyclohexanone (yield 13.7%) are recovered. The yields are calculated to the amount of converted cyclohexane.

The aqueous phase is evaporated until a boric acid solution results which is virtually saturated at a temperature of 60 to 65° C. The vapor discharge during the evaporation is condensed, the condensate containing small amounts of alkane monocarboxylic acids, cyclohexanol, and cyclohexanone. After that, the evaporated boric acid solution is passed through a column containing pumice (1.5 litres) at a temperature of 60 to 65° C.

At a temperature of 80 to 85° C. the aqueous solution is then further evaporated to 9 kg., in which 2 kg. of boric acid are present. This boric acid solution is re-used by mixing with additional hydrocarbon, evaporating the water to obtain a boric acid suspension in hydrocarbon and subjecting this suspension to oxidation as aforesaid.

The anion exchanger is regenerated by passing dilute nitric acid through it at a temperature of 60 to 65° C. As a result, an aqueous solution of alkane dicarboxylic acids is obtained, the solution being advantageously evaporated to dryness.

As a further feature of the invention, it has been found that, in lieu of subjecting the aqueous phase obtained by hydrolyzing the oxidation reaction product to treatment with ion exchanger, the aqueous phase may be directly mixed with hydrocarbon so oxidized after which the water and volatile carboxylic acids, namely the lower alkane monocarboxylic acids, are evaporated from the resulting mixture. This is usually accomplished at a temperature of about 100 to 110° C. until all of the water is evaporated. Any hydrocarbon which is also evaporated along with the water and volatile carboxylic acids may be re-circulated after condensation. Evaporation causes the boric acid to precipitate and this is then separated from the hydrocarbon in any convenient fashion, e.g., by filtration or centrifuging. The hydrocarbon re-contains in solution the non-volatilized carboxylic acids, mainly alkane dicarboxylic acids, among them succinic acid, glutaric acid, adipic acid and higher alkane dicarboxylic acids. These acids may be extracted from the hydrocarbon with water and can be readily recovered from the resulting aqueous solution. The boric acid, previously precipitated and separated from the hydrocarbon may be dissolved in water, the resulting solution of hydroboric acid and this mixture appropriately processed by evaporating water to prepare the boric acid suspension in hydrocarbon for oxidation.

The following example illustrates the alternative procedure referred to in the preceding paragraph:

**Example 6**

A hot solution of 2 kg. of boric acid in 8 kg. of water is mixed with 25 kg. of cyclohexane at a temperature of 80 to 85° C. and a pressure of 25 atm. in an autoclave with a capacity of 50 litres. The autoclave is provided with a propeller stirrer which rotates in a tube, as a result of which intimate mixing is achieved. After that, water and cyclohexane are evaporated from the autoclave at a temperature of 100 to 110° C. until a suspension of solid boric acid in cyclohexane has been obtained. Following condensation and phase separation, the cyclohexane evaporated in this step is returned to the autoclave. The temperature is then raised to 164 to 165° C., and a gas consisting of nitrogen and oxygen (5% by volume of oxygen) is passed through the autoclave at the rate of 5 m³ per hour (measured at 0° C. and 1 atm.), the pressure being kept at 25 atm. The water formed during the oxidation is removed in the vapor state, while hydroboric acid evaporated along with the water is recirculated after condensation.

After 4 hours the oxidation is stopped, and the non-converted cyclohexane is separated off by distillation. 21.5 kg. of cyclohexane are recovered, which corresponds to a degree of conversion of 14%.

The raw oxidation product is mixed with 10 kg. of water and hydrolyzed at a temperature of 80 to 90° C. after which the oil is separated from the aqueous phase. From the oil thus obtained 2.76 kg. of cyclohexanol (yield 79%) and 0.25 kg. of cyclohexanone (yield 10%) are recovered. These yields are based on the amount of converted cyclohexane.

The aqueous phase is mixed with the 21.5 kg. of recovered cyclohexane, and water and volatile carboxylic acids are removed from the mixture by evaporation, while the cyclohexane evaporated along with these substances is recirculated after condensation. The solid boric acid (2 kg.) precipitated in this operation is separated off.

The carboxylic acids present in the cyclohexane are extracted with water. The aqueous carboxylic acid solution is evaporated to dryness and the cyclohexane purified in this way is returned to the autoclave, where the amount is made up to 25 kg., while the boric acid previously separated off is dissolved in 8 kg. of water, and also introduced into the autoclave to prepare additional boric acid suspension in cyclohexane for further oxidation.

While the foregoing examples are directed specifically to the oxidation of cyclohexane, the invention is not restricted thereto and other saturated cyclic hydrocarbons may also be similarly oxidized into the appropriate alcohols. Thus, for example, the process herein may be employed to oxidize other saturated cyclic hydrocarbons as cyclopentane, cycloheptane, cyclo-octane and cyclocodexane to give the corresponding cyclic alcohols.

Other modifications may be made in the invention described herein. Hence, the scope of the invention is set forth in the following claims wherein:

**What is claimed is:**

1. In a process for the preparation of a cyclic alcohol by the oxidation of a saturated cyclic hydrocarbon selected from the group consisting of cyclopentane, cyclohexane, cycloheptane, cyclo-octane and cyclocodexane by preparing a suspension of boric acid in said hydrocarbon and then contacting said suspension with molecular oxygen at a temperature of 100 to 300° C. followed by hydrolysis of the resulting oxidation product, the improvement which comprises preparing said suspension by mixing said hydrocarbon with an aqueous solution of boric acid and then evaporating all of the water from said mixture to leave behind a suspension of solid boric acid in said hydrocarbon.

2. The process of claim 1 wherein said aqueous solution of boric acid includes a boric acid salt.

3. The process of claim 2 wherein said salt is an alkalai metal borate.

4. The process of claim 1 wherein said aqueous solution contains 15 to 20% by weight of said acid and said solution is mixed with hydrocarbon at 40 to 60° C.

5. The process of claim 4 wherein said hydrocarbon is cyclohexene.

6. The process of claim 1 wherein the amount of acid used is in excess of the amount of alcohol formed.

7. The process of claim 1 wherein said oxidation reaction product is hydrolyzed to give an oil phase containing the desired alcohol and an aqueous phase containing boric acid and acid by-products, said acid by-products being removed from said aqueous phase by contacting said aqueous phase with a basic anion exchanger.

8. The process of claim 7 wherein the aqueous boric acid phase after removal of said acid by-products is mixed with hydrocarbon to prepare additional suspension for said oxidation.

9. The process of claim 8 wherein water is evaporated from said aqueous phase before mixing with the hydro-
carbon, said evaporation continuing until a boric acid solution is obtained which is saturated at a temperature of 40° to 83° C.

10. The process of claim 1 wherein said oxidation reaction product is hydrolyzed to give an oil phase containing the desired alcohol and an aqueous phase containing boric acid, followed by separating said phases, then mixing said aqueous phase directly with hydrocarbon and evaporating the water from the resulting mixture whereby boric acid is precipitated in said hydrocarbon, recycling any hydrocarbon evaporated with said water, separating the precipitated boric acid from said hydrocarbon, recovering by-product carboxylic acids from said hydrocarbon by extraction with water and utilizing the boric acid separated from said hydrocarbon to prepare additional suspension for use in said oxidation.

11. The process of claim 10 wherein said separated boric acid is dissolved in water, the resulting solution mixed with hydrocarbon and water thereafter evaporated from said mixture to prepare said suspension.

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