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RECOVERY OF EPSILON-CAPROLACTONE AND ALKANE DICARBOXYLIC ACID BY ACID TREATMENT AND VACUUM DISTILLATION

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ABSTRACT OF THE DISCLOSURE

The recovery of epsilon caprolactone and of alkane dicarboxylic acids from mixtures such as are obtained in the individual washing steps of the process for oxidation of cyclohexane with air at elevated temperature and at superatmospheric pressure and containing substantially monocarboxylic acids, dicarboxylic acids and epsilon-hydroxycaproic acid (if desired after part of the adipic acid present has been separated) by removing water (if present) and the major portion of the monocarboxylic acids (if present) by distillation, adding 1 to 30% by weight of phosphoric acid or a compound forming the same or boric acid, heating the mixture obtained under subatmospheric pressure at 180° to 250° C., distilling off the volatile components, condensing the individual fractions and rectifying and/or crystallizing the fractions. Distillation temperatures above 150° C. are avoided. Epsilon caprolactone is useful for the production of caprolactam, a starting material for the production of fibers.

This invention relates to the recovery of epsilon-caprolactone and alkane dicarboxylic acids from byproducts obtained in the oxidation of cyclohexane with air.

It is known that in the oxidation of cyclohexane with air in the liquid phase at elevated temperature and superatmospheric pressure, preferably in the presence of metal catalysts, there are obtained, in addition to cyclohexanol and cyclohexanone, the following byproducts: acids, for example monocarboxylic acids having one to six carbon atoms, such as formic acid, acetic acid, propionic acid, butyric acid, valeric acid and caproic acid; dicarboxylic acids having two to six carbon atoms, such as oxalic acid, succinic acid, glutaric acid and adipic acid; hydroxycarboxylic acids, such as epsilon-hydroxy-caproic acid; aldehydic acids, keto acids and other compounds not yet identified, each having up to six carbon atoms. The major portion of these byproducts remains as a residue in the distillation of the reaction products. They are however preferably removed in the prior art methods prior to the distillation of the end products by washing with water or weakly alkaline solutions, for example alkali metal hydroxide or carbonate solutions, either after the oxidation of the cyclohexane has been completed or between the individual stages of the oxidation, for example by the method described in U.S. patent specification No. 2,938,-924. Since considerable amounts of these washing solutions are obtained in industrial cyclohexane oxidation, which is carried out on a large scale, an endeavour has been made to make use of the products dissolved therein. It is known that the organic byproducts contained in the washing solutions can be oxidized with nitric acid, a mixture of monocarboxylic and dicarboxylic acids being obtained. It is also known that adipic acid (which constitutes a considerable proportion of the byproducts) can be partly crystallized out after the washing solution has been concentrated. It is said to be advantageous for the mixture of oxidation byproducts first to be extracted with chloroform because adipic acid then crystallizes more readily. Furthermore it is known from U.K. patent specification No. 997,340 that solutions which have been obtained in the alkaline hydrolysis of the byproducts formed in the oxidation of cyclohexane may be separated into the main components by a combined extraction process wherein (after acidification) the monocarboxylic acids are first removed by means of a hydrocarbon, then the dicarboxylic acids and lactones and esters of hydroxycaproic acid are taken up by means of another organic solvent, the solvent is distilled off, the adipic acid crystallized and separated and finally the lactone and the ester of hydroxycaproic acids are recovered. Finally it is known that epsilon-hydroxycaproic acid may be obtained in monomeric and/or polymeric form from the aqueous or alkaline washing solutions obtained in the oxidation of cyclohexane with air by extraction with alcohols which are not miscible with water (cf. U.S. patent specification No. 3.277,168).

In this way however mixtures of epsilon-hydroxycaproic acid with the lactone and intermolecular esters thereof (estolides) and esters with other acids are obtained. The recovery of the main components (epsilon-hydroxycaproic acid or the lactone thereof) is therefore difficult because the monomeric acid very readily forms esters with itself and the other acids, especially adipic acid.

It is an object of this invention to provide a process for the recovery of epsilon-caprolactone and alkane dicarboxylic acids from mixtures such as are obtained in the washing stages of the process for oxidizing cyclohexane with air in a relatively simple manner and with a good yield. It is a further object of the invention to provide a process for the recovery of the said lactone in which it is obtained in the form of monomeric epsilon-caprolactone and not in the form of a polymeric lactone as in the prior art methods.

These and other objects and advantages will be better understood from the following detailed specification.

We have now found that epsilon-caprolactone and alkane dicarboxylic acids having up to six carbon atoms can be obtained in a relatively simple manner and with a good yield from mixtures such as are contained in the washing solutions obtained in the oxidation of cyclohexane with air at elevated temperature and superatmospheric pressure and containing substantially monocarboxylic acids having up to six carbon atoms, dicarboxylic acids having up to six carbon atoms and epsilon-hydroxycaproic acid, with or without previous separation of a part of the adipic acid present, by first distilling off all or substantially all of any water present and if desired the major portion of the monocarboxylic acid, heating the residue at 180° to 250° C. at a pressure of 1 to 20 mm. Hg. with an addition of 1 to 30% by weight, advantageously 5 to 10% by weight, with reference to the residue, of phosphoric acid, phosphorus pentoxide and/or boric acid, thus distilling off the volatile constituents containing epsilon-caprolactone and alkane dicarboxylic acids, condensing the vapors, preferably while fractionating them, and if desired rectifying or crystallizing the individual fractions, distillation temperatures of more than 150° C. being avoided.

The starting material may be an aqueous or aqueous-alkaline solution which has been obtained by washing oxidation mixtures such as are obtained in the oxidation of cyclohexane with air in the liquid phase at elevated temperature, for example at 130° to 160° C., and at superatmospheric pressure, for example at 2 to 50 atmospheres preferably in the presence of oxidation catalysts, particularly cobalt compounds, with water or aque-

ous-alkaline solutions, for example up to 30 wt. percent alkali hydroxide solutions either after the oxidation of cyclohexane or between the individual oxidation stages. They contain from about 30 to 50% by weight of organic substances. The percentage contents of the most important components are about within the following limits, in each case with reference to the total amount of organic substances:

(a) monocarboxylic acids: acetic acid, propionic acid, butyric acid, up to about 10% by weight valeric acid, caproic acid, up to about 20% by weight,
(b) dicarboxylic acids: succinic acid, glutaric acid, about 5 to 10% by weight, adipic acid up to about 30% by weight,
(c) hydroxycaproic acid and other carboxylic acids, omega-hydroxy caproic acid (also as lactone), about 25 to 40% by weight.

When starting from alkaline solutions, these are first acidified, preferably with a mineral acid such as hydrochloric acid or sulfuric acid and then the inorganic salts formed are separated, for example by extracting the free organic acids (for example with ketones such as acetone, methyl ethyl ketone or cyclohexanone, or with aromatic hydrocarbons such as toluene or xylene) before or after the water is separated, and the extracted acid mixture is used as starting material for the process. Such mixtures in general contain only very little water so that separate dehydration can often be dispensed with.

In addition to the said acids, there is a number of other byproducts formed in the oxidation of cyclohexane, some of which are not precisely known, contained in the said washing liquids. It is also possible however to use mixtures of this type from which some of the adipic acid has already been separated, for example after concentration and crystallization of some of the adipic acid. These solutions (which for the sake of simplicity are also referred to as "washing solutions") contain up to 75% by weight of organic substances of the same types as specified above, the percentage content varying according to the extent of the separation of adipic acid. Finally it is possible to use any mixtures of monocarboxylic acids, dicarboxylic acids and hydroxycarboxylic acids whose composition is similar to that of the said washing solutions.

Monomeric epsilon-caprolactone is obtained by the process according to this invention from epsilon-hydroxycaproic acid or polymers or esters thereof. More or less of various byproducts, for example hexenoic acid, δ-methyl-δ-valerolactone or γ -ethyl-γ-butyrolactone, are obtained depending on the conditions used.

The water is first substantially evaporated, for example down to a content of 5 to 10% by weight but preferably practically completely. In general not more than 5% by weight of water remains in the residue. The water is distilled off advantageously first at atmospheric pressure and then in a second stage at subatmospheric pressure, for example down to 5 mm. Hg. Volatile carboxylic acids, for example acetic acid and homologues up to caproic acid, and also remainders of cyclohexanol and/or cyclohexanone evaporate together with the water. During evaporation at subatmospheric pressure, small amounts of epsilon-caprolactone and also keto acids (mainly laevulinic acid) and succinic anhydride also pass over. The water is distilled off practically completely for example by heating at subatmospheric pressure, for example up to about 220° C. at 20 mm. Hg. During evaporation, epsilon-hydroxycaproic acid is converted, with elimination of water, into polymers and into ester compounds with the dicarboxylic acids. The monocarboxylic acids can readily be distilled off from this high boiling point residue. Purification of the lactone to be recovered is thus simplified. Phosphoric acid, phosphorus pentoxide, boric acid or boric anhydride is added to the residue obtained (with or without cooling, for example to a temperature below 200° C.) advantageously in an amount of 3 to 20%, particularly 5 to 10%, by weight with reference to the residue. It is advantageous for the phosphoric acid or boric acid used to be substantially anhydrous, for example an 80% or more highly concentrated solution.

After these acids have been added, the residue is further heated at a pressure of 1 to 20 mm. Hg to 180° to 250° C. A mixture of lactones and dicarboxylic acids distills over. It is condensed, preferably with fractionation, and then if desired pure lactone is recovered from the distillate by rectification and if desired pure dicarboxylic acids are obtained advantageously by crystallization. Fractional condensation is advantageously carried out in the first stage at about 140° to 170° C. and in a second stage at room temperature. In the first fraction separated at the higher temperature, a mixture of adipic acid, glutaric acid and small amounts of lactone (about 10%) are obtained and in the second fraction separated at room temperature mainly lactones are obtained with small amounts of dicarboxylic acids or anhydrides.

The effects of phosphoric acid and boric acid are not entirely equivalent. When using boric acid mainly epsilon-caprolactone is obtained in addition to the dicarboxylic acids and only a small amount of hexenoic acid as a by-product. When using phosphoric acid, there is formed not only epsilon-caprolactone but also methylvalerolactone and ethylbutyrolactone, which are formed by secondary reactions, and there is a general rule that the amount of byproducts increases when higher pressure and temperature are used and when a larger amount of phosphoric acid is added. The presence of steam also increases the proportion of byproducts. Practically only ethylbutyrolactone is obtained in a steam distillation at atmospheric pressure. In continuous operation it is advantageous to remove continuously from the bottoms (which is heated at 200° to 250° C.) a portion, for example 20 to 30% by weight, of the amount supplied and to keep the proportion of phosphoric acid or boric acid in the bottoms at a constant value, for example at 5 to 10% by weight of the bottoms, by adding the said acid.

The distillate or the fractions of the distillate are as a rule not uniform in composition. They may be separated into the individual components however by simple crystallization and rectification. Appreciable changes, for example by fresh esterification with the carboxylic acids or by the formation of estolides, do not take place when temperatures below 150° C. are maintained during the distillation. It is advantageous to convert the anhydrides with a small amount of water at 60° to 80° C. into the high boiling point acids and to separate the lactones from these by rapid distillation. The lactones are separated by subsequent rectification, advantageously at pressures of less than 10 mm. Hg. The dicarboxylic acid fraction is advantageously purified by fractional crystallization from water or solvents such as xylene; adipic acid is recovered as a crystallization product; glutaric acid, lactone and impurities are contained in the mother liquor.

The epsilon-caprolactone obtained after rectification is equivalent to epsilon-caprolactone obtained by other methods, for example from cyclohexanone by the Bayer-Villiger reaction, is stable and can be used in the same way as the said other product. It may be further purified if necessary by crystallization from the melt (melting point −5° C.).

The phosphoric acid or boric acid in the distillation residue can easily be recovered because these residues are substantially soluble when boiled, advantageously at super atmospheric pressure and elevated temperature, for example at 5 atmospheres gauge and 150° C., in once to twice the amount of aqueous starting solution, and can be used as additions after insoluble material has been filtered off and water removed. The small amount of organic compounds which is recycled in this way is not troublesome.

The invention is illustrated by the following example.

EXAMPLE

When washing with water an oxidation mixture obtained by oxidation of cyclohexane with air, a solution is obtained containing 30% by weight of organic constituents which comprise 38% by weight of epsilon-hydroxycaproic acid (present in monomeric form, in polymeric form or as hydroxycaprolactone), 2% by weight of monocarboxylic acids (acetic acid, caproic acid and valeric acid), 40% by weight of dicarboxylic acids (adipic acid, glutaric acid and succinic acid), 3% by weight of keto acids, mainly laevulinic acid, and 17% by weight of unknown condensation products. This aqueous solution is first substantially freed from water at atmospheric pressure by heating to 150° C., acetic acid and traces of cyclohexanol and cyclohexanone distilling off with the steam. 1,000 g. of the concentrate thus obtained is heated to 220° C. while gradually decreasing the pressure. 83 g. of an aqueous distillate distils over up to 200° C. and at a pressure of down to 20 mm. Hg. In the range up to 220° C. and a pressure decrease to 5 mm. Hg, another 69 g. of organic products distil over. They comprise 27.8% by weight of epsilon-hydroxycaprolactone, 26.5% by weight of keto acids (mainly laevulinic acid) and succinic anhydride with a small amount of adipic acid.

10% by weight of 85% phosphoric acid is added to the practically anhydrous residue and then the solution is distilled at 5 mm. Hg and 214° C. The vapor is first passed through a cooler cooled with boiling xylene where mainly high boiling point dicarboxylic acids are condensed. In a second cooler charged with cooling water at room temperature, a fraction condenses consisting mainly of lactones. From 3,000 g. of the practically anhydrous residue there are obtained by the addition of 300 g. of 85% phosphoric acid the following fractions: 1,050 g. of lactone fraction (containing 75% of lactones and 20% of hexenoic acid; the remainder is glutaric anhydride, glutaric acid and adipic acid); 790 g. of a dicarboxylic acid fraction (adipic acid and glutaric acid); 270 g. of readily volatile constituents, including cyclohexene, cyclopentanone and water (separated by strong cooling upstream of the vacuum pump. Any CO_2 formed is sucked off by the vacuum pump).

A residue of 1,130 g. remains in the evaporator. It is liquid. If it is mixed while heating to 150° C. at 5 atmospheres gauge with an equal amount of aqueous washing solution such as has been used as starting material the major portion dissolved and 90% of the phosphoric acid is found in this solution. After this solution has been dehydrated it is used again as an addition of phosphoric acid. The insoluble residue (320 g.) becomes solid at temperatures of about +10° C., is soluble in acetone but cannot be hydrolized with caustic soda solution. 50 g. of water is

added to the lactone fraction (1,050 g.) and the whole heated to 80° C. in order to convert the anhydrides into acids. The lactones are separated from the high boiling point dicarboxylic acids by rapid distillation at 10 mm. Hg and temperatures of up to 130° C. 525 g. of epsilon-caprolactone, 210 g. of γ-ethyl-γ-butyrolactone and 53 g. of δ-methyl-δ-valerolactone are recovered in pure form from this lactone fraction by rectification.

The dicarboxylic acid fraction is dissolved in an equal weight of hot xylene. Adipic acid crystallizes out upon cooling. 70% of the dicarboxylic acid fraction is recovered as pure adipic acid. Small amounts of adipic acid, glutaric acid, lactone and impurities remain in the mother liquor.

We claim:

1. An improved process for recovering epsilon-caprolactone and alkane dicarboxylic acids from solutions which are formed by washing mixtures obtained in the oxidation of cyclohexane with air at elevated temperatures and at superatmospheric pressures with water or weakly alkaline solutions, said formed solutions containing monocarboxylic acids, dicarboxylic acids, and epsilon-hydroxycaproic acid, said improved process comprising: distilling off substantially all of any water present in the washing solution together with the major part of any monocarboxylic acids that are present; heating the residue and from 1 to 30% by weight, with reference to the residue, of at least one member of the group consisting of phosphoric acid, phosphorus pentoxide, and boric acid, to a temperature of from 180° to 250° C. at a pressure of 1 to 20 mm. Hg, whereby the volatile constituents in the residue are distilled off; and thereafter fractionally condensing the vapor to obtain a fraction containing mainly epsilon-caprolactone and a fraction containing mainly alkane dicarboxylic acids.

2. A process as claimed in claim 1, wherein the fraction containing mainly epsilon-caprolactone is subsequently rectified at a temperature up to 150° C.

3. A process as claimed in claim 1, wherein the fraction containing mainly alkane dicarboxylic acids is crystallized.

4. A process as claimed in claim 1 wherein the amount of acid added to said residue is from 5 to 10% by weight based on the weight of the residue.

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