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OXIDATION OF CYCLIC COMPOUNDS

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This invention relates to the production of aliphatic dibasic acids and more particularly to the production of aliphatic dibasic acids by oxidation of cyclic saturated hydrocarbons with an oxygen-containing gas.

Processes have previously been proposed for the oxidation of cyclic saturated hydrocarbons, but these proposals have been directed toward production of cyclic partial oxidation products. If, in fact, under the conditions specified in the art, an attempt is made to continue the oxidation beyond the partial oxidation stage, I have observed that excessive oxidative degradation occurs with loss of carbon as CO_2 and CO and formation of a very complex mixture of oxidation products.

It is an object of the present invention to provide a process for the controlled oxidation of cyclic saturated hydrocarbons, particularly cyclohexane, cyclopentane, cyclobutane and their substituted derivatives, to aliphatic dibasic acids.

It is a further and more specific object of the present invention to provide a new and improved process for the production, from cyclic saturated hydrocarbons, of dibasic acids containing the same number of carbon atoms as the hydrocarbon treated, and more particularly to obtain adipic acid from cyclohexane, substituted adipic acids from the homologs of cyclohexane, glutaric acid and substituted glutaric acids from the corresponding cyclopentanes, and succinic acid or substituted succinic acids from the corresponding cyclobutanes.

Other objects and advantages of the present invention will be apparent by reference to the following specification.

I have found that simultaneous oxidation and ring cleavage of cyclic saturated hydrocarbons with production in good yield of aliphatic dibasic acids of the general formula $\text{COOH}(\text{CH}_2)_X\text{COOH}$ wherein X is an integer of from 2 to 4 inclusive can be accomplished by subjecting the said hydrocarbons to oxidation in the liquid phase by means of an oxygen-containing gas, for example oxygen or air or air enriched with oxygen.

In this manner it is possible to oxidize saturated cyclic hydrocarbons, such as cyclohexane, cyclopentane, cyclobutane and the like or homologs such as the methyl-, dimethyl-, ethyl- or like substituted cyclic hydrocarbons, with production of aliphatic dibasic acids such as glutaric, succinic or the corresponding adipic acids. Although dibasic acids of a smaller number of carbon atoms than the hydrocarbon treated may be formed, I have found that the conditions

may be so controlled that the dibasic acids produced are predominantly of the same number of carbon atoms as the original hydrocarbons. Thus, while my process may be carried out at various temperatures ranging upward from about 60°C. to about 160°C. , generally speaking the use of the lower temperatures, e. g., not in excess of about 120°C. , tends, other conditions remaining the same, to give less of partial oxidation products (cyclic alcohols and ketones), less loss of carbon to oxides of carbon, and a higher proportion of dibasic acids of the same number of carbon atoms as the hydrocarbons oxidized.

I have further discovered three factors which, all taken together, produce the optimum result but which, nevertheless, individually contribute to an improved result as will appear hereinafter. Each of these factors, or methods, facilitate oxidation at low temperatures, improved results are obtained when any two of them are employed and the best results are secured when all three methods are used simultaneously. These factors exert their favorable influence upon the oxidation, whether dibasic acids generally are being produced or whether dibasic acids of the same number of carbon atoms as the parent hydrocarbon are the predominant dibasic acids in the final product.

As one of the three factors previously mentioned, I have found that the yields of dibasic acid produced according to my invention may be considerably increased by carrying on the oxidation in the presence of an oxidation catalyst, such, specifically as the solid polyvalent metals having an atomic weight between about 50 and about 200. For example, I may use such metals in the finely divided metallic state or as organic and inorganic salts or oxides including such specific metals as cerium, cobalt, copper, manganese, and uranium, with or without inorganic acids such as nitric, phosphoric and hydrochloric acids or mixtures of any two or more of these substances. As specific catalysts under the above description there may be employed vanadium, cerium and cobalt chlorides, manganese acetate alone or together with barium acetate, barium or cobalt permanganate, sodium cobalt nitrite or mixtures of two or more of such compounds. In addition to the oxidation catalysts, promoters such as the alkali and alkaline earth metals may also be employed, if desired, such, for example as the barium, magnesium and potassium acetates, butyrates, propionates, and the like.

I have also found that enhanced yields of

aliphatic dibasic acids are obtained if the oxidation is carried on in the presence of a solvent for the hydrocarbons. Various liquids substantially inert to the oxidation and capable of dissolving the hydrocarbons such as carbon tetrachloride and benzene can be used, but I prefer to use as solvent an organic acid, such as acetic, propionic, butyric, trimethyl acetic and isobutyric, such aromatic acids as phenyl acetic, such hydroxy acids or derivatives as methoxy acetic, and the like. Varying proportions of these acids, based upon the weight per cent present in the saturated cyclic hydrocarbon being oxidized, may be utilized, such as from 1 to 99 per cent by weight although I prefer to utilize about 37 to 80 per cent. Within these indicated ranges I have found that the solvents effect a considerable increase in the yield of dibasic acid obtained by oxidation of the hydrocarbon.

As a further feature of the invention I have found that, especially when operating at the lower temperatures, say 120° or below, the yields and efficiency of the process may be even further improved by carrying on the oxidation, whether with or without the solvents referred to, in the presence of one or more "initiators", which term I employ herein to designate substances capable of initiating attack on the hydrocarbon molecule which may not readily react with molecular oxygen under my preferred low temperature conditions. For example, there may be employed inorganic peroxides, such as sodium or hydrogen peroxide; organic peroxides, such as benzoyl peroxide; peracids, such as peracetic and perbenzoic acids, the aldehydes, such as acetaldehyde, propionaldehyde, and isobutyraldehyde; ketones, such as acetone, methyl ethyl ketone, diethyl ketone, and cyclohexanone; ethers, such as diisopropyl, diethyl and diamyl ethers; olefins, such as cyclohexane and octylene, and, in fact, any organic compound which tends to form peroxide bodies under the reaction conditions.

The initiator may be added to the reactants at the start or continuously during the oxidation or both; or, if preferred, the oxidation may be begun at a temperature and pressure at which partial oxidation products, capable of being oxidized to or acting as oxygen carriers are formed, and the partially oxidized hydrocarbons thus produced may thereafter act as an oxygen carrier capable of attacking other hydrocarbon molecules at the relatively low temperatures which I have generally outlined and will hereinafter more specifically describe. The constant maintenance of a concentration of initiator is important, however, and therefore, in general, I deliberately add the initiator to the reactants as described hereinafter. The oxygen carrier is thus able to initiate the oxidation which then may become at least partially self-sustaining at temperatures very much lower than otherwise possible.

The proportions of initiators which are desirable according to this invention range from about 0.1 to 10 per cent based upon the weight of the hydrocarbon being treated. I do not wish to be restricted to these proportions, however, for I have found that as much as 50 per cent initiator may be utilized without deleterious effect upon progress of the oxidation and at the same time as low as 0.05 per cent initiator may be employed with an increased efficiency and yield of dibasic acid. Although primarily applicable to ketones such as acetone, dimethyl or methyl ethyl ketones, or cyclohexanone, or mixtures thereof, these ranges describe satisfactorily the amounts

of other initiators which are suitable according to my invention.

While the process is operable at ordinary pressures I prefer to use elevated pressures ranging upwards from about 2 atmospheres to about 100 atmospheres. Higher pressures, for example as much as 1000 atmospheres, may be used. The minimum pressure is that required to permit effecting the reaction in the liquid phase, by which is meant that the hydrocarbon is preferably oxidized in the liquid or dissolved state. Pressures in excess of this minimum may be used, however, since pressure has been found to favor the reaction rate.

Having described separately some of the features of my invention, the following description will illustrate by example of cyclohexane oxidation how these features may be combined for oxidation of saturated cyclic aliphatic compounds generally.

Example 1

A mixture containing 422 g. cyclohexane, 247 g. acetic acid, 10.5 g. cyclohexanone, 0.033 g. cobalt chloride hexahydrate, and 0.5 g. hydrogen chloride is charged into a tantalum lined converter of 1000 cc. capacity, provided with suitably valved gas outlet and inlet lines at top and bottom, respectively. The mixture is heated to 94°, and air is introduced through the inlet line at the base of the converter until the pressure reaches 10 atmospheres. Air is then bubbled through the mixture for 4.0 hours at the rate of 300 liters per hour, the pressure being maintained at 10 atmospheres and the temperature at 94-120°. The exit gas is directed through a condenser, and then through a series of cold ethyl benzene traps to scrub out most of the cyclohexane vapor. Solid adipic acid may be removed from the converter and recovered, for example, by cooling the final product to crystallize the adipic acid or by distillation of the other products from the adipic acid. The total weight of cyclohexane recovered is 311.2 g. Cyclohexane lost by vaporization is found to be 10.9 g. The weight of cyclohexane oxidized is, therefore, 99.9 g. The residue obtained after recovery of cyclohexane and acetic acid is steam distilled for recovery of cyclohexanol, cyclohexanone (1.8 g.) and cyclohexyl acetate (5.7 g.). This leaves in the stillpot an aqueous mixture containing non-volatile cyclohexyl esters, lactone compounds, and dibasic acids. To this mixture 5 g. sulfuric acid is added, and the steam distillation is continued, liberating sufficient cyclohexanol to bring the total to 11.9 g. The sulfuric acid in the distillation residue is removed from the hot solution as barium sulfate. Upon filtration a clear solution is obtained. Chilling this filtrate causes the precipitation of 84.5 g. pure adipic acid, or a yield of 48.7 per cent based on the cyclohexane oxidized.

Example 2

A mixture containing 520 grams cyclohexane, 296 grams acetic acid, 13.9 grams cyclohexanone, .0596 grams of a mixture of copper, acetate, cobalt acetate, and manganese acetate, was charged into a stainless steel converter of 1000 cc. capacity. The mixture was heated to 104° C., and air introduced through an inlet line at the base of the converter until the pressure reached 10 atmospheres. Air was then bubbled through the mixture for 2.0 hours at the rate of 288 liters per hour. Temperature of the reaction was maintained at 100-104° C. Adipic acid was removed from the converter and recovered by cooling the

final product to crystallize the adipic acid. The yield of adipic acid based upon the cyclohexane oxidized was 46.0%.

Example 3

A mixture containing 537 grams cyclohexane, 308 grams acetic acid, 13.79 grams cyclohexanone, and 0.043 grams cobalt acetate was charged into an aluminum converter of 1000 cc. capacity. The mixture was heated to 125° C., and air was introduced through an inlet line at the base of the converter until the pressure reached 10 atmospheres. Air was then bubbled through the mixture for 5.75 hours at the rate of 225 liters per hour. Temperature of the reaction was maintained at 103–125° C. Adipic acid was removed from the converter and recovered by cooling the final product to crystallize the adipic acid. The yield of adipic acid based upon the cyclohexanone oxidized was 23.0%.

It will be understood that some variation in the yield of dibasic acids is to be expected depending upon the specific conditions employed. For example, continuation of the oxidation beyond the times stated in the examples tends to greater formation of oxides of carbon, while shorter times of contact favor a greater production of intermediate oxidation products, such as cyclic alcohols and ketones.

Although specific disclosure has been made in the examples of methods for carrying on my invention in a batch process, it should be understood that this invention may also be practiced in a continuous manner. Thus, after completion of the adipic acid or other dibasic acid production, such as shown in the specific examples, the materials (cyclic hydrocarbon, alcohol and ketone) capable of being converted to the desired dibasic acid, plus the catalyst, solvent, and initiator may be recovered and recycled to the reaction zone together with further quantities of cyclic hydrocarbon. In a continuous process it will also be found desirable to make such additions of catalyst, solvent, and initiator as will maintain the reaction rate and yield of dibasic acid at the desired high degree.

While the process as described in the examples involves passage of the oxidizing gas through a body of liquid, it will be understood that other means of assuring the desired liquid-gas contact may be employed, as, for example, passage of liquid and gas co-current or counter-current through a tube or tower, which may be supplied with plates, packing or other devices for enhancing contact.

I claim:

1. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of an oxidation catalyst.

2. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of a solvent for the hydrocarbon which is substantially inert to the reaction, and in the proportions of from 1 to 99% by weight.

3. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the pres-

ence of an oxidation initiator of the group consisting of peroxides and compounds which form peroxides under the reaction conditions.

4. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of an organic acid solvent for the hydrocarbon and an oxidation catalyst.

5. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of acetic acid solvent for the hydrocarbon and an oxidation catalyst.

6. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of an organic acid solvent for the hydrocarbon, a ketone and an oxidation catalyst.

7. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of acetic acid solvent for the hydrocarbon, a ketone and an oxidation catalyst.

8. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of acetic acid, a ketone and an oxidation catalyst comprising a mixture of cobalt, copper and manganese acetates.

9. A method of producing adipic acid which comprises subjecting cyclohexane, in the liquid phase, and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of an oxidation catalyst.

10. A method of producing adipic acid which comprises subjecting cyclohexane, in the liquid phase, and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of a solvent for the cyclohexane which is substantially inert to the reaction and an oxidation catalyst.

11. A method of producing adipic acid which comprises subjecting cyclohexane, in the liquid phase, and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of acetic acid and an oxidation catalyst.

12. A method of producing adipic acid which comprises subjecting cyclohexane, in the liquid phase, and at a temperature of at least 60° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% by weight of an organic acid, from 0.05 to 50% by weight of an oxidation initiator of the group consisting of peroxides and compounds which form peroxides under the reaction conditions.

13. A method of producing adipic acid which comprises subjecting cyclohexane, in the liquid phase, and at from about 80 to about 120° C. to oxidation by means of an oxygen-containing gas

in the presence of from 1 to 99% of acetic acid, 0.05 to 50% by weight of cyclohexanone and an oxidation catalyst.

14. A method of producing adipic acid which comprises subjecting cyclohexane, in the liquid phase, and at from about 80 to about 120° C. to oxidation by means of an oxygen-containing gas in the presence of from 1 to 99% of acetic acid, 0.05 to 50% by weight of cyclohexanone and an oxidation catalyst comprising a mixture of cobalt, copper and manganese acetates and separating adipic acid from the reaction mixture.

15. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C., to oxidation by passage therethrough of an oxygen-containing gas in the presence of from 1 to 90% by weight of a solvent for the hydrocarbon substantially inert to the reaction.

16. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C., to oxidation by passage therethrough of an oxygen-containing gas in the presence of from 37-80% by weight of

a solvent for the hydrocarbon which is substantially inert to the reaction.

17. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C., to oxidation by passage therethrough of an oxygen-containing gas in the presence of from 0.05 to 50% by weight of an oxidation initiator of the group consisting of peroxides and compounds which form peroxides under the reaction conditions.

18. A method of producing aliphatic dibasic acids which comprises subjecting a saturated cyclic hydrocarbon, in the liquid phase and at a temperature of at least 60° C., to oxidation by passage therethrough of an oxygen-containing gas in the presence of from 1-99% by weight of a solvent for the hydrocarbon which is substantially inert to the reaction, from 0.05 to 50% by weight of an oxidation initiator selected from the group consisting of peroxides and compounds which form peroxides under the reaction conditions, and in the presence of an oxidation catalyst.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 46, for "actate" read --acetate--; page 3, second column, line 71, claim 12, after "conditions" and before the period insert --and an oxidation catalyst--; page 4, first column, lines 1 and 8, claims 13 and 14 respectively, after "99%" insert the words --by weight--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of February, A. D. 1941.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.