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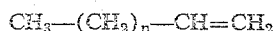
ALIPHATIC ACID PROCESS

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This invention relates to a process by which an alkene-1 hydrocarbon is oxidized with molecular oxygen to produce an aliphatic monocarboxylic acid product and more specifically pertains to the oxidation of certain alkene-1 hydrocarbons to aliphatic monocarboxylic acid products containing an aliphatic monocarboxylic acid and a keto derivative thereof of one less carbon atom than in the alkene-1 hydrocarbon.

Many processes have been proposed for the oxidation of aliphatic hydrocarbons to produce aliphatic monocarboxylic acids by subjecting the aliphatic hydrocarbon in a liquid phase to oxidation with molecular oxygen. By these processes acidic oxidation products result. The oxidation products have generally been mixtures of aliphatic monocarboxylic acids of varying chain length and in some cases are even aliphatic dicarboxylic acids. When saturated paraffinic hydrocarbons are oxidized in a catalytic liquid phase system under selected temperature conditions and controlled rate of addition of molecular oxygen, in general, these processes produce mainly carbon monoxide, carbon dioxide, water, formic acid and acetic acid. In many of the processes for oxidizing aliphatic hydrocarbons in the liquid phase with air, especially where monocarboxylic acids were produced, the acidic products were formed in admixture with dark-colored resinous polymerized materials which precluded recovery of the desired acids as satisfactory, useful products. To avoid the formation of such contaminants, low oxidation temperatures and low conversions were suggested to obtain only partial oxidation of the aliphatic hydrocarbon feed stock. However, the use of either or both of these means to avoid the dark-colored high molecular weight contaminants markedly reduces the reaction rates, thus resulting in relatively long reaction periods. The use of various special catalyst, promoters and special apparatus, together with the selected operating conditions, have been proposed to obtain especially long chain aliphatic monocarboxylic acids. However, no commercial process is available for producing and readily recovering relatively long chain aliphatic monocarboxylic acids by the oxidation of aliphatic hydrocarbons with air in a liquid phase process.

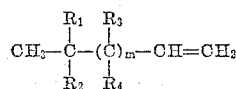
It has now been discovered that an alkene-1 hydrocarbon containing 3 to 20 or more carbon atoms can be oxidized in a liquid phase with molecular oxygen in the presence of a catalyst comprising bromine and a heavy metal catalyst to produce a normal aliphatic monocarboxylic acid product containing one less carbon atom than present in the alkene-1 hydrocarbon. When the alkene-1 hydrocarbon is a normal alkene-1 containing at least five carbon atoms, there is produced a mixture containing the normal aliphatic monocarboxylic acid of one less carbon atom and a keto, i.e., acetyl, derivative thereof. Alkene-1 hydrocarbons of less than five carbon atoms; i.e., two to four carbon atoms oxidize to produce normal aliphatic monocarboxylic acids as the product. Thus, when normal alkene-1 hydrocarbons,



wherein n is a number of from 0 to 17 or higher, are oxidized, the aliphatic monocarboxylic acid product is, when n is 0, acetic acid; n is 1, propionic acid; n is 2, n-butyric acid and acetyl acetic acid; n is 3, n-valeric

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acid and 3-acetyl propionic acid; n is 4, n-hexanoic acid and 4-acetyl butyric acid; n is 5, n-heptanoic and 5-acetyl pentanoic acid; etc. Branched chain alkene-1 hydrocarbons having the formula:



wherein R_1 , R_2 , R_3 and R_4 are hydrogen or methyl and at least one of R_1 or R_2 or R_3 or R_4 is methyl and m is a number from 0 to 16 or higher; i.e., a branched chain alkene-1 hydrocarbon containing five or more carbon atoms can also be oxidized according to the process of this invention to aliphatic monocarboxylic acid products containing the aliphatic monocarboxylic acid of one less carbon atom than the alkene-1. When both R_1 and R_2 are hydrogen, then a keto aliphatic acid will also be formed. Accompanying by-products of the oxidation are carbon monoxide, carbon dioxide, water, formic acid and acetic acid. Since acetic acid and propionic acid are readily available from other processes, the process of this invention is preferably carried out with normal alkene-1 hydrocarbons and their methyl substituted derivatives which contain a terminal $-\text{CH}=\text{CH}_2$ group as the feed stock to be oxidized. These alkene-1 hydrocarbons will contain five or more carbon atoms. The alkene-1 hydrocarbons containing both a CH_3-CH_2 group and a $-\text{CH}=\text{CH}_2$ group as terminal groups are preferred for the preparation of acetyl aliphatic monocarboxylic acids and aliphatic monocarboxylic acids of one less carbon atom than the feed stock alkene-1.

The present process is conducted in the liquid phase at a temperature below 200°C ., preferably at a temperature in the range of about 50 to 200°C . The temperature at which the process is carried out will determine to an appreciable extent the minimum pressure to be employed to maintain the liquid phase of the reaction mixture. The pressure at any specific temperature will be governed by the vapor pressures of the materials in the reaction mixture. When the reaction mixture contains the alkene-1 hydrocarbon, the pressure to be maintained will be that required to keep at least a portion of the alkene-1 in the liquid phase. It is advantageous during the course of the reaction to subject the vapors in contact with the reaction mixture to partial condensation to condense out of said vapors at least the alkene-1 hydrocarbon contained therein. However, there are also advantages in carrying out the process of this invention in the presence of a reaction solvent or diluent. For this purpose any inert solvent may be employed. It is preferred that the solvent or reaction medium dissolve at least a portion of the alkene-1 being oxidized and also dissolve the heavy metal oxidation catalyst. Monocarboxylic acids containing 2 to 8 carbon atoms can be used as reaction solvents or reaction media. Such monocarboxylic acids include benzoic acid and the lower aliphatic monocarboxylic acids such as acetic acid, propionic acid, butyric acid, valeric acid, enanthic acid and caprylic acid. It will be appreciated that many of these acids are produced in the process of this invention. Whether or not the acids used as the reaction solvents or reaction media are produced in the process of this invention, the separation of the desired products from the reaction mixture can be readily accomplished. Because of its resistance to oxidation under the conditions of the process of this invention, acetic acid is the preferred lower aliphatic monocarboxylic acid for use as the reaction solvent or reaction medium.

The use of such a reaction solvent or reaction medium either permits a convenient means for removing heat of reaction since the vaporized reaction solvent can be condensed and returned to the liquid phase or, in the case of

the use of the higher boiling monocarboxylic acids, a lower pressure reaction can be conducted and still maintain the liquid phase.

Air is the most readily available source of molecular oxygen. However, substantially pure oxygen; i.e., commercial oxygen, oxygen plus ozone, mixtures of oxygen and inert gas, and mixtures of air and inert gases can be employed as the source of molecular oxygen for the process of this invention. Molecular oxygen-containing gases having from 5% to 100% oxygen by volume can be employed.

In the practice of this invention the catalyst system comprises bromine and a heavy metal oxidation catalyst. The bromine may be employed as elemental, combined, or ionic bromine. More specifically, as a source of bromine for the catalyst system there may be employed molecular bromine, ammonium bromide, hydrogen bromide, and other bromine-containing compounds soluble in the reaction mixture. Satisfactory results can be obtained, for example, by the use of potassium bromate, tetrabromoethane, benzyl bromide and the like as a source of bromine.

The heavy metal oxidation catalyst portion of the catalyst system employed in the process of this invention includes the heavy metals and derivatives thereof which are soluble in the reaction medium to the extent necessary to provide a catalytically effective amount of the heavy metal oxidation catalyst component. The term "heavy metal" is employed herein in the same sense as employed in connection with the metals shown in the "Periodic Chart of Elements," appearing on pages 56 and 57 of the "Handbook of Chemistry," 8th edition, published by Handbook Publishers, Inc., Sandusky, Ohio (1952). From this group there have been found heavy metal oxidation catalysts desirably applicable to the process of this invention for furnishing the heavy metal oxidation component of the catalyst system. Of the heavy metal group, those metals having an atomic number not greater than 84 have been found most useful. Excellent results are obtained by the utilization of metals having an atomic number of from 23 to 28 inclusive. Particularly excellent results are obtained with a metal of the group consisting of manganese, cobalt, nickel, iron, chromium, vanadium, molybdenum, tungsten, tin and cerium. The catalytic amount of the heavy metal may be provided either by a single metal or a combination of the metals. The heavy metal oxidation catalyst component of the catalyst system in the process of this invention may be provided by the addition of the metal in elemental form, as its oxide or hydroxide, or in the form of a salt of the metal. For example, the metal manganese may be employed as the manganese salt of an organic carboxylic acid, such as manganese naphthenate, manganese toluate, manganese acetate, etc., or in the form of an organic complex, such as the acetylacetonate, the 8-hydroxy-quinolate and the ethylene diamine tetra-acetate, as well as inorganic manganese salts such as the borates, halides and nitrates. The catalyst system may also be provided by the use of a heavy metal bromide or mixtures of heavy metal bromides.

The amount of metal catalyst employed is not critical and may be in the range of about 0.01 to about 10% by weight or more based on the feed stock reactant. Where the heavy metal is introduced as a bromide salt, for example as manganese bromide, the proportions of manganese and bromine will be in their stoichiometric proportions. The ratio of metal to bromine may be varied from such proportions within the range of about 1 to 10 atoms of heavy metal oxidation catalyst per atom of bromine to about 1 to 10 atoms of bromine per atom of heavy metal.

The amount of solvent or reaction medium employed will vary over wide limits as will be readily appreciated by those skilled in the art. The amount of solvent or reaction medium employed is not critical but typically will

be in the range of from about 0.1 to about 10, desirably 0.5 to 4 times the weight of oxidizable feed stock.

In order to facilitate a clear understanding of the invention, the process of this invention is illustrated by the following preferred embodiments described in detail.

Example 1

As an oxidation reactor there is employed a vertical tubular reactor into the bottom of which air or other source of molecular oxygen containing gas can be charged. The bottom of said reactor is also suitably adapted to the removal of the mixture resulting from the oxidation process. The top of the reactor is provided with a means for closing the reactor through which is connected a vapor line for transfer of vapors to a condenser from which condensate may be recycled to the reaction zone. A condenser is provided with means for removing the uncondensed materials through a pressure regulating valve with which the reaction pressure is maintained to obtain a liquid phase throughout the reaction. The reactor is constructed of corrosion-resistant material such as highly corrosive resistant alloys, or is glass-lined. To such a reactor there is charged a mixture containing 112.2 grams (1 mole) of 1-octene, 120.1 grams (2 moles) glacial acetic acid and 10 milliliters of an aqueous solution containing cobalt acetate and manganese acetate, each in a 0.25 molar concentration. There is also added 1.0 milliliter of 5 molar ammonium bromide dissolved in water. The resulting mixture is heated to 170° C. in the presence of sufficient nitrogen so that the resulting pressure is 400 p.s.i.g. Air at a pressure of about 400 p.s.i.g. is introduced into the reactor at a flow rate of about 3 liters per minute. After 5 hours of air addition, the reactor contents are cooled and distilled.

As a first fraction there are collected all materials boiling up to 50° C. at 140 mm. Hg. This mixture contains primarily formic acid, acetic acid and water. The total amount of acetic acid collected in this mixture is 128 grams.

As a second fraction there is collected material boiling in the range of 63° C. at 2.2 mm. Hg to 94° C. at 1.8 mm. Hg. This fraction when redistilled has a boiling point of 206–203° C. and has a refractive index of n_D^{20} of 1.4218. This second fraction is n-heptanoic acid for which the literature reports a boiling point of 202° C. and a refractive index of $n_D^{19.8}$ of 1.4216.

As a third fraction there is collected material boiling at 121–143° C. at 1.7 mm. Hg. This material has a refractive index of n_D^{20} of 1.4464. Analysis of this material (third fraction) shows 60.0% carbon and 9.4% hydrogen. The neutral equivalent of this fraction is 146. Acetyl pentanoic acid has a calculated neutral equivalent of 145 and a calculated carbon and hydrogen content of 58.0% and 9.0%, respectively. The third fraction is substantially all 5-acetyl pentanoic acid.

Only a small amount of residue remains, about 7.3 grams, which was not further characterized.

When the process of the foregoing example is carried out at a temperature of 150° C., the yield of n-heptanoic acid is increased, and the yield of the keto-acid is decreased. By carrying out the process of the foregoing example at a temperature of about 180 to 185° C., the yield of the keto-acid is increased while the yield of n-heptanoic acid is decreased.

The use of manganese bromide in place of ammonium bromide in the process of the foregoing example in an amount to provide an equivalent amount of metal will produce substantially equivalent results. Also in place of employing both manganese acetate and cobalt acetate there may be employed either manganese acetate or cobalt acetate. Other members of the heavy metal oxidation catalyst can be employed to produce substantially the same results.

As additional feed stocks of the process of this invention there may be specifically employed 1-hexene, 3,3-dimeth-

yl hexene-1, 1-decene, 1-hexadecene, 1-heptadecene, and the like.

What is claimed is:

1. A process for the preparation of saturated normal aliphatic monocarboxylic acid products of from 4 to 19 carbon atoms which comprises oxidizing in the liquid phase an alkene-1 hydrocarbon containing 5 to 20 carbon atoms with molecular oxygen at a temperature in the range of 50° to 200° C. in the presence of a catalyst consisting essentially of bromine and a heavy metal oxidation catalyst and distilling the resulting reaction mixture to recover the resulting saturated normal aliphatic monocarboxylic acids.

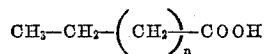
2. The process of claim 1 wherein air is the source of molecular oxygen.

3. A process for the preparation of saturated normal aliphatic monocarboxylic acid products of from 4 to 19 carbon atoms which comprises oxidizing in the liquid phase an alkene-1 hydrocarbon containing 5 to 20 carbon atoms with molecular oxygen at a temperature in the range of 50° to 200° C. in the presence of a monocarboxylic acid of from 2 to 8 carbon atoms selected from the class consisting of benzoic acid and lower alkanolic acids and in the presence of a catalyst consisting essentially of bromine and a heavy metal oxidation catalyst and distilling the resulting reaction mixture to recover the resulting saturated normal aliphatic monocarboxylic acids.

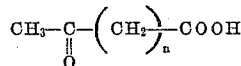
4. A process for the preparation of saturated normal aliphatic monocarboxylic acid products of from 4 to 19 carbon atoms which comprises oxidizing in the liquid phase an alkene-1 hydrocarbon containing 5 to 20 carbon atoms with molecular oxygen at a temperature in the range of 50° to 200° C. in the presence of acetic acid and in the presence of a catalyst consisting essentially of bromine and a heavy metal oxidation catalyst and distilling the resulting reaction mixture to recover the resulting saturated normal aliphatic monocarboxylic acids.

5. The process for the preparation of a mixture of normal aliphatic monocarboxylic acid products contain-

ing a normal aliphatic monocarboxylic acid and a keto derivative thereof having the respective formulae:



and



wherein n is an integer of from 1 to 16 by oxidizing in the liquid phase an alkene-1 hydrocarbon containing 5 to 20 carbon atoms with molecular oxygen at a temperature of from about 50° C. to about 200° C. in the presence of acetic acid and in the presence of a catalyst consisting essentially of bromine and a heavy metal oxidation catalyst, distilling the resulting reaction mixture to remove a mixture containing acetic acid and low boiling reaction by-products, which mixture is characterized by boiling up to 50° C. at 140 mm. Hg. and recovering from the residue said aliphatic acid and its keto derivative.

6. The process for preparing heptanoic acid and 5-acetyl pentanoic acid comprising oxidizing octene-1 in the liquid phase with air in the presence of acetic acid and in the presence of a catalyst consisting essentially of bromine and a heavy metal oxidation catalyst at a temperature of from about 50° to about 200° C., distilling the resulting reaction mixture to remove a mixture characterized by boiling up to 50° C. at 140 mm. Hg. and containing acetic acid, formic acid and water, and distilling the residue to recover heptanoic acid and 5-acetyl pentanoic acid as separate products.

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