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PREPARATION OF POLYCARBOXYLIC ACIDS

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The present invention relates to a process for the preparation of carboxylic acids, and more particularly to an improved process for the preparation of polycarboxylic acids by oxidation of readily available hydrocarbon materials.

Aliphatic dibasic acids have been prepared heretofore by oxidation of hydrocarbon materials such as relatively long chain paraffins (i. e., oils, waxes) or cycloparaffins having about 4–12 carbon atoms. The prior art processes, in general, comprise treating the foregoing types of hydrocarbons directly with an oxidizing agent such as oxygen or oxygen-containing gas, nitric acid, potassium permanganate, and potassium chromate, usually at an elevated temperature of about 212° F. or higher and under atmospheric to superatmospheric pressure. The oxidation step has been modified by varying conditions such as reaction time, temperature and pressure, or by using a combination of oxidizing agents, such as partial air oxidation followed by a final oxidation step with nitric acid.

The foregoing prior art processes are not entirely satisfactory for a number of reasons, among the more important reason being the extremely low yield of a given polycarboxylic acid obtainable heretofore by oxidation of paraffins. The cycloparaffins usually give better yields of polycarboxylic acids than the open-chain paraffins but have the disadvantage of being difficult to procure in large volume and at a competitive price. Paraffins such as oils and waxes are readily available from petroleum sources in almost unlimited quantities and at very low cost. Thus it will be readily apparent to those skilled in the art that it would be advantageous, particularly from an economic standpoint, to provide a process for producing aliphatic polycarboxylic acids in improved yield from low cost paraffins.

It is an object of the present invention to provide an improved process for producing polycarboxylic acids from hydrocarbon materials.

It is a further object of the present invention to provide a process for producing aliphatic dibasic acids from a wide variety of hydrocarbon starting materials.

It is still a further object of the present invention to provide an improved process for producing succinic acid and its simple derivatives from hydrocarbons derivable from petroleum sources.

Still other objects of the present invention and the attendant advantages thereof will be apparent to those skilled in the art by reference to the following detailed description.

Broadly stated, I have discovered that if a wide variety of essentially paraffinic hydrocarbon materials having a carbon chain of a length greater than four carbon atoms are first treated with a suitable sulfurizing agent under conditions which will introduce sulfur into the hydrocarbon molecule, the sulfurized hydrocarbon derivative thus produced may be reacted with well known oxidizing

agents of the prior art to produce aliphatic polycarboxylic acids in improved yield.

While almost any aliphatic hydrocarbon having a carbon chain of a length greater than four carbon atoms is suitable as a starting material, the preferred starting materials for economic reasons are those derived from petroleum sources such as heavy distillate, heavy oils of the lube stock type, other very viscous petroleum distillates, and waxes. These preferred starting materials are essentially paraffinic in nature, but in some instances materials known to contain considerable quantities of cyclic hydrocarbons having an aliphatic side chain suitable for sulfurizing and oxidizing in accordance with the process of the invention may be used.

The introduction of sulfur into the hydrocarbon molecule may be accomplished by reacting the hydrocarbon with a number of suitable sulfurizing agents such as sulfur, sulfur monochloride, sulfur dichloride, or the phosphorus sulfides. The sulfurizing treatment preferably should be carried out at temperatures sufficiently elevated to cause the evolution of a gas such as hydrogen sulfide, but below the cracking temperature of the particular hydrocarbon. Temperatures between 200° F. and 600° F. are found to be generally suitable in most instances. The time required to effect the sulfurizing treatment will vary somewhat depending upon the temperature and other factors, but preferably should be such as to effect the combination of a substantial amount of sulfur with the hydrocarbon. A sulfurized hydrocarbon product containing 0.5–10% by weight sulfur has been found to give a very satisfactory yield of polycarboxylic acids on oxidation. However, a higher sulfur content may be present in some instances and may be preferred for a particular starting material.

Oxidation of the sulfurized hydrocarbon product may be effected by a number of suitable well known oxidizing agents such as nitric acid, potassium permanganate, potassium chromate, and oxygen or oxygen-containing gas. The reaction time and temperature for the oxidation step will vary with the nature and strength of the specific reagent selected. Generally satisfactory conditions for the oxidation step are a reaction temperature of about 212° F. or at about reflux temperature, and a reaction time of from several hours up to 48 hours and longer in some instances. Oxidation with nitric acid at reflux temperature and for a period of from several hours up to 48 hours is preferred in most instances. Where an oxidation with nitric acid appears in the specification and claims, it is understood that the oxides of nitrogen are also intended to be included.

I prefer to treat paraffin waxes or heavy oils of the lube stock type with elemental sulfur at a temperature varying between 200–500° F., depending upon the nature of the particular starting material, for not more than 8–12 hours. The temperature should be sufficiently high to cause evolution of hydrogen sulfide from the reactants, and the reaction preferably should not be continued for an extended period of time after evolution of hydrogen sulfide has sharply diminished. The sulfurized hydrocarbon product thus produced may be oxidized with concentrated nitric acid at an elevated temperature up to reflux temperature for about 32–48 hours. The reaction mixture then may be vacuum distilled to remove most of the unreacted nitric acid and water, and any traces of nitric acid remaining in the crude oxidation product may be destroyed by a suitable reducing agent such as the alkali metal sulfites or sulfur dioxide. Small quantities of water remaining in the crude oxidation product may be removed by azeotropic distillation with heptane, mineral spirits, or other suitable solvent.

One method for obtaining aliphatic dibasic acids in pure form from the crude anhydrous oxidation product obtained as outlined above comprises esterifying the acidic material with a lower alcohol, such as butyl alcohol. The butyl esters of dibasic acids having up to about 8 carbon atoms then may be separated by vacuum distillation and are frequently obtained sufficiently pure for use directly as plasticizers without further purification. The low molecular weight dibasic acids also may be separated from the crude anhydrous oxidation product by sublimation or distillation at very low pressure, such as at a pressure of about 4 mm. of mercury.

The following examples further illustrate the process of the present invention.

Example I

A heavy oil was obtained from petroleum asphalt by propane deasphaltizing. Such heavy oils are particularly known to the art as asphaltic oil and are essentially paraffinic in nature but may contain minor quantities of cyclic hydrocarbons which have paraffinic side chains containing as many as 4 or more carbon atoms, as well as other cyclic hydrocarbon material.

A 600 g. sample of the above prepared asphaltic oil dissolved in sufficient pentane to give a very fluid mixture was slowly introduced beneath the surface of 6 liters of concentrated nitric acid held at its reflux temperature. This reaction mixture was then allowed to react for a period of 36 hours. The reason for diluting the asphaltic oil with pentane was to permit controlled addition to the refluxing nitric acid, and also to provide a ready means for controlling the reaction.

After the reaction was completed, the reaction mixture was distilled at 80° F. and at 40 mm. pressure to remove the unreacted nitric acid and water. The residue was then treated with sodium sulfite and the last traces of water removed by azeotropic distillation with toluene. The crude oxidized product remained as a dry material and was distilled at 1 mm. pressure. The yield of succinic acid recovered from this distillate was 1.61% by weight based on the asphaltic oil starting material.

Example II

A 200 g. sample of asphaltic oil identical with that of Example I was treated with elemental sulfur at a temperature of 500° F. for a period of 6 hours. Evolution of hydrogen sulfide gas had practically ceased at the end of the reaction time and the resulting sulfurized asphaltic oil was a black, soft asphalt-like material.

A 146 g. sample of the above sulfurized asphaltic oil was oxidized at reflux temperature for a period of 32 hours with 600 ml. of concentrated nitric acid. The nitric acid was removed from the reaction mixture by distillation at reduced pressure and last traces of nitric acid were destroyed with sodium sulfite. The crude oxidized product was then thoroughly dried by azeotropic distillation with toluene. The crude dry oxidized product thus obtained was distilled at 1 mm. pressure and the yield of succinic acid recovered from the distillate was 2.8% by weight based on unsulfurized asphaltic oil. A portion of the crude oxidized product was given a second nitric acid oxidation at reflux temperature for a period of 24 hours. The yield of succinic acid from this further oxidation was 3.9% by weight based on unsulfurized asphaltic oil.

Example III

A refined paraffin wax derived from petroleum sources and having a melting point of 155° F. was obtained from the Barnsdall Oil Company, this particular wax being a proprietary product of the Barnsdall Oil Company, referred to as Bareco Victory Wax, and was essentially a mixture of long-chain paraffinic hydrocarbons.

A 50 g. sample of the above wax was oxidized at reflux temperature for a period of 24 hours with 325 parts of concentrated nitric acid. At the end of this 24 hour period, an additional 110 g. of nitric acid was added to the reaction mixture and refluxing continued for an additional 8 hour period. The oxidized reaction mixture was then distilled under vacuum to remove unreacted nitric acid and water present, and finally an oily distillate was obtained. From this oily distillate upon crystallization from cold ether was obtained 8.8% by weight of a material identified as succinic anhydride. The yield was based upon the quantity of paraffin wax used as starting material.

Example IV

A 200 g. sample of paraffin wax identical with that of Example III was treated with 20 g. of sulfur at a temperature of 400–450° F. until the rate of evolution of hydrogen sulfide gas began to decrease. A 50 g. sample of the sulfurized paraffin wax thus produced was oxidized with 315 g. of concentrated nitric acid at reflux temperature for a period of 24 hours, and then an additional 110 g. of concentrated nitric acid was added to the reaction mixture and the oxidation continued for an additional 24 hours. The reaction mixture was distilled at reduced pressure to remove unreacted nitric acid and water, and the distillation was continued at very low pressure to give an oily distillate which upon crystallization from cold ether yielded 11.1%, based on unsulfurized paraffin wax, of a product identified as an aliphatic dibasic acid having a melting point of 295–305° F., and a neutralization equivalent of 66.57. This product depressed the melting point of authentic adipic acid to give a mixture melting at 284–289° F. The product was tentatively identified as being a substituted succinic acid and probably a mixture of dimethyl succinic acids. It is apparent that the product thus obtained was definitely different from that obtained in Example III by paraffin wax oxidation without sulfurization.

The crude oxidized product remaining after the foregoing distillation step was soluble in sodium hydroxide solution and also gave other indications of being a mixture of higher polycarboxylic acids. The yield of such higher polycarboxylic acids is greatly increased by sulfurization prior to oxidation.

The reaction mechanism promoting improved yield of aliphatic dibasic acids by sulfurization of hydrocarbons prior to oxidation is not fully understood at the present time.

The foregoing detailed description and the specific examples are for the purpose of illustrating the present invention, and are not to be taken as limiting to the scope or spirit of the appended claims.

What is claimed is:

1. A process for preparing a succinic acid selected from the class consisting of succinic acid and lower alkyl substituted succinic acids comprising reacting a paraffinic hydrocarbon having a carbon chain of a length greater than four carbon atoms with a sulfurizing agent to produce a sulfurized hydrocarbon product, and then oxidizing the sulfurized hydrocarbon product with an oxidizing agent to produce the succinic acid.

2. The process of claim 1 wherein the sulfurizing agent is elemental sulfur.

3. The process of claim 1 wherein the oxidizing agent is nitric acid.

4. The process of claim 2 wherein the oxidizing agent is nitric acid.

5. A process for preparing a succinic acid selected from the class consisting of succinic acid and lower alkyl substituted succinic acids comprising reacting a paraffinic hydrocarbon having a carbon chain of a length greater than four carbon atoms with a sulfurizing agent to produce a sulfurized hydrocarbon product having a sulfur content of 0.5–10% by weight, and then oxidizing the sulfurized hydrocarbon product with an oxidizing agent to produce the succinic acid.

6. The process of claim 5 wherein the sulfurizing agent is elemental sulfur.

7. The process of claim 5 wherein the oxidizing agent is nitric acid.

8. The process of claim 6 wherein the oxidizing agent is nitric acid.

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