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MANUFACTURE OF CARBOXYLIC ACIDS

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The present invention relates to the manufacture of carboxylic acids. An object of the invention has been to provide a process whereby aliphatic carboxylic acids can be produced by an economical procedure, from raw materials which are readily available in large quantities.

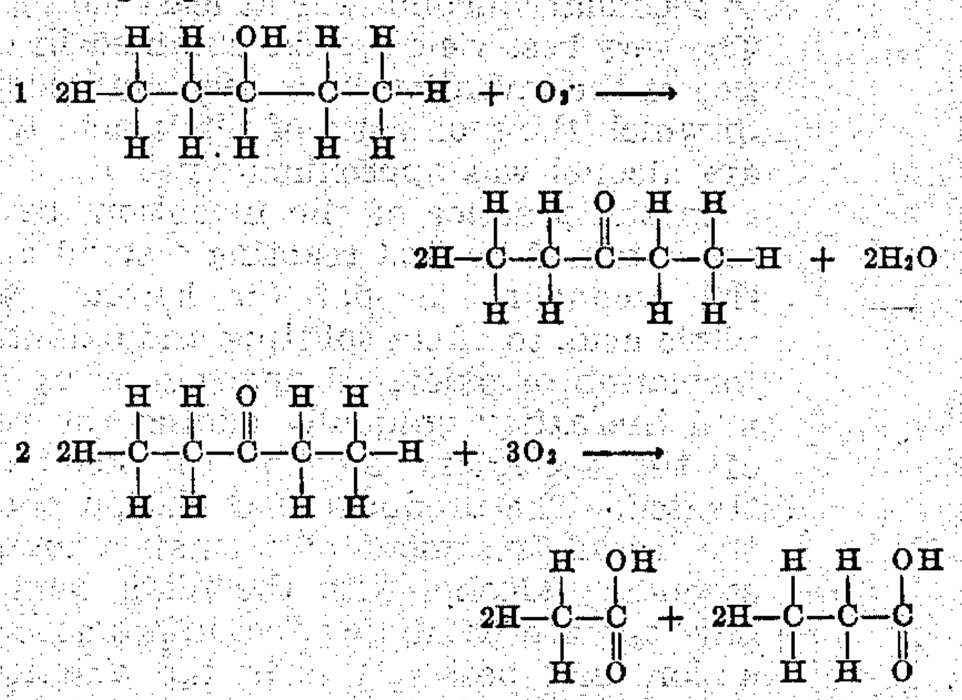
It is well known that primary alcohols may be oxidized to produce acids. When pantanol-1, for example, is oxidized, valeric acid may be obtained together with other oxidation products, and when primary iso-amyl alcohol is oxidized, isovaleric acid is produced among the oxidation products.

The oxidation of a tertiary alcohol is extremely difficult, and when it is effected, ketones and acids are obtained, but the acids so formed are usually oxidized further with the result that the bulk of the alcohol is converted into carbon dioxide and water.

A secondary alcohol cannot be converted into an acid by simple oxidation, and such oxidation, therefore, results in the production of ketones without forming any acid. An object of the present invention has been to provide a process of oxidizing secondary alcohols and ketones to produce carboxylic acids. Since secondary alcohols can be produced in large quantities by the simple hydration of olefins derived from petroleum or other sources, the use of this plentiful and economical source of raw material for the preparation of carboxylic acids affords a highly desirable process.

The present invention is based upon the reaction of a secondary aliphatic alcohol, or an aliphatic ketone, is treated with nitric acid of appropriate concentration, to cause the alcohol or ketones to undergo a series of reactions including scission of the aliphatic hydrocarbon radical at the point of attachment of the hydroxyl radical, or ketone oxygen thereto, and an oxidation at the point of scission to produce two molecules of carboxylic acid from the secondary alcohol or ketone molecule. The alcohol or ketone molecule thus undergoes a combined splitting and oxidation reaction.

Various carboxylic acids, such as acetic, propionic, butyric, valeric, caproic, caprylic, capric, etc., and mixtures of these various acids can be produced by the technique of the invention. Thus, when 3-hydroxy normal pentane is oxidized by means of nitric acid in the practice of the invention, a mixture is obtained containing acetic acid and propionic acid, by scission of the alcohol molecule at the hydroxyl radical and oxidation of the compounds or radicals resulting from such scission. While we do not wish to be limited to any specific theory as to the mechanism of the reactions obtained in the practice of the invention, it is believed that the results obtained may be explained on the basis that the secondary alcohol is first oxidized to produce the corresponding ketone, and that this ketone is then split and oxidized to produce acetic acid and propionic acid simultaneously by oxidation of the compounds or radicals resulting from the splitting operation. If this theory is correct, the reactions involved may be illustrated by the following equations:



While the invention may be practiced to effect simultaneous oxidation and splitting of various secondary alcohols and ketones, containing from 3 to 20 carbon atoms, for example, it will be described (for the sake of simplicity of explanation), in connection with the conditions of temperature, acid concentration, method of purifying the crude reaction mixture, and other details, found to be most suitable for the manufacture of alcohols by performance of combined splitting and oxidation reactions on such alcohols (or ketones) containing between 3 and 8 carbon atoms. Since the application of the principles of the invention to the splitting and oxidation of ketones involves a procedure which is identical to that involved in the treatment of secondary alcohols, except with respect to time of reaction, the invention will be described in its application to the oxidation of secondary alcohols containing between 3 and 8 carbon atoms, with the understanding that similar treatment may be applied to the manufacture of similar acids from ketones of corresponding carbon content, as well as from the corresponding alkyl sulfates. In the treatment of secondary alcohols

in the practice of the invention, the combined splitting and oxidizing reaction referred to above may be accomplished by treatment of the alcohol with nitric acid having a concentration between 35 and 70%. The reaction may be accomplished at temperatures between 23 and 65° C., although temperatures toward the upper limit of this range are preferred. Reaction temperatures which are much higher than 65° C. are undesirable in the treatment of lower secondary alcohols, since a part of the alcohol is lost by distillation in case higher temperatures are employed. The best yields from the practice of the invention have been obtained in connection with operations in which the reaction temperature was maintained between 45 and 55° C. during the major part of the course of the reaction. When very dilute nitric acid is used, higher temperatures should be employed in order to speed up the reaction, and when relatively strong nitric acid (e. g. between 55 and 70% concentration) is used, the temperatures should ordinarily be below 60° C. in order to avoid reaction of such violence as might result in an explosion, and uncontrollable oxidation to produce undesired highly oxidized by-products.

It is preferred that the quantity of nitric acid used in the practice of the process be in considerable molecular excess of the total quantity of secondary alcohol treated, and best results in the practice of the invention have been obtained in cases in which the mol. ratio of nitric acid to secondary alcohol was at least as high as 2:1. The very best yields so far obtained in the practice of the invention have been obtained in cases in which the mol. ratio of nitric acid to secondary alcohol was approximately 3:1.

In the practice of the invention, best results are obtained by first reacting a small amount of the secondary alcohol (or ketone) with the nitric acid, to effect splitting and oxidation, with formation of oxides of nitrogen as by-products, and thereafter gradually adding the remainder of the secondary alcohol (or ketone) to be treated. The products of oxidation obtained by the initial treatment of a small amount of the secondary alcohol with the nitric acid seem to have an auto-catalytic effect in promoting the reaction, and best results in the practice of the invention have been, therefore, obtained in cases in which reaction is first accomplished to produce a small quantity of these reaction products before adding the bulk of the secondary alcohol. This inital reaction may be accomplished, for example, by charging the nitric acid of appropriate concentration to a reactor and heating this acid to a temperature in excess of 70° C., and preferably between 90 and 95° C., and thereafter adding a small amount of the secondary alcohol to the acid in the reactor. In connection with this operation, oxidation takes place promptly, and is accompanied by the evolution of brown fumes resulting from the formation of oxides of nitrogen. When the evolution of such fumes, in connection with the small amount of secondary alcohol initially added, has ceased, the oxidation of the main bulk of the secondary alcohol to be treated may be commenced.

In the oxidation of the main bulk of the secondary alcohol, after oxidation of a small quantity of such alcohol has been acomplished, as described above, the mixture of nitric acid and reaction products in the reactor is first cooled to a temperature between 23 and 65° C., preferably between 45 and 55° C., when nitric acid having a concentration between 45 and 55% is employed. The remainder of the secondary alcohol is next gradually added to the reaction mixture, and the mixture is stirred and artificially cooled during the addition of this remaining alcohol, in order to maintain the reaction mixture within the temperature limits discussed above. Care should be taken to avoid adding the alcohol so rapidly as to build up a high concentration of alcohol, with subsequent rapid reaction causing a rise of temperature substantially above the limits above indicated, since rapid rise of temperature causes too rapid reaction with danger of explosion, and promotion of undesired side reactions to produce highly oxidized products. The time required to add the secondary alcohol, while avoiding undue temperature rise, has varied between 1¼ and 5 hours in experiments conducted in the practice of the invention, depending upon operating conditions.

After all of the alcohol to be oxidized has been passed into the reactor, stirring of the reaction mixture is continued (usually for a period between 15 and 50 minutes), until the splitting and oxidation reaction to produce the desired acids has been completed, as indicated by the fact that no more gas is evolved.

After the reaction is completed, the reaction mixture is diluted to precipitate from solution products of side reactions which are insoluble in water, such as aldehydes, ketones and esters. The aqueous solution so obtained, contains the desired carboxylic acids and nitric acid. In order to separate unreacted nitric acid from the carboxylic acids, the aqueous solution of this mixture of acids is extracted with a solvent which selectively dissolves the carboxylic acids while leaving the nitric acid in aqueous solution. Care should be taken in the choice of the selective solvent to be used for this purpose, to avoid use of a solvent, which will, itself, be oxidized by the nitric acid. The various aliphatic ethers, such as di-ethyl ether, di-propyl ether, di-butyl ether, and particularly di-iso-propyl ether, have been found to be excellent solvents for effecting this selective extraction of the carboxylic acids from the nitric acid solution.

Gases evolved during the course of the reaction are passed, together with air, through a scrubber system, which may be a system for counter-currently extracting the oxides of nitrogen by treatment with water. Such a treatment has the advantage that it effects regeneration of nitric acid, and this nitric acid may be used in the subsequent practice of the process on another batch of alcohol. The use of acid derived from the scrubbing system in this way has the advantage that such acid contains a small quantity of the by-products of reaction and of incompletely oxidized material. The return of acid containing such material has two advantages. In the first place, the return of inadequately oxidized alcohols or ketones enables these materials to be subjected to treatment in a subsequent batch for adequate oxidation, and thus improves the yield. In the second place, the return of by-products of reaction, which are not desired in connection with the oxidation of a further batch of secondary alcohol, depresses the formation of similar compounds in the treatment of this second batch, in accordance with the principles of the law of mass action. The solution of nitric acid obtained by selective extraction of the organic acids from the reaction mixture, by means of isopropyl ether, for example, may similarly be returned to

the reactor for treatment with the next batch of nitric acid and alcohol, with similar advantageous results, as may the oil phase separated from the supernatant aqueous acid phase formed by addition of water to the reaction mixture.

In the practice of the process as described above, a certain amount of nitric acid is reduced to free nitrogen, and the reduction of the oxides of nitrogen to elemental nitrogen represents a total loss in the practice of the process. In cases in which di-ethyl carbinol is split and oxidized in the practice of the invention, it frequently happens that between 30 and 40% of the nitric acid employed in the reaction is reduced to nitrogen, and this undesired reduction is not avoided even in cases in which extremely high molecular ratios of acid to alcohol are employed.

After considerable experimentation, the applicants have discovered that the reduction of the nitric acid to produce nitrogen may be minimized by incorporating in the reaction mixture a compound chosen from the class consisting of mercuric oxide, antimony tri-chloride, stannous chloride, cobalt nitrate and nitrates of mercury. These compounds are effective to inhibit reduction to produce nitrogen regardless of the proportions in which they are incorporated. They are effective as reduction inhibitors when incorporated in proportions even as small as 0.1%, and their effect is, therefore, obviously a catalytic one. The best results have been obtained in instances in which these reduction inhibitors are employed in ratios varying between 0.3 and 5%, and a concentration of approximately 0.3% has been found to be just as effective as higher concentrations in most cases.

As an alternative to the continuation of the reaction after the complete charge of alcohol has been added to the nitric acid, water may be added to the reaction mixture immediately upon the completion of the addition of the secondary alcohol, and the mixture may then be promptly stratified into an aqueous phase containing the organic acids and dilute nitric acid, and a supernatant oil phase containing other products. The addition of water promptly, without waiting for the completion of the oxidation reaction, has the advantage that the reaction mixture can be more easily and effectively separated into its constituents in the case of such prompt water dilution. In case the water is added promptly and extraction promptly effected, it will, of course, be desirable to return the oil phase stratified from the aqueous phase to the next batch of material to be treated, since this oil phase contains a considerable proportion of inadequately oxidized material.

Examples

Example 1.—12 mols. of HNO_3 (in 50% solution) was heated to 90–95° C. While stirring, a small portion (2 cc.) of di-ethyl carbinol was added. As soon as oxidation started, the mass was cooled to 60–65° C. and the alcohol (3 mols.) was charged at a rate at which the temperature could be maintained and the excessive evolution of gas avoided. 1¼ hours were required for charging the alcohol. The mass was stirred for ¼ hour after completing the charge. It was then diluted, but no oil layer separated. Extraction of the diluted mass with di-isopropyl ether and fractionation of the mass yielded 1.78 mols. of acetic acid and 1.82 mols. of propionic acid. The alcohol to acid yield was 60%. 38.3% of the HNO_3 was reduced to nitrogen.

Example 2.—By adding 10 g. $SnCl_3$ to the hot HNO_3 along with 2 cc. of alcohol and proceeding as above, the amount of HNO_3 reduced to nitrogen decreased to 20% with approximately the same yield of alcohol to acid.

Example 3.—When 3 mols. of methyl ethyl carbinol (sec. butyl alcohol) was oxidized by the use of 10 mols. of HNO_3 as in Example 1. 1.72 mols. of acetic acid and 0.6 mol. of propionic acid were obtained to give an alcohol yield of 38.6% to the acids.

Example 4.—3 mols. of pentanol-2 were reacted with 12 mols. of nitric acid at a temperature of 55° C., after initiating the reaction by adding a very small quantity of pentanol-2 to the nitric acid at a temperature between 90 and 95° C. as described in Example 1. The technique followed in this operation was otherwise identical as that of Example 1. 1.73 mols. of acetic acid, 1.78 mols. of propionic acid and 0.62 mol. of butyric acid were formed. A conversion of 68.5% of the alcohol to acids was thus obtained.

Further modifications will be obvious to those skilled in the art and we do not, therefore, wish to be limited except by the scope of the subjoined claims. When secondary alcohols are referred to in these claims, it is to be understood that this expression is not to be interpreted as limited to the simple monohydric secondary alcohols, since the expression is used to designate the broad class of compounds having a hydroxyl radical attached to an internal carbon atom of an aliphatic chain. The expression thus includes poly-hydric alcohols, and also hydroxy acids in which the hydroxyl radical is attached to a non-terminal carbon atom (these may be considered as carboxy secondary alcohols.) Thus, in the practice of the invention, oleic acid may be hydrated to produce 9-hydroxy stearic acid, and this stearic acid may thereafter be oxidized by treatment with nitric acid in accordance with the invention, to produce, from one molecule of 9-hydroxy stearic acid, a molecule of mono-carboxylic 9-carbon atom acid and a molecule of di-carboxylic 9-carbon atom acid, and such procedure is intended to be included, when reference is made in the subjoined claims to treatment of a secondary alcohol.

We claim:

1. In the manufacture of carboxylic acids, the process comprising reacting secondary oxy compounds of the open chain type chosen from the class consisting of ketones, secondary alcohols and the sulfuric acid esters of secondary alcohols with nitric acid to split the alkyl radical of said compound and oxidize said compound to produce two molecules of carboxylic acid from a single molecule of said compound, said reaction being accomplished by first mixing a very small proportion of said compound with nitric acid at a temperature substantially in excess of 70° C., and reacting said added compound with the nitric acid, thereafter cooling the reaction mixture to a temperature below 65° C., and adding the remaining quantity of said compound to be reacted with said nitric acid to said reaction mixture gradually while cooling the reaction mixture to maintain it at a temperature below 65° C. during the reaction of the remaining alcohol with the nitric acid to complete the formation of carboxylic acids.

2. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the

improvements that comprise heating together initially a small quantity of the compound with the acid until substantially reacted and thereafter completing the oxidation by adding further quantities of the compound to the acid at a rate substantially equal to the rate of oxidation of the compound to carboxylic acids while maintaining the temperature of the reaction mixture substantially constant.

3. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise reacting initially at a temperature above 70° C. a small quantity of the compound with the acid and thereafter completing the oxidation by adding and reacting within the temperature range 23° to 65° C. further quantities of the compound to the acid at a rate substantially equal to the rate of oxidation of the compound to carboxylic acids.

4. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise reacting initially within the temperature range 90° to 95° C. a small quantity of the compound with the acid and thereafter completing the oxidation by adding and reacting within the temperature range 23° to 65° C. further quantities of the compound to the acid at a rate substantially equal to the rate of oxidation of the compound to carboxylic acids.

5. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise reacting initially within the temperature range 90° to 95° C. a small quantity of the compound with the acid and thereafter completing the oxidation by adding and reacting within the temperature range 45° to 55° C. further quantities of the compound to the acid at a rate substantially equal to the rate of oxidation of the compound to carboxylic acids.

6. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise adding the compound in small incremental quantities to the nitric acid while maintaining the acid initially at a temperature above 70° C. and thereafter at a temperature below 65° C.

7. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise adding the compound in small incremental quantities to the nitric acid while maintaining the acid initially at a temperature above 70° C. and thereafter at a temperature within the range 23° to 65° C.

8. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise adding the compound in small incremental quantities to the nitric acid while maintaining the acid initially at a temperature above 70° C. and thereafter at a temperature below 65° C., the concentration of the nitric acid used being about 50% based on weight.

9. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise adding the compound in small incremental quantities to the nitric acid while maintaining the acid initially at a temperature above 70° C. and thereafter at a temperature within the range 23° to 65° C., concentration of the nitric acid used being about 50% based on weight.

10. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise heating together initially a small quantity of the compound with the acid until substantially reacted and thereafter completing the oxidation by adding further quantities of the compound to the acid at a rate substantially equal to the rate of oxidation of the compound to carboxylic acids, the concentration of the nitric acid used being about 50% based on weight, while maintaining the temperature of the reaction mixture substantially constant.

11. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols, the improvements that comprise heating together initially a small quantity of the compound with the acid until substantially reacted and thereafter completing the oxidation by adding further quantities of the compound to the acid at a rate substantially equal to the rate of oxidation of the compound to carboxylic acids, the reactions being performed at substantially constant temperature and in the presence of catalytic quantities of a substance selected from the class consisting of antimony trichloride, stannous chloride, cobalt nitrate, and nitrates of mercury.

12. In the process of manufacturing carboxylic acids by oxidation with nitric acid of an open chain type oxy compound selected from the class consisting of ketones and secondary alcohols. the improvements that comprise adding the compound in small incremental quantities to the nitric acid while maintaining the acid initially at a temperature above 70° C. and thereafter at a temperature below 65° C., the reactions being performed in the presence of catalytic quantities of a substance selected from the class consisting of antimony trichloride, stannous chloride, cobalt nitrate, and nitrates of mercury.

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