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PROCESS FOR THE PREPARATION OF ALIPHATIC ETHERS

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The present invention relates to a process for preparing aliphatic ethers. More particularly it relates to the preparation of aliphatic ethers by electrolysis of aliphatic carboxylic acid salts.

It has previously been proposed by Kolbe to electrolyze aqueous solutions of aliphatic carboxylic acid salts to produce hydrocarbons according to the overall equation:

$$2RCH_2COONa + 2H_2O \xrightarrow{\text{Electrolysis}} \underbrace{RCH_2.CH_2R + 2CO_2}_{\text{Anode}} + \underbrace{2NaOH + H_2}_{\text{Cathode}}$$

It has also previously been proposed to electrolyze alcoholic aqueous solutions of aliphatic carboxylic acid salts under certain special conditions so as to prepare mixtures of alcohols and olefines which contain one less carbon atom than the original salt from which they are prepared.

It has now been discovered that electrolysis of aliphatic carboxylic acid salts using a graphite anode and substantially anhydrous conditions results in the production of high yields of aliphatic ethers. In accordance with the present invention a process for the preparation of aliphatic ethers comprise electrolyzing, using a graphite anode, a substantially anhydrous solution of aliphatic carboxylic acid salt containing more than one carbon atom in a solvent therefor selected from the group consisting of lower monohydric and dihydric alcohols, and recovering an aliphatic ether of a carbon content equal to one less than the sum of the carbon contents of said aliphatic carboxylic acid salt and said alcoholic solvent. This electrolysis is preferably carried out using relatively low current densities, and dilute anhydrous alcoholic solutions of aliphatic carboxylic acid salts in the presence of stable, electrically conductive inorganic salts as set forth in detail below.

It is essential to the present invention that electrolysis be carried out under anhydrous or substantially anhydrous conditions, as the presence of relatively small proportions, e. g. about 10% of water, results in a marked decrease in the yield of the instant ethers.

The alcoholic solvent employed in carrying out the present process is selected from the group consisting of lower monohydric and dihydric alcohols containing up to about 3 carbon atoms, e. g. methanol, ethanol, ethylene glycol, and the propanols. In general it has been found that excellent yields are realized when using methanol, probably because of its stability and superior solvation characteristics. Good yields may also be obtained when ethylene glycol is used, however under unfavorable conditions some oxidation, e. g. to glycol aldehyde, is experienced.

The alcoholic solvents are used in considerable excess. Preferably, solutions to be electrolyzed are less than about 0.5 to 0.75 molar with respect to the aliphatic carboxylic acid salt, as at higher concentrations considerable amounts of the Kolbe hydrocarbon form. In the case of potassium laurate dissolved in methanol, the maximum yields of 1-methoxyhendecane have been found to occur

when the solvent is 0.335 molar or less in potassium laurate.

The aliphatic carboxylic acid salts employed in the instant novel process are metallic salts of saturated or unsaturated aliphatic carboxylic acids containing more than one carbon atom. These salts may be pure or in admixture, however it is essential that they have at least slight solubility in the alcoholic solvent used. Suitable carboxylic acid salts for carrying out the present invention include the alkali metal salts such as sodium propionate, potassium caprylate, sodium laurate, sodium myristate, potassium oleate, potassium stearate and the potassium salts of tridecanoic acid, pentadecanoic acid and margaric acid. While free aliphatic carboxylic acids are not suitable to initiate the instant process, they may be added after electrolysis has commenced using carboxylic acid salt. On such addition, the free acid will react with metal hydroxide liberated at the cathode to form metal salt which will then enter the electrolysis reaction.

It is a preferred embodiment of the invention to carry out the instant electrolysis in the presence of electrically conductive inorganic salts, e. g. ionically bonded inorganic salts, stable in the electrolysis medium. The particular salt employed is not critical, suitable salts including for instance the alkali metal chlorides, sulfates and persulfates. Specific examples thereof are potassium and sodium-chlorides, -sulfates, and -persulfates. The salts are generally employed by preparing a saturated solution or suspension thereof in the alcoholic solvent which is used.

While the use of these inorganic salts somewhat diminishes the current efficiency of the electrolytic system employed, their presence is essential to the procurement of high yields of ether and suppression of side reactions. Thus it has been found that whereas in the presence of such salts, relatively high yields may be realized, a similar process carried out in the absence of such salts results in the production of a product consisting of about only one-third ether and two-thirds hydrocarbons. Coating of the carbon anode is also experienced in the absence of these salts, and the coating must be periodically scraped to maintain the desired current density.

The yield of ether obtained is further influenced by the current density employed in the electrolysis cell, i. e. current densities up to about 40 amperes per square decimeter of anode surface favoring the production of ethers. Although the instant ethers are also generated at higher current densities, side reactions such as the Kolbe reaction become increasingly prevalent under such conditions.

It is essential that graphite be employed as the anode material. Substitution of another material therefore, e. g. platinum, results in the production of products lacking any analytically detectable amounts of ether. A large variety of materials are suitable for use as cathodes, suitable substances being platinum, stainless steel, carbon, copper, silver, nickel and the like.

The following examples are given to additionally illustrate the nature of the invention and it will be understood that the invention is not limited thereto.

EXAMPLE I

1-methoxyhendecane

A direct current of 3.5 amperes at a potential of 90 volts is passed through 200 ml. of a well stirred, refluxing methanolic solution containing 16.0 grams (0.067 mole) of potassium laurate and 2 grams of potassium chloride for 6.5 hours. The anode is a graphite cylinder having a surface area of 0.1 square decimeter, thus the current density is 35 amperes per square decimeter. The cathode is a coiled platinum wire.

The electrolyzed reaction mixture is poured into 600 ml. of water and extracted three times with diethyl ether. The combined extracts are washed once with water and dried over anhydrous magnesium sulfate.

The dried ethereal solution is then concentrated and rapidly distilled, yielding 12.0 grams of material boiling from 40 to 85° C. (0.25 mm.). Rough fractionation of this distillate gives three major fractions. The first fraction amounts to 1.75 grams and is predominantly 1-hendecene. The second fraction amounts to 6.75 grams and is predominantly 1-methoxyhendecane. The third fraction 2.25 grams is predominantly methyl laurate. The 1-methoxyhendecane fraction is identified by infrared analysis by comparison with 1-methoxyhendecane prepared by reacting methyl sulfate with the sodium alcoholate of hendecanol.

The combined aqueous residues are acidified and the residual ether is then removed on a steam bath. No lauric acid is thus recovered, indicating that all of the potassium laurate starting material has been consumed.

EXAMPLE II

2-hendecyloxyethanol

A solution of 16.0 g. (0.067 mole) of potassium laurate and 4.0 g. of potassium chloride in 190 ml. of ethylene glycol is subjected to electrolysis at 110 volts, 3.5 amperes at 70–100° C. for 6.5 hours. The cathode and anode are as described in Example I above. The reaction mixture is worked up as described in Example I and yields 5.0 g. of 2-hendecyloxyethanol, B. P. 90–115° (0.25 mm.), most at 115°, which crystallizes in ice water. The acidified aqueous residue yields 6.8 g. of lauric acid.

While there has been disclosed and described what is at present considered to be the preferred embodiment of the invention it will be understood, of course, that many changes, modifications, and substitutions may be made therein without departing from the true scope of the invention as defined in the appended claims.

What is claimed is:

1. A process for the preparation of aliphatic ethers which comprises electrolyzing, using a graphite anode, a substantially anhydrous solution of aliphatic carboxylic acid salt containing more than one carbon atom in a solvent therefor selected from the group consisting of lower monohydric and dihydric alcohols, and recovering an aliphatic ether of a carbon content equal to one less than the sum of the carbon contents of said aliphatic carboxylic acid salt and said alcoholic solvent.

2. A process for the preparation of aliphatic ethers as set forth in claim 1 wherein said solvent is methanol.

3. A process for the preparation of aliphatic ethers as set forth in claim 1 wherein said solvent is ethylene glycol.

4. A process for the preparation of aliphatic ethers which comprises electrolyzing, using a graphite anode, a substantially anhydrous solution of aliphatic carboxylic acid salt containing more than one carbon atom in a solvent therefor selected from the group consisting of lower monohydric and dihydric alcohols, said electrolysis being carried out in the presence of an electrically conductive inorganic salt, and recovering an aliphatic ether of a carbon content equal to one less than the sum of the carbon contents of said aliphatic carboxylic acid salt and said alcoholic solvent.

5. A process for the preparation of aliphatic ethers as set forth in claim 4 wherein said solution is less than about 0.5 to 0.75 molar with respect to aliphatic carboxylic acid salt.

6. A process for the preparation of 1-methoxyhendecane which comprises electrolyzing, using a graphite anode, an anhydrous solution of potassium laurate in methanol, said electrolysis being carried out in the presence of potassium chloride, and recovering 1-methoxyhendecane as a product of said electrolysis.

7. A process for the preparation of 2-hendecyloxyethanol which comprises electrolyzing, using a graphite anode, an anhydrous solution of potassium laurate in ethylene glycol, said electrolysis being carried out in the presence of potassium chloride, and recovering 2-hendecyloxyethanol as a product of said electrolysis.

References Cited in the file of this patent

Glasstone et al: Electrolytic Oxidation and Reduction (1936), pp. 289–290.