Patented Feb. 1, 1944 2,340,689

UNITED STATES PATENT OFFICE

2,340,689

PROCESS FOR FORMING ALCOHOLS

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No Drawing. Application May 27, 1943, Serial No. 488,736

8 Claims. (Cl. 260—638)

Our invention relates to a process for forming alcohols by reacting hydrogen with certain metallic salts of carboxylic acids.

The present application is a continuation-in-part of our applications Serial Nos. 380,072 and 380,073, filed February 21, 1941, and of application Serial No. 438,852, filed April 13, 1942. The first of these discloses a general process for forming alcohols and esters by hydrogenating the corresponding carboxylates of certain metals at high temperature and pressure, the second discloses a similar process directed specifically to forming unsaturated alcohols and esters from corresponding unsaturated carboxylates of certain metals, and the third discloses specific and advantageous applications of the process to mixtures of cadmium carboxylates and carboxylates of certain other metals.

Among the carboxylates which respond to the process of the above mentioned applications are those of cadmium. When subjected to reaction with hydrogen under the conditions of our general process cadmium soaps, for example, are converted to alcohols and esters corresponding to the fatty acid radicals of these soaps, with liberation of metallic cadmium and water:

$$(RCOO)_2Cd+5H_2 \rightarrow 2RCH_2OH+2H_2O+Cd$$

and

$$(RCOO)_2Cd+3H_2 \rightarrow RCOOCH_2R+2H_2O+Cd$$

If the R group of the carboxylate contains one or more double carbon bonds, the alcohol and ester products will for the most part also contain these linkages.

In the absence of free or combined metals other than cadmium among the reactants, the second of the above reactions predominates, with production mainly of esters, and only relatively small amounts of free alcohol are produced.

The subject matter and claims of the present application are based upon our discovery that unexpectedly beneficial results are obtained when mixtures of cadmium carboxylate with carboxylates of one or more of the metals iron, cobalt, or nickel are hydrogenated, as compared with the results obtainable under comparable hydrogenating conditions with carboxylates of any one of these metals alone. This improvement in results manifests itself in a higher percentage reduction of carboxyl groups to alcohol groups than the percentage obtained when cadmium carboxylates alone are hydrogenated; also, as compared with the hydrogenation of carboxylates of any of the metals iron, cobalt, and nickel alone, it manifests itself either in a higher percentage reduction of carboxyl groups to alcohol groups or in a greater preservation of double carbon bonds in unsaturated fatty radicals, or in both of these effects simultaneously. In other words, hydrogenating mixtures of carboxylates of different metals as specifically claimed in the present application results in unexpectedly high yields of alcohols and/or alcohols of an unexpectedly high iodine value.

Thus our present process provides an improved means of forming higher alcohols, which may contain unsaturated carbon-carbon linkages if the starting materials are unsaturated. Such a process, which is not dependent upon added metallic or metal oxide catalysts, has great advantages over previously described methods of making higher fatty alcohols. The reaction is rapid, the yields of the desired product are high, and the metals are readily recoverable for reuse in making fresh lots of carboxylates for hydrogenation.

The following examples will illustrate typical small scale applications of our process. In each of these examples the hydrogenation was carried out in a reaction vessel consisting of a stainless steel bomb of 300 cubic centimeters capacity. The mixed fatty acids present in commercial oleic acid, or "red oil," are for convenience referred to as "oleic acid," and the alcohols resulting from the process are referred to as "oleyl alcohol."

The extent of the reduction of carboxyl groups is calculated from the saponification value of the original oleic acid and the saponification value of the acid washed, water washed, and dried reaction product. The per cent total alcohol in the acid washed (and water washed and dried) product is determined either by calculation from the hydroxyl value determined on the unsaponifiable matter in the acid washed product, or by calculation from the acid value, saponification value, and hydroxyl value of the acid washed product. In either case the per cent total alcohol includes both free oleyl alcohol and oleyl alcohol combined as ester, the latter being liberated when the acid washed product is saponified.

Example 1.—Cadmium oleate and iron oleate were separately prepared by treating solutions of "red oil" sodium soaps with solutions of cadmium nitrate and iron sulfate respectively, and washing and drying the precipitated metallic soaps. A mixture of 50 grams of this cadmium oleate and 50 grams of this iron oleate was placed in the

reaction bomb at room temperature, air was displaced from this vessel by admitting hydrogen and venting the bomb, and then hydrogen was introduced to build up the pressure in the bomb to about 2000 pounds per square inch. The bomb was sealed and heated to about 340° C. The contents were agitated by rocking the bomb while maintaining a pressure of 4000 pounds per square inch by adding more hydrogen when necessary, for two hours. The bomb was then allowed to cool to a temperature convenient for handling, excess gas pressure was released, and the non-gaseous organic contents were removed, boiled with a 10% aqueous solution of hydrochloric acid to remove free and combined metal, water washed until free from mineral acid, and dried. This acid washed product was found to have about 71% of the original carboxyl groups reduced, and to contain slightly over 74% of free and combined oleyl alcohol.

Free alcohol was obtained from the acid washed material by reacting fatty acids and esters in this material with caustic alkali, extracting with ether, and distilling off this solvent.

When cadmium oleate alone was similarly hydrogenated, only about 53% of the carboxyl groups were reduced, and the acid washed hydrogenation product contained only about 47% total alcohol.

When iron oleate alone was similarly hydrogenated, about 75% of the carboxyl groups were reduced, but the acid washed hydrogenation product was found to contain almost no alcohol and to consist mostly of hydrocarbons.

Example 2.—A mixture of 90 grams of cadmium oleate and 10 grams of nickel oleate was subjected to hydrogenation under conditions comparable with those of Example 1.

The resulting acid washed product was found to have about 90% of the original carboxyl groups reduced, and to contain about 82% free and combined alcohol having an iodine value above 70.

When nickel oleate alone was hydrogenated under comparable conditions only 20% of the carboxyl groups were reduced and the hydrogenation product had an iodine value of only 4.

Example 3.—A mixture of 90 grams of cadmium oleate and 10 grams of nickel oleate was subjected to hydrogenation under conditions similar to those of Example 1 except that the time at the elevated reaction temperature and pressure was only one hour.

The resulting acid washed and water washed product contained less than 1% of free oleic acid, about 80% of free oleyl alcohol, and about 5% of oleyl alcohol combined as ester. The iodine value of the product was 75, indicating that about 79% of the double carbon bonds remained unsaturated.

When nickel oleate alone was hydrogenated under similar conditions no significant amount of free or combined alcohol was formed.

Example 4.—A mixture of 90 grams of cadmium oleate and 10 grams of cobalt oleate was subjected to hydrogenation under conditions comparable with those of Example 1.

The resulting acid washed product was found to have about 57% of the original carboxyl groups reduced and to have an iodine value of 90.

When cobalt oleate alone was hydrogenated under comparable conditions the percentage reduction of carboxyl groups was even higher, namely 93%, but the iodine value of the product was only 2.4.

Our process as exemplified by the above specific applications is applicable to treatment of soaps of all fatty acids occurring in natural vegetable, animal, and marine fats and oils. Thus carboxylates of our preferred metals and of fatty acids derived from coconut oil, tallow, vegetable oils, fish oils, hydrogenated oils, etc., may be treated to produce the corresponding fatty alcohols. Similarly, our process is applicable to hydrogenation of metallic salts of carboxylic acids generally, although we do not claim that it is equally efficient as applied to conversion of all such salts to alcohols. It is well known, of course, that carboxylic acids and their derivatives differ in thermal stability and the outstanding merit of our process as applied to production of the higher alcohols is due in large part to the resistance of the salts of the fatty acids to decomposition by side reactions under the conditions employed in our process.

It is to be understood that whereas mixtures of carboxylates of cadmium and of one or more of the other three metals Fe, Co, Ni are the essential ones to be employed in the process claimed herein, and are to be employed in substantial quantities to obtain the advantages of the invention, the process is not limited to mixtures composed entirely of carboxylates of these metals, and that carboxylates of other metals, such as those disclosed in our co-pending application 380,072, namely those of lead, copper, chromium, zinc, and manganese, may also be included in the reaction mixture.

Preferred conditions for our process include the maintenance of temperatures between about 240° C. and about 400° C., pressures in excess of 2000 pounds per square inch, the provision of some form of agitation to promote intimate contact between the hydrogen and the reacting salts, the maintenance of a constant supply of hydrogen, and time under these reaction conditions sufficient for the attainment of substantial completion of the reaction.

The relative proportions of the preferred metals in the carboxylate mixtures subjected to our process may be varied greatly, with the results more advantageous than those obtained by using carboxylates of the respective individual metals. The relative proportions referred to in the foregoing examples have been found to be quite favorable.

Having thus described our invention, what we claim and desire to secure by Letters Patent is:

1. In a process for forming alcohols, the step which consists essentially of subjecting to reaction with hydrogen a mixture of salts of carboxylic acids corresponding to said alcohols, said mixture of salts comprising essentially carboxylates of cadmium and of at least one metal selected from the group consisting of iron, nickel, and cobalt, the reaction temperature and hydrogen pressure being sufficiently above atmospheric to effect substantial reduction of the carboxylic group —CO—O— of said salts to the group —CH_2—O— of said alcohols.

2. In a process for forming fatty alcohols, the step which consists essentially of subjecting to reaction with hydrogen a mixture of soaps of fatty acids corresponding to said alcohols, said mixture of soaps comprising essentially soaps of cadmium and of at least one metal selected from the group consisting of iron, nickel, and cobalt, the reaction temperature and hydrogen pressure being sufficiently above atmospheric to effect sub-

stantial reduction of the carboxylic group —CO—O— of said soaps to the group

$$-CH_2-O-$$

of said alcohols.

3. The process of forming fatty alcohols, which comprises subjecting to reaction with hydrogen, at a temperature between about 240° and 400° C. and at a hydrogen pressure above 2000 pounds per square inch, a mixture of soaps of fatty acids corresponding to said alcohols, said mixture of soaps comprising essentially soaps of cadmium and of at least one metal selected from the group consisting of iron, nickel and cobalt.

4. The process of claim 3, in which the soaps are soaps of unsaturated fatty acids whereby the alcohols formed are for the most part unsaturated alcohols.

5. The process of claim 3, in which the soaps comprise soaps of oleic acid.

6. The process of claim 3, in which the soaps comprise soaps of coconut oil mixed fatty acids.

7. The process of forming fatty alcohols which comprises subjecting to reaction with hydrogen, at a temperature between about 240° and 400° C. and at a hydrogen pressure above 2000 pounds per square inch, a mixture of soaps of fatty acids corresponding to said alcohols, said mixture consisting of soaps of cadmium and nickel.

8. The process of forming higher alcohols which comprises: subjecting to reaction with hydrogen, at a temperature between about 240° and 400° C. and at a hydrogen pressure above 2000 pounds per square inch, a mixture of soaps of fatty acids corresponding to said alcohols, said mixture of soaps comprising essentially soaps of cadmium and of at least one metal selected from the group consisting of iron, nickel and cobalt, removing free and combined metal from the organic reaction products of said hydrogenating step by treating with mineral acid; reacting fatty acids and esters in the resulting acid washed material with caustic alkali; and separating free alcohols from the resulting mixture.

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