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1,839,974

UNITED STATES PATENT OFFICE

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HYDROGENATION OF CARBOXYLIC ACIDS

No Drawing. **Application filed March 5, 1931. Serial No. 520,474.**

This invention relates to a process for the direct catalytic reduction of carboxylic acids. More specifically, it relates to a process for the catalytic hydrogenation of carboxylic acids wherein the acids are converted to the corresponding alcohols or to esters formed by combination of the corresponding alcohols with a part of the acids undergoing hydrogenation.

The more common members of the aliphatic system of organic compounds may be regarded as derivatives of the simple hydrocarbons in which oxygen, nitrogen or other substituents have been introduced in place of hydrogen atoms. This system comprises among other compounds the alcohols, aldehydes, ketones, acids, esters, salts, acid chlorides, anhydrides, amides, nitriles, and amines. By treatment with suitable reagents it is possible to convert any one of these compounds into any other, a fact which has contributed largely to their widespread commercial exploitation.

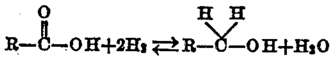
Among these interconversions, the reduction of acids to aldehydes or to alcohols has probably presented the greatest difficulty of all. Professor Moureau in his Fundamental Principles of Organic Chemistry states: "Whereas the transformation of aldehydes into primary alcohols is always effected by direct hydrogenation, the conversion of acids into aldehydes is, in general, only possible by indirect means".

Higher alcohols are compounds of considerable technical importance, but owing to the difficulties heretofore involved in their preparation on a large scale, they have with few exceptions never become articles of commerce. The higher alcohols containing from six to eighteen carbon atoms have been obtainable only through the reduction by chemical means of esters of the corresponding fatty acids.

One of the indirect methods, described by Bouveault and Blanc in 1904, consists of reducing an ester of the acid to the corresponding alcohol with metallic sodium in anhydrous alcoholic solution. Although very expensive, this method has been, and is still being operated on a commercial scale. One other method depending on the use of an acid derivative makes use of the direct hydrogenation of an acid chloride to the corresponding aldehyde in the presence of a palladium catalyst, according to the method of Rosenmund. Sabatier and Mailhe have described a reaction in which acetic acid may be reduced to acetaldehyde by passing it together with formic acid or carbon monoxide over a manganese oxide catalyst. In my co-pending application, Serial No. 445,224, filed April 17, 1930, I have described a process for the direct catalytic hydrogenation of esters to alcohols, but so far as I am aware the direct catalytic hydrogenation of acids to alcohols or esters has never been known prior to my discovery thereof.

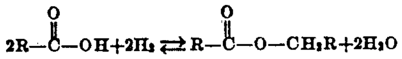
This invention has as an object a new process of converting carboxylic acids into the corresponding alcohols, or esters or mixtures of the alcohols and esters. A further object resides in conducting my new process so as to produce as desired either the alcohols or the wax-like esters as the main products of the reaction.

According to the present invention the only reducing agent required is molecular hydrogen which is applied in the presence of a suitable hydrogenating catalyst. One molecule of hydrogen is required to remove the oxygen from the C=O group of the acid in the form of a molecule of water, while still another molecule of hydrogen takes up the position of the oxygen atom removed, according to the equation:



$$R-\overset{O}{\overset{\|}{C}}-OH+2H_2 \rightleftarrows R-\overset{H\;\;H}{\overset{\diagdown\diagup}{C}}-OH+H_2O$$

where R represents an alkyl group preferably of the aliphatic or hydroaromatic series. A secondary reaction consists of esterification of a portion of the alcohol formed with a portion of the unchanged acid. The proportion of ester present in the product depends chiefly on the completeness of the hydrogenation, and when conducting the reaction under conditions which yield only partial reduction of the acid, the process may be altered to give esters as the main products according to the equation:



$$2R-\overset{\overset{O}{\|}}{C}-OH+2H_2 \rightleftarrows R-\overset{\overset{O}{\|}}{C}-O-CH_2R+2H_2O$$

My process is characterized by hydrogenation of the acid with a suitable hydrogenating catalyst at temperatures and pressures somewhat higher than those ordinarily employed for such liquid phase hydrogenations as are carried out for the purpose of hardening fats and fatty acids. In conducting the reaction I prefer to use an excess of hydrogen and a special hydrogenation catalyst hereinafter described.

If R in the formula above is an unsaturated radical, reduction or partial reduction of the carbon-carbon unsaturation may occur as in the usual hydrogenation process, but in the present process this is only incidental to the more important reaction which results in the formation of alcohols and esters. As an added step in my invention I sometimes prefer, after conducting the reaction as indicated above to favor alcohol and ester formation, to hydrogenate the reaction products at low pressure and temperature with a nickel catalyst in the usual manner. This brings all the reaction products up to the same level of hydrogen saturation, yielding new compositions, usually solid products from which the alcohols and esters may be separated if desired. This second hydrogenating step also saturates any unsaturated alcohols or esters that may be present as a result of using acids containing unsaturated acid radicals.

One method of carrying out the invention consists of melting the acid, if a solid, and passing the liquid acid together with hydrogen under high pressure over a heated hydrogenation catalyst. Preferably the catalyst is a mixture of hydrogenating metals and their oxides prepared in a granular form and held in place in a suitable pressure resisting tube. Whereas carboxylic acids would ordinarily be decomposed at the high temperatures employed for the hydrogenation, I have found that under hydrogen pressure the acids are much less susceptible to decomposition than would be supposed from their behavior when heated in air. Under reducing conditions and in the presence of a catalyst the decomposition, if such it may be termed, takes place in a controlled manner and with the absorption of hydrogen and the production of alcohols or esters or both.

Catalysts especially suitable for the purposes of the present invention may consist of a mixture of difficulty reducible oxides of hydrogenating metals. I prefer to use compositions in which the oxides are in the form of the chromites of the metals. An effective catalyst comprising a mixture of the chromites or chromates of different hydrogenating metals and containing also some of the oxides of these metals may be made in the following manner: A solution is prepared by dissolving 245 parts by weight of crystallized zinc nitrate, 23 parts of hydrated cadmium nitrate and 24 parts of copper nitrate (trihydrate) in about 750 parts of water. A second solution is prepared by dissolving 100 parts by weight of chromic anhydride (CrO_3) in 500 parts of water and then adding 135 parts of 28% ammonium hydroxide. Precipitation of the hydrogenating metals of the first solution as chromates is effected by stirring and adding at room temperature the second solution. The mixture is exactly neutralized with additional ammonium hydroxide and allowed to settle. The clear supernatant liquid is poured off and the precipitate is washed several times by decantation with an adequate volume of wash water, after which it is filtered and dried at about 100° C. The next step consists of igniting the dried filter cake at 400° C. for four hours. This process converts the double ammonium chromates of the copper, zinc, and cadmium to metallic chromites in which form they are employed as catalysts. Suitable physical form is obtained by granulating the friable chromite powder and briquetting it into the form of tablets, which may or may not be broken up into grains of various size. In some cases it is advisable to prereduce the hydrogenation catalyst with hydrogen or other reducing gas prior to loading into the converter. In other cases the catalyst reduction is carried out in situ by heating up slowly in a stream of reducing gas, prior to introduction of the acid to be hydrogenated.

The following examples are illustrative of the method of carrying out my invention:

Example I

Fifty cubic centimeters of the acid hydrogenation catalyst prepared as described above was placed in a steel reaction vessel capable of withstanding high pressures, and was slowly heated to 390° C. in a stream of hydrogen. The exit valve was then closed and the hydrogen pressure was allowed to rise to 3,000 lbs. per sq. in. At this temperature and pressure pure lauric acid was pumped over the catalyst at the rate of about 200 cc. per hour while hydrogen was simultaneously drawn thru the system at the rate of about 15 cu. ft. per hour as measured at ordinary conditions of temperature and pressure at the exit of the reaction system. The pressure was controlled at a constant value by maintaining a large supply of hydrogen at the required pressure. The flow of acid was regulated by adjusting the rate of pumping, and the rate of hydrogen flow was controlled by manipulation of the gas expansion valve at the end of the reaction system. The liquid products were separated from the exit gas by passage through a cooled trap located between the reaction tube and the expansion valve.

Ninety-six per cent by volume of acid injected was recovered as liquid products consisting of a very small water layer and a very much larger oily layer. The oily layer was separated and subjected to analysis. The acid number was 31, indicating the presence of only 11% of unchanged acid. The saponification number of 38 represented a lauryl laurate content of about 25% while the acetyl number of 149 indicated the presence of about 61% of lauryl alcohol. Hydrocarbons were formed in very small amounts if present at all. The presence of large quantities of lauryl alcohol in the product was confirmed by distilling it out of the crude condensate under diminished pressure.

Example II

A commercial grade of butyric acid was successfully hydrogenated at a temperature of 390° C. and pressures varying between 2,500 lbs. and 3,000 lbs. per sq. in. As in Example I, 50 cc. of the standard hydrogenation catalyst already described was slightly reduced in hydrogen prior to the introduction of the organic acid. The butyric acid was passed over the catalyst at the rate of 225 cc. per hour while hydrogen was put through at the rate of 11.9 cu. ft. per hour. This rate of hydrogen flow was roughly equivalent to 3.5 moles per mole of acid treated. The condensed product consisted of a water and an oil layer. The latter was separated and dried by distilling off the water-butanol binary and returning the oil to the still. After all of the water had been removed, 50% of the product distilled over at 117° C., the boiling point of normal butanol and about 10% at 164° C., the boiling point of normal butyl normal butyrate. Similar percentages were converted to compounds having boiling points higher or lower than these compounds. There was no evidence that the volatile acid had impaired the activity of the catalyst at any stage of the reduction process.

Example III

Glacial acetic acid was hydrogenated under conditions similar to those used for butyric acid in Example II. Analogously, there was formed a mixture of products containing chiefly ethanol and ethyl acetate.

Example IV

In this experiment a good commercial grade of mixed coconut oil acids were hydrogenated continuously in high yields to the corresponding mixed alcohols. The zinc, copper, cadmium chromite catalyst already described was used at a temperature of about 380° C. The acids were pumped over 100 cc. of the catalyst at the rate of about 200 cc. per hour. The hydrogen pressure was 2500–3000 lbs. per sq. in. and rate of flow of the hydrogen about 15 cu. ft. per hour. Analysis of the crude product gave 6% ester calculated as lauryl laurate and 0.8% acid calculated as lauric acid. 850 g. of coconut oil acids yielded 681 g. of mixed alcohols, corresponding to a yield of about 85% of the theoretical. By fractional distillation in vacuo it was found that the mixed synthetic alcohols contained about 25% of normal decyl alcohol, about 55% of lauryl alcohol, and about 10% of alcohols of higher molecular weight.

Example V

The acids from castor oil were hydrogenated in accordance with the procedure set forth in Example IV and were thereby converted into a viscous product containing about 40% of esters and practically no free acid. The acetyl number of this product was 178.

Example VI

Oleic acid provides a very suitable starting point for the synthesis of oleyl and stearyl alcohols and their esters. Owing to its low melting point, oleic acid is more convenient to pump than stearic acid, and the selection of optimum conditions for its hydrogenation has been more thoroughly investigated than for some of the other acids. Pure oleic acid was pumped over 100 cc. of the preferred catalyst at the rate of 400 cc. per hour. The hydrogen flow was about 15 cu. ft. per hour and the pressure 2800 lbs. per sq. in. The temperature was varied between 350° C. and 420° C. and the product collected at each temperature was analyzed for acid, ester, and alcohol. The results are shown in the following table:

Temperature °C.	% acid	Composition of product		% total
		% ester	% alcohol	
350	19	36	39	94
360	8	36	50	94
370	6	34	58	98
390	2	30	68	100
400	2	29	67	98
410	2	26	65	93
420	1	21	60	82

It is apparent that the lower temperatures favor the formation of waxes, which at the higher temperatures are hydrogenated further to the free alcohols. The optimum temperature is about 390° C.

Although the efficiency of hydrogenation of the carboxyl group may be very high, the saturation of the carbon-carbon linkages in the unsaturated acids, alcohols, and esters may be only partial. In a typical run with oleic acid the acid was 65% hydrogenated as judged by the decrease in the acid and saponification numbers while the iodine number decreased from an initial value of 88 to a value of only 50. The product from the hydrogenation of oleic acid therefore contains both oleyl alcohol and stearyl alcohol. Oleyl alcohol may be separated from the mixture by use of a selective solvent.

In order to obtain pure stearyl alcohol a portion of the mixed alcohols was subjected to hydrogenation in the liquid phase in the presence of a reduced nickel catalyst. A 1000 g. sample of the mixed alcohols was vigorously stirred with 50 g. of nickel on kieselguhr catalyst at 125–150° C. under a hydrogen pressure of 150 lbs. per square in. Hydrogen absorption was rapid and complete after one and one-half hour. On cooling, the product congealed to a white solid having an iodine number less than 10 and consisting chiefly of stearyl alcohol.

Acids which are solid at ordinary temperature have been hydrogenated by melting them and pumping them into the reaction system while still in the liquid state. A more convenient method consists of dissolving the solid acids in a suitable solvent and treating the solution as for a pure acid as indicated in the following example:

Example VII

Thirty-eight hundred and fifty cc. of a solution containing 750 g. of stearic acid in normal butanol was pumped over the catalyst described above at the rate of 200 cc. per 100 cc. of catalyst per hour. The temperature was 390–400° C., the pressure 2500–3000 lbs. and the hydrogen flow about as indicated in the other examples. The recovery of material was nearly quantitative. The butanol was distilled off and the high boiling material subjected to vacuum distillation. Seventy-seven per cent distilled over as a stearyl alcohol cut which was free from acid and had a saponification number of 6 and an acetyl number of 153. The residue was composed of about two thirds wax and about one third alcohol.

Example VIII

A solution of 180 g. of sebacic acid in 900 cc. of absolute ethyl alcohol was hydrogenated in a manner similar to that of Example VII, yielding the corresponding glycol. The crude condensate was distilled to remove the ethanol and the oily residue was subjected to analysis. This material was found to have an acid number of 9, a saponification number of 64 and an acetyl number of 260. From these values, it was estimated that the hydrogenation of the carboxyl groups of the sebacic acid had been about 80% complete.

While the catalyst previously described is preferred because of the high conversion obtained, it is to be understood that other suitable hydrogenating catalysts can be used. The cataylst composition contributes in an important way to the yield of alcohols and freedom from side reactions, but it is only necessary to employ any good hydrogenation catalyst under the conditions described in order to effect the reduction of acids. Such a catalyst may be composed of one or more metals or metallic oxides prepared in an active form and preferably selected from the group known as the hydrogenating metals or metallic oxides. Some well known members of this group are copper, cadmium, nickel, cobalt, tin, zinc oxide, magnesium oxide, and manganese oxide. These may be combined with promoters of the oxide type in the form of mixtures or compounds with the same. In general the catalysts which have found use in methanol synthesis are applicable to the present process. Particularly good results have been obtained in acid hydrogenation by preparing such a catalyst according to the method described in U. S. Patent 1,746,783, wherein a double ammonium chromate of a hydrogenating metal is heated to form a chromite catalyst. As indicated in the examples success has attended the use of mixtures of the chromites of two or more hydrogenating metals. The catalyst compositions prepared according to the manner described on page 2 and corresponding to those catalysts disclosed in my copending application, Serial No. 470,238, filed July 23, 1930, are eminently suited to use in the present invention. I prefer to use a chromite composition consisting substantially of zinc chromite but containing lesser quantities of the chromates or chromites of copper and cadmium.

Temperatures as low as 200° C. may be used in conducting the reaction, but the most satisfactory results are obtained between 300 and 400° C., depending somewhat on the catalyst composition selected and the chemical nature of the acid to be reduced.

The minimum pressure at which it is desirable to operate is about 13.5 atmospheres, the best results being obtained at higher pressures, usually between 100 and 205 atmospheres. Elevated temperatures and pressures are essential to the success of the process but within the operative limits of temperature and pressure, the temperature is the most important factor in determining the yield of hydrogenation products. Thus, when the reaction is conducted at the higher temperatures with the lower operative pressures the yield is much greater than is obtained when the lower temperatures are used with the higher pressures. The higher temperature limit is determined by the temperature at which undesirable decomposition takes place and in so far as I am aware the higher operative pressures are limited only by practical considerations for obtaining exceptionally high pressures. The optimum pressures will vary somewhat depending upon the acid treated and the degree of hydrogenation and freedom of the product from side products desired.

The ratio of hydrogenation to acid may also be varied over a wide range. While it may not always be strictly necessary, I prefer to use an excess of hydrogen, say from 2 to 10 moles per mole of acid hydrogenated.

The rate of which the acid may be passed over the catalyst is a function of the molecular weight of the acid and the catalytic activity of the contact mass. For the ordinary acids I prefer to pass from 2 to 8 volumes per hour per unit volume of catalyst, but higher rates may be employed at the expense of slightly lower conversions.

The acid may be employed in liquid form or, if it is a solid, it may be dissolved in a solvent and the solution treated as for the pure acid. Mixtures of acids such as are obtained from naturally occurring products may be reduced as well as the individual acids in a pure state.

As demonstrated in the examples, the process may be operated to produce either alcohols or esters as the major products. Thus, a high rate of flow and the lower operative temperatures favor the formation of esters, whereas conditions tending to cause more complete hydrogenation, i. e., a low rate of flow and high temperatures, favor the formation of alcohols.

The process of the present invention is unique in the success that has attended control of the expected side reactions. It was well known prior to my discovery that alcohols, particularly those of high molecular weight, are very susceptible to dehydration to hydrocarbons at high temperatures, a reaction which is not appreciably inhibited by application of pressure. Another reaction which is characteristic of carboxylic acids is decarboxylation with the formation of carbon dioxide and a hydrocarbon having a lesser number of carbon atoms. By careful control of the operating conditions and selection of catalyst, these troublesome side reactions have been suppressed to such an extent that they are now of negligible importance.

As a method for the preparation of alcohols and esters, the hydrogenation of acids possesses distinct advantages over the hydrogenation of either the simple esters or glycerides of the acids. The esters of acids with the simple alcohols occur only rarely in nature and must usually be synthesized specifically for use in the hydrogenation process. After hydrogenation the desired products must be removed from the undesired alcohols introduced in the esterification process. Both extra operations are avoided by use of the free acids. Glycerides, while relatively inexpensive, lead to products on hydrogenation which are rather difficult to separate, owing to the presence of glycerol and its decomposition products.

The present invention is applicable to the synthesis of alcohols and esters from a very great number and wide variety of carboxylic acids. The configuration of the acid is relatively unimportant. Best results are obtained by use of the classes of acids known as aliphatic and hydroaromatic acids, but the invention is not limited to these as the process may also be applied to hydroxy or ketonic acids, monobasic or dibasic acids, or aromatic acids containing the carboxyl group in an aliphatic side chain.

From the foregoing it will be apparent that I have developed a new process for producing higher alcohols cheaply and in unlimited quantities starting with the acids derived from the naturally occurring fats and oils and without the use of expensive chemical reagents. The practice of my invention makes available a new and economical source of supply for these alcohols which will tend to develop important uses for the higher alcohols and their derivatives.

No claims are made herein to the various catalysts which have been described or to the use of any of the described catalysts for reactions other than the hydrogenation of acids. Certain of the catalysts described, their preparation, and their use broadly and specifically in hydrogenation and dehydrogenation reactions, in so far as this subject matter is novel, are described and claimed in copending applications to W. A. Lazier, Serial No. 445,-224, filed April 17, 1930, Serial No. 470,238, filed July 23, 1930, and Serial No. 520,473, filed March 5, 1931.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for producing alcohols and esters which comprises heating carboxylic acid with hydrogen above 200° C. and above 13.5 atmospheres pressure in the presence of a hydrogenating catalyst.

2. A process for producing alcohols and esters which comprises heating carboxylic acid with hydrogen within a temperature range of 300–400° C. and within a pressure range between 100 and 205 atmospheres in the presence of a hydrogenating catalyst.

3. A process for producing alcohols and

esters which comprises heating carboxylic acid and excess hydrogen above 200° C. and above 13.5 atmospheres pressure in the presence of a hydrogenating metallic oxide.

4. A process for producing alcohols and esters which comprises heating carboxylic acid and excess hydrogen above 200° C. and above 13.5 atmospheres pressure in the presence of a mixture of hydrogenating metallic oxides.

5. A process for producing alcohols and esters which comprises heating carboxylic acid and excess hydrogen above 200° C. and above 13.5 atmospheres pressure in the presence of a difficultly reducible hydrogenating metallic chromite.

6. A process for producing alcohols and esters which comprises heating carboxylic acid and excess hydrogen above 200° C. and above 13.5 atmospheres pressure in the presence of a mixture of zinc, copper, and cadmium chromite.

7. The process of claim 1 in which the carboxylic acid is aliphatic.

8. The process of claim 1 in which the carboxylic acid is monobasic.

9. The process of claim 1 in which the carboxylic acid is oleic acid.

10. The process of claim 1 in which the carboxylic acid is stearic acid.

11. The process of claim 1 in which the carboxylic acid is lauric acid.

12. The process of claim 1 in which a molar excess of hydrogen is used.

In testimony whereof, I affix my signature.

WILBUR A. LAZIER

Certificate of Correction

Patent No. 1,839,974. Granted January 5, 1932, to

WILBUR A. LAZIER.

It is hereby certified that error appears in the printed specification of the above-numbered patent requiring correction as follows: Page 2, line 67, for the word "difficulty" read *difficultly;* page 3, lines 114 to 124 inclusive, strike out the table and insert the following:

Temperature °C.	Composition of product			
	% acid	% ester	% alcohol	% total
350	19	36	39	94
360	8	36	50	94
370	6	34	58	98
390	2	30	68	100
400	2	29	67	98
410	2	26	65	93
420	1	21	60	82

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page 5, line 11 for "hydrogenation" read *hydrogen;* same page, line 16, for "of" read *at;* and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23d day of February, A. D. 1932.

[SEAL.]

M. J. MOORE,
Acting Commissioner of Patents.