

## UNITED STATES PATENT OFFICE

2,105,540

CATALYTIC HYDROGENATION PROCESS  
FOR THE PRODUCTION OF ALDEHYDESWilbur A. Lazier, Marshallton, Del., assignor to  
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mington, Del., a corporation of DelawareNo Drawing. Application January 9, 1935,  
Serial No. 951

27 Claims. (Cl. 260—138)

This invention relates to a process for the catalytic hydrogenation of carboxylic acids containing at least two carbon atoms and the esters and anhydrides of such acids to the corresponding aldehydes, and more specifically it relates to a process for the hydrogenation of carboxylic acids containing eight or more carbon atoms, and the esters and anhydrides of such acids to the corresponding aldehydes.

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, lactones, 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 direct reduction of acids to aldehydes has probably presented the greatest difficulty of all. Professor Moreau 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 aldehydes 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 available commercially.

Of the known methods for obtaining aldehydes, the following may be mentioned. One process, depending upon 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. Acids may also be converted to aldehydes by distilling a dry mixture of the calcium or barium salt of the acid with the same salt of formic acid (Cohen's "Theoretical Organic Chemistry", second edition, page 127). However, so far as I am aware, the processes for the production of aldehydes described in the pres-

ent invention have never been, known prior to my discovery thereof.

This invention has as an object a new process of converting carboxylic acids containing at least two carbon atoms per carboxyl group to the corresponding aldehydes by means of hydrogenation. A further object is the conversion of esters and anhydrides of such acids to aldehydes. Another object is the employment of highly efficient hydrogenation catalysts to effect the desired conversions. Further objects will appear hereinafter.

The above objects are accomplished according to the present invention by processes which in a general way comprise the treatment of carboxylic acids, their esters or anhydrides, with hydrogen at elevated temperatures and substantially atmospheric pressure in the presence of suitable efficient hydrogenating catalysts.

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 mol of hydrogen is required to convert the  $\text{—COOH}$  group to a  $\text{—CHO}$  group in the case of an acid, while a similar reaction occurs in the case of an ester or anhydride. The process is characterized by hydrogenation of the acids, esters, or anhydrides with a suitable hydrogenating catalyst at elevated temperatures, and at pressures that are in the neighborhood of atmospheric. In conducting the reactions, an excess of hydrogen is preferred, and a special hydrogenation catalyst described hereinafter.

Catalysts especially suitable for the purposes of this invention may consist of a mixture of difficultly reducible and easily reducible oxides of hydrogenating metals. By the term "difficultly reducible oxides" as used herein and in the claims, I refer to those which remain substantially in the oxide form after several hours' exposure in a pure state to the action of hydrogen at  $400^{\circ}\text{C}$ . The preferred catalysts are those oxygen compositions in which the elements are at least partially associated in the form of chromites. An effective catalyst comprising a mixture of the chromites 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, 25 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 ( $\text{CrO}_3$ ) in 500 parts of water and then adding 135 parts of 28

per cent 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 sizes. In some cases it is advisable to pre-reduce the 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 the invention.

#### Example 1

Twenty-five cubic centimeters of a hydrogenation catalyst prepared as described above and crushed to 8-25 mesh size was placed in a steel reaction vessel and slowly heated to 300° C. in a stream of hydrogen. The temperature was then raised to 376° C. and ethyl acetate was pumped over the catalyst together with hydrogen at atmospheric pressure. The ethyl acetate and hydrogen were passed over the catalyst at rates of 8.35 cc. and 35.6 cu. ft. per hour, respectively. During the last 1.5 hours of a 5-hour run a solid carbon dioxide trap was placed in the exit line and the products collected. In addition to unchanged ethyl acetate and ethyl alcohol, a substantial quantity of acetaldehyde was obtained.

#### Example 2

Fifty cubic centimeters of the catalyst already described was crushed to 8-14 mesh size and pre-reduced with hydrogen for one hour at 375° C. in a steel tube. Then with the temperature still at 375° C., and at atmospheric pressure, lauric acid and hydrogen were pumped over the catalyst at respective rates of 25 cc. per hour and 26.9 liters per hour. The products of hydrogenation were condensed and upon separation by fractional distillation under reduced pressure yielded a substantial quantity of lauric aldehyde and in addition dodecyl, laurate, dodecyl alcohol, and unchanged lauric acid. The lauric acid was recycled to produce additional dodecyl laurate.

#### Example 3

A run was made as in Example 2 except that the lauric acid and hydrogen were pumped over the catalyst at the respective rates of 50 cc. per hour and 53.8 liters per hour. Thus, the time of contact with the catalyst was reduced and a larger yield of lauric aldehyde resulted.

#### Example 4

Ninety cubic centimeters of 8-14 mesh catalyst, the preparation of which has been described, was pre-reduced with hydrogen for one hour at 375° C. in a reaction tube. Then at a temperature of 375° C. and at atmospheric pressure,

ethyl laurate and hydrogen were pumped over the catalyst at rates of 18 cc./hr. and 20.4 l./hr., respectively. Separation of the condensed products of hydrogenation gave ethyl alcohol, unchanged ethyl laurate and a quantity of lauric aldehyde.

#### Example 5

Under the conditions of Example 2, caproic anhydride and hydrogen were passed over the catalyst at respective rates of 30 cc. per hour and 50 liters per hour. The condensed products of hydrogenation yielded a substantial quantity of caproic aldehyde and also some unchanged acid and the corresponding alcohol.

While the catalyst previously described is preferred because of the yield of aldehydes obtained, it is to be understood that other suitable hydrogenating catalysts may be used.

Mild-acting hydrogenating catalysts such as metallic copper and zinc oxide, which are well known to be suitable for the synthesis of methanol from carbon oxides and hydrogen, are in general also suitable catalysts for the production of aldehydes in the manner set forth. On the other hand, there are certain very energetic catalysts such as metallic nickel and iron which are known to catalyze the formation of hydrocarbons from the oxides of carbon and hydrogen. These ferrous metal catalysts, when employed in the hydrogenation of acids, anhydrides and esters to aldehydes, tend to carry the reaction too far with the formation of hydrocarbons. To make the hydrogenation operative for the production of aldehydes to the substantial exclusion of hydrocarbons, I select as the catalyst a composition comprising a member of the group of non-ferrous hydrogenating metals such as copper, tin, silver, cadmium, zinc, lead, their oxides and chromites, and oxides of manganese and magnesium. Especially good results are obtained with finely divided copper oxide, either wholly or partially reduced and preferably supported upon an inert surface-extending material such as kieselguhr, or promoted by such promoters as manganese oxide, zinc oxide, magnesium oxide, or chromium oxide.

The above mentioned mild-acting catalysts may be termed the alcohol-forming catalysts to distinguish them from the more energetic hydrocarbon-forming elements of the platinum and ferrous metal groups.

Elementary nickel, cobalt and iron, when suitably supported on kieselguhr, may be used to effect the reduction of the acids, anhydrides and esters with hydrogen, but in these cases the product contains besides aldehydes a preponderance of hydrocarbons. This disadvantage in most cases will prove so serious as to preclude the use of these catalysts unless the hydrocarbons themselves are the desired products.

Particularly good results have been obtained in acid hydrogenation with catalysts prepared 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 chromites of two or more hydrogenating metals. The catalyst compositions prepared according to the manner disclosed in co-pending application Serial No. 470,238, filed June 23, 1930, and issued June 26, 1934 as U. S. Patent No. 1,964,001, are eminently suited to use in the present invention. I prefer to use a chromite composition consisting substantially of zinc chromite but con-

taining 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 compound to be reduced.

An important feature of the present invention is the employment of pressures which are substantially atmospheric. Low pressures favor the formation of aldehydes, whereas elevated pressures favor the formation of alcohols and esters as described in my United States Patent No. 1,839,974, issued January 5, 1932. It is preferred to operate at atmospheric pressure or at pressures not greatly above normal. However, when it is desired to produce mixtures of alcohols and aldehydes, a somewhat higher pressure may be used, providing it does not exceed about 10 atmospheres.

The ratio of hydrogen to acid, ester or anhydride may also be varied over a wide range. While it may not always be strictly necessary, the use of an excess of hydrogen is preferred, say from 2 to 10 moles per mole of compound to be hydrogenated.

The rate at which the acid, ester or anhydride may be passed over the catalyst is a function of the molecular weight of the compound and the catalytic activity of the contact mass. In general, it will be found desirable to use a rather high rate to obtain the best yield of aldehyde, say in the neighborhood of 10 volumes of compound per unit volume of catalyst, but higher rates may be employed successfully.

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

From the foregoing, it will be apparent that I have developed an entirely new process for the production of aldehydes which is superior to the older indirect methods for obtaining the same. The aldehydes which are obtained by the processes of this invention may be used as sources of amines and are valuable as intermediates. They may also be used for the production of addition compounds and for condensation reactions. The higher aldehydes will be particularly valuable, as in the past they have not been readily obtainable.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. A process of producing aldehydes by the catalytic hydrogenation of a carboxyl group to an aldehyde group, which comprises heating the vapor of a compound containing the radical of an aliphatic monocarboxylic acid having at least two carbon atoms, said compound being selected from the group consisting of the acid, its anhydride, and its alkyl esters, with hydrogen to a temperature of at least 300° C. and at a pressure

less than 10 atmospheres, while in contact with a mild-acting hydrogenation catalyst.

2. The process in accordance with claim 1 characterized in that the reaction is carried out at a temperature between 300° C. and 400° C.

3. The process in accordance with claim 1 characterized in that the reaction is carried out at substantially atmospheric pressure.

4. The process in accordance with claim 1 characterized in that the catalyst is a mixture of 10 hydrogenating metal chromites.

5. The process in accordance with claim 1 characterized in that the catalyst is a mixture of hydrogenating metal chromites at least one of which is a chromite of a hydrogenating metal whose oxide is difficultly reducible.

6. The process according to claim 1 characterized in that the catalyst comprises essentially a difficultly reducible hydrogenating metal oxide.

7. The process according to claim 1 characterized in that the catalyst comprises essentially a mixture of hydrogenating metal oxides at least one of which is a difficultly reducible metal oxide.

8. The process according to claim 1 characterized in that the catalyst comprises essentially a hydrogenating metal chromite.

9. The process according to claim 1 characterized in that the catalyst comprises essentially a mixture of zinc, copper and cadmium chromites.

10. A process of producing aldehydes by the catalytic hydrogenation of a carboxyl group to an aldehyde group, which comprises heating the vapor of a compound containing the radical of an aliphatic monocarboxylic acid having at least eight carbon atoms, said compound being selected from the group consisting of the acid, its anhydride, and its alkyl esters, with hydrogen to a temperature of at least 300° C. and at a pressure less than 10 atmospheres, while in contact with a mild-acting hydrogenation catalyst.

11. The process in accordance with claim 10 characterized in that the catalyst is a mixture of hydrogenating metal chromites.

12. The process in accordance with claim 10 characterized in that the catalyst is a mixture of hydrogenating metal chromites at least one of which is a chromite of a hydrogenating metal whose oxide is difficultly reducible.

13. The process in accordance with claim 10 characterized in that the reaction is carried out at a temperature between 300° C. and 400° C.

14. The process in accordance with claim 10 characterized in that the reaction is carried out at substantially atmospheric pressure.

15. The process according to claim 10 characterized in that the catalyst comprises essentially a difficultly reducible hydrogenating metal oxide.

16. The process according to claim 10 characterized in that the catalyst comprises essentially a mixture of hydrogenating metal oxides at least one of which is a difficultly reducible metal oxide.

17. The process according to claim 10 characterized in that the catalyst comprises essentially a hydrogenating metal chromite.

18. The process according to claim 10 characterized in that the catalyst comprises essentially a mixture of zinc, copper and cadmium chromites.

19. A process of producing lauric aldehyde by the catalytic hydrogenation of a carboxyl group to an aldehyde group, which comprises heating the vapor of a compound containing the radical of lauric acid, said compound being selected from the group consisting of the acid, its anhydride, and its alkyl esters, with hydrogen to a

temperature of at least 300° C. and at a pressure less than 10 atmospheres, while in contact with a mild-acting hydrogenation catalyst.

5 20. The process in accordance with claim 19 characterized in that the reaction is carried out at a temperature between 300° C. and 400° C.

21. The process in accordance with claim 19 characterized in that the reaction is carried out at substantially atmospheric pressure.

0 22. The process in accordance with claim 19 characterized in that the catalyst is a mixture of hydrogenating metal chromites.

15 23. The process in accordance with claim 19 characterized in that the catalyst is a mixture of hydrogenating metal chromites at least one of which is a chromite of a hydrogenating metal whose oxide is difficultly reducible.

24. The process according to claim 19 characterized in that the catalyst comprises essentially a difficultly reducible hydrogenating metal oxide.

25. The process according to claim 19 characterized in that the catalyst comprises essentially a mixture of hydrogenating metal oxides at least one of which is a difficultly reducible metal oxide. 5

26. The process according to claim 19 characterized in that the catalyst comprises essentially a hydrogenating metal chromite. 10

27. The process according to claim 19 characterized in that the catalyst comprises essentially a mixture of zinc, copper and cadmium chromites. 15

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