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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Synthesis of Organic Oxygen-containing Compounds

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, of Wilmington, Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the synthesis of organic oxygen-containing compounds.

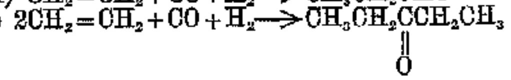
It was early observed by Patart (French Patent 593,648)) that when a mixture containing ethylene, carbon monoxide, and hydrogen was heated under a pressure of 150—250 atmospheres at a temperature of 300° C. in the presence of a zinc chromate catalyst, a reaction product was obtained which consisted essentially of methanol and hydrocarbons, but which also contained very small quantities of aldehydes and higher alcohols. Smith, Hawk, and Golden (J.A.C.S., 52, 3221) reported that oxygen-containing compounds other than methanol were formed in 25—35% yield when mixtures of ethylene, carbon monoxide, and hydrogen were heated at temperatures of 206°—245° C., under atmospheric pressure in the presence of a cobalt-copper-manganese oxide catalyst. The nature of these oxygen-containing compounds was not ascertained, although aldehyde boiling below 100° C., were shown to be present. Later it was reported (German Patents 539,990 and 660,619) that mixtures of hydrogen and carbon monoxide react with ethylene at high temperature (500° C.) under increased pressures (150 atmospheres) to give a mixture of hydrocarbons, higher alcohols, and ketones. More recently Roelen (U.S. Patent 2,327,066) found that propionaldehyde could be obtained in yields considerably higher than previously, e.g. 40%, together with other oxygen-containing products, by processing mixtures of ethylene, carbon monoxide, and hydrogen at a temperature of about 40°—200° C., under a pressure within the range 20—300 atmospheres in the presence of hydrogenation catalysts.

According to the present invention there is provided a process for the production of oxygen-containing organic compounds which comprises reacting an olefinic compound, carbon monoxide and hydrogen at a pressure exceeding 300 atmospheres gauge in the presence of a hydrogenation catalyst and at a temperature of 75°—250° C.

This invention involves the surprising discovery that at pressures in excess of 300 atmospheres gauge, the formation of ketones from compounds containing olefinic unsaturation, carbon monoxide and hydrogen, in the presence of hydrogenation catalysts is completely or almost completely avoided, and aldehydes are formed in very high yields. More particularly, it has been discovered in accordance with the invention that the reaction between olefinic compounds, carbon monoxide, and hydrogen produces aldehydes in yields as high as 70% to 100% at pressures in excess of 300 atmospheres, preferably within the range of about 325 to 1500 atmospheres, at a temperature of about 75° to 250° C. preferably 100° C. to 200° C., in the presence of certain catalysts to be hereinafter disclosed.

In one of its important aspects the invention may be viewed as a novel method for controlling competing reactions in the olefine-$H_2$-CO system, so that the desired aldehyde products are obtained selectively. Thus, for example when ethylene is the olefine, two competing reactions are involved as follows:—

(1) $CH_2=CH_2+CO+H_2 \rightarrow CH_3CH_2CHO$

(2) 
$$2CH_2=CH_2+CO+H_2 \rightarrow CH_3CH_2\underset{\underset{O}{\parallel}}{C}CH_2CH_3$$

in the processes of the prior art these two reactions (and others) take place simultaneously at pressures up to 300 atmospheres. The normal effect of increased pressure would be to suppress reaction (1) and to favour reaction (2) since the former is accompanied by the smaller volume decrease. It was therefore a surprising and unexpected discovery that increase of pressure did not produce such a result, but, on the contrary, suppressed reaction (2) instead of reaction (1).

The following table, based on experimental data obtained by procedures described more fully in the Examples which follow, brings out this anomalous effect. The experiments were made by heating mixtures containing 75 cc. diethyl ether, 28 grams of ethylene and 10 grams of metallic cobalt catalyst in a shaker tube in the presence of a gas containing two volumes of hydrogen per volume of carbon monoxide. Temperatures were held within the range 120°—160° C. The reaction is exothermic and heat-removing means was required, especially at higher pressures. The table indicates that at pressures above about 300 atmospheres propionaldehyde formation was selectively favoured.

Reaction between Ethylene, Hydrogen and Carbon Monoxide.

| Gauge pressure (atm.) | Reaction time (min.) | Weight of propionaldehyde (monomer and trimer) (grams) | Weight of other oxygen-containing products (grams) |
|---|---|---|---|
| 200 | 66 | 4.6 | 4.4 |
| 280 | 60 | 4.7 | 10.4 |
| 350 | 71 | 35 | 14.8 |

This advantage is observed not only with ethylene but also with olefinic compounds generally. A further advantage resulting from the use of pressures greater than 300 atmospheres gauge when the olefinic reactant is propylene, is that the butyraldehyde fraction contains a much higher ratio of *n*-butyraldehyde relative to isobutyraldehyde than does the corresponding product obtained at pressures below 300 atmospheres gauge.

The effect of pressure in selectively favouring aldehyde formation is very pronounced when the molar ratio of $CO:H_2$ is initially from about 1:1.5 to about 1:10. These improved results are realised not only with relatively stable olefines such as ethylene but also with olefinic materials which polymerise rapidly, such as the dienes, although loss by polymerisation of the reactant when the latter type of olefinic materials is used sometimes occurs. Such loss may be reduced by the use of an inhibitor such as hydroquinone.

Unsaturated compounds containing olefinic unsaturation which may be used in accordance with this invention are the olefinic hydrocarbons and other organic compounds containing at least one nonbenzenoid double bond between carbon atoms. Examples of such compounds are the olefinic hydrocarbons themselves, e.g. ethylene, alkyl-substituted ethylenes (such as propylene, butene-2, isobutylene, pentene-1, tetramethyl ethylene, di-isobutylene, and cracked gasoline fractions), cyclohexene, butadiene, isoprene, polymerised dienes, styrene, alpha-methyl styrene, vinyl cylclohexene, pinene, limonene, mixed olefine fractions obtainable by cracking and/or dehydrogenating petroleum, cyclohexadiene, dicyclopentadiene; unsaturated oxygenated compounds such as allyl alcohol, allyl acetate, allyl ethers, methallyl alcohol, vinyl acetate, furan, methyl methacrylate, methyl acrylate, methallyl propionate, methyl oleate, methyl vinyl ketone, methyl vinyl ether, cyclohexene carboxylic acids, esters of cyclohexene carboxylic acids, (such as methyl $\Delta^3$-tetrahydro benzoate), methallyl methacrylate, acrolein; and, in general, the unsaturated hydrocarbons, esters, ethers, carboxylic acids, amides, aldehydes and ketones containing non-benzenoid olefinic unsaturation. The olefinic reactants employed in the practice of this invention should preferably be deoxidized prior to use.

The catalysts which may be employed include the hydrogenation catalysts generally, such as nickel, cobalt, iron, copper, ruthenium, and mixtures or compounds thereof. These materials may be used in combination with each other or with inert materials, such as kieselguhr or pumice, or with promoters such as thoria or manganese. The proportion of catalyst employed is generally about 0.1 to 10.0% by weight of the total reaction mixture.

The pressure is limited only by the strength of the retaining vessel and may be as high as 3000 atmospheres or even higher. The reaction may be conducted either batchwise or continuously. The relative proportions of reactants employed may be stoichiometrically-required quantities, although other proportions may be employed if desired. Excellent results are obtained when the molal ratio of $CO:H_2$:olefine is within the range, 1:2:1 to about 1:4:1, but the invention is not limited to this range. In one method of practising the invention the olefinic compound, catalyst, and solvent are placed in a pressure vessel, and a mixture of carbon monoxide and hydrogen is injected under very high pressure. After the reaction is complete, the resulting liquid product is removed from the reaction vessel and the aldehydes are separated therefrom by any suitable method, for example by fractional distillation. In some instances, the product contains the desired aldehydes in polymeric (particularly trimeric) form, and such products may be readily depolymerised during distillation to obtain the monomers.

If desired, any inert liquid may be employed as a reaction medium. Moreover, it has been discovered that in certain cases the yield of product and, in fact, the nature and rate of the reactions occurring are determined, at least in part, by the nature of the reaction medium. Thus, when water is employed, the reaction yields relatively large amounts of unsaturated aldehydes. Examples of solvents suitable for the production of saturated aldehydes are cyclohexane, exylene, methyl formate and diethyl ether.

The advantages of the present invention are that very high yields of aldehydes are obtained with such olefines as ethylene, and that aldehydic products can be obtained from olefinic reactants which do not give appreciable yields of aldehydes at lower pressures. In many instances, the aldehydes thus obtained can be hydrogenated *in situ* to the corresponding primary alcohols. Formation of ketones, or products derived therefrom, is virtually completely avoided.

While the process of the invention is applicable to the preparation of saturated and unsaturated aldehydes, it is to be understood that the method can be adapted to the manufacture of other organic compounds derivable therefrom. Thus condensation products of such aldehydes as are produced from the unsaturated compound, carbon monoxide, and hydrogen, may be converted to cyclic trimers or high-boiling products under the reaction conditions. Furthermore, if the hydrogenation is prolonged ,it is possible to convert the aldehydes to the corresponding alcohols. Alternatively, the aldehydes may be hydrogenated to the corresponding alcohols in a separate step in the absence of carbon monoxide. At temperatures above 180°—190° C., hydrogenation of carbon monoxide readily occurs and the alcohols produced either by CO hydrogenation or by aldehyde hydrogenation may react with aldehydes simultaneously formed, so that the resultant product may contain acetals.

The process of the invention may be practised by heating the reactants in any suitable pressure-resistant vessel such as an autoclave or tubular converter preferably made of, or lined with, inert materials such as glass, porcelain, inert metals and the like. If desired, constructional materials yielding small amounts of metallic carbonyls which are effective as catalyst may be employed. Outstanding results, however, are obtained in reaction vessels lined with silver or copper. In the continuous process, the reactants may be introduced at one or more points within the reaction vessel if desired. In certain instances it is preferred to employ a tubular reaction vessel in which the temperature and pressure are not uniform throughout the length of the vessel.

In most cases it is preferred to employ mixtures containing carbon monoxide and hydrogen in the proportions of about 1:2 to 1:4, but other mixtures of carbon monoxide and hydrogen, containing inert gases may be used, if desired. The use of an excess of one of the reactants or of an inert diluent gas assists in dissipating the heat of the reaction.

The products obtained in accordance with this invention are widely useful, and are especially valuable as intermediates for the manufacture of alcohols, glycols, esters, and numerous other materials.

The invention is illustrated but not limited by the following Examples.

### EXAMPLE 1.

A reaction mixture having the composition $H_2:CO:C_2H_4$ 4:1:1 was continuously passed at a gauge pressure of 500 atmospheres over reduced fused cobalt catalyst at a temperature of 140°—150° C. and the liquid product was distilled for recovery of the oxygen-containing constituents. As shown in the table below monomeric propionaldehyde formed 95.5% of the product.

Details of two like runs in which the high range of pressure was employed and in which the relative proportions of the reactants were varied are also given. The higher yield of aldehyde obtained at these higher pressures is well brought out by comparing these figures with those obtained for a pressure of 125 atmospheres gauge. (See the fourth line of the table).

| Charge | Reaction Time (Min.) | Pressure (atmospheres) | Reacting % | Monomeric propionaldehyde in liquid product % | Diethyl ketone in liquid product % |
|---|---|---|---|---|---|
| $4H_2:CO:C_2H_4$ | 0.5 | 500 | 33.5 | 95.5 | — |
| $H_2:CO:C_2H_4$ | 0.5 | 500 | 34 | 92.0 | — |
| $2H_2:CO:C_2H_4$ | 0.6 | 700 | 63 | 91 | — |
| $H_2:CO:C_2H_4$ | 6.8 | 125 | 70 | 50 | 22 |

### EXAMPLE 2.

A mixture containing 10 grams of reduced fused alkali-free cobalt catalyst, 75 cc. of diethyl ether and 42.1 grams of propylene was heated in a silver-lined shaker tube for 2 hours at a temperature of 108°—120° C. under a pressure of 470—790 atmospheres gauge with a $CO:2H_2$ mixture. Distillation of the resulting product gave 69.9 grams of *n*-butyraldehyde, corresponding to a conversion of 97.1%. Part of the product was trimer, which depolymerised during the distillation.

### EXAMPLE 3.

A mixture containing 140 grams of ethylene, 140 grams of carbon monoxide and 20 grams of hydrogen was pumped through a 20″ long × 1″ diam. (inside dimension) silver-lined tube at a temperature of 140° C. under a pressure of 700 atmospheres gauge (during one hour). The reaction vessel contained 65 ccs. of metallic cobalt catalyst, 8 to 14 mesh, arranged in 3 beds separated by copper rivets. Analysis of the product showed that propionaldehyde was produced in 80% conversion based on the ethylene charged. The rate of production of propionaldehyde was 140 lb. per cubic foot of catalyst per hour.

### EXAMPLE 4.

The run described in Example 3 was repeated exactly except that the reaction mixture also contained 900 grams of cyclohexane. The conversion of ethylene to propionaldehyde was 80%. The rate of production of propionaldehyde was 180 lb. per cubic foot of catalyst per hour.

### EXAMPLE 5.

A mixture containing 128 cc. cyclohexane, 28 grams of ethylene and 10 grams of copper molybdate catalyst was heated for 3 hours at 155°—165° C. under 605—810 atmospheres of $CO:2TH_2$. The resulting reaction product contained substantially no diethyl ketone, and was chiefly a mixture of propionaldehyde and *n*-propanol.

### EXAMPLE 6.

A mixture containing 66.1 grams of dicyclopentadiene, 75 cc. of diethyl ether and 10 grams of reduced, fused cobalt catalyst containing 3% of copper was processed in a copper-lined shaker tube with $CO:2H_2$ at 610 to 795 atmospheres gauge for 4.3 hours at a temperature of 110°—132°C. On distillation the reaction product yielded 22.5 grams of mono-aldehyde (B.P. 79° C. at 3 mm., carbonyl number 340, calc., 346), and 27.3 grams of unidentified aldehyde-containing products having a boiling range of from 95° C. at 8 mm. to 158° C. at 7 mm.

The carbonyl number is the number of milligrams of KOH per gram of sample required to neutralise the acid liberated by reaction between the material tested and hydroxylamine hydrochloride.

### EXAMPLE 7.

A mixture containing 82.1 grams (1.0 mols) of cyclohexane, 75 cc. of diethyl ether and 10 grams of reduced, fused cobalt catalyst containing 3% of copper was processed in a copper-lined shaker tube for 2 hours under a pressure of 580—790 atmospheres of $CO:4H_2$ at a temperature of 110°—112° C. On distillation the products yielded 41.5 grams of hexahydrobenzaldehyde, B.P. 55°—60° C. at 19 to 20 mm. (carbonyl number, 507.5. 508.1; Calc., 501), 11.8 grams of high-boiling products (103°/7 mm.—194°/5 mm.) and 8.6 grams of a distillation heel which appeared to be about half hexahydrobenzaldehyde trimer.

### EXAMPLE 8.

A mixture containing 58.8 grams (0.716 mol) of cyclohexene, 75 cc. of cyclohexane and 10 grams of a reduced, fused cobalt catalyst was processed in a copper-lined shaker tube for 2 hours. Sufficient CO and $H_2$ in the molar ratio of 1:4 was injected to maintain a pressure of 183—196 atmospheres gauge at the operating temperature of 160°—170° C. Distillation of the resulting product at atmospheric pressure yielded 93.3 grams of a mixture of cyclohexane and unconverted cyclohexene (B.P. 81°—83° C.: cyclohexene content about 41 grams), and 3.9 grams of impure material boiling in the range, 66° C./18 mm.—81° C./2 mm. and having a carbonyl number 196. There remained only 0.9 gram of distillation heel. The results of this experiment, when compared with those of the experiment described in Example 7, show the poor conversion obtained at relatively low pressure.

### EXAMPLE 9.

A mixture comprising 43 grams of methyl acrylate, 0.5 gram of hydroquinone, 100 cc. of methyl formate and 10 grams of reduced, fused cobalt catalyst was processed in a shaker tube with $CO:2H_2$ under 390—730 atmospheres gauge pressure at 145°—167° C. for one hour. On distillation the product gave methyl γ-aldehydobutyrate in 57.4% yield (B.P. 62° C./10 mm.), characterised by hydrogenation to tetramethylene glycol using copper chromite catalyst, and reaction conditions circa 230° C. and 700 atmospheres.

### EXAMPLE 10.

A mixture comprising 75 cc. of diethyl ether, 20 grams of reduced, fused cobalt catalyst and 44 grams of butadiene was heated in a shaker tube for 2 hours at 142° to 220° C. under a pressure of 400—575 atmospheres of $CO:H_2$. On distillation the resulting product under atmospheric pressure gave 11.4 grams of a fraction which boiled within the range 101°—121° C. and had a carbonyl number of 449.

### EXAMPLE 11.

A mixture comprising 100 cc. of water, 10 grams of a reduced cobalt-iron catalyst containing the components in the relative proportions by weight 65:35 and 28 grams of ethylene was heated for 1.5 hours at 110°—178° C. under a $CO:2H_2$ pressure of 550—730 atmospheres in a stainless steel shaker tube. On distillation the product yielded 13.3 grams of propionaldehyde (B.P. 49° C.) and 15 grams of alpha-methyl-beta-ethylacrolein (B.P., water azeotrope, 94° C.; B.P. after separation from water, 135°—139° C.).

### EXAMPLE 12.

The following table records a series of experiments showing how various olefinic compounds react with carbon monoxide and hydrogen under the conditions stated. The reaction was conducted in a shaker tube and reaction times of 0.5—2.0 hours were employed.

| Olefinic Compound | Catalyst | Ratio $CO:H_2$ | Temperature °C. | Pressure: atmospheres gauge | Product | Approximate yield % |
|---|---|---|---|---|---|---|
| Allyl cyanide | Cobalt (cyclohexane = diluent) | 1:1 | 130 | 630—750 | γ-cyanobutyraldehyde | 36 |
| Methyl $\Delta^3$-tetrahydrobenzoate | ,, | 1:1 | 165—185 | 600—750 | Methyl formyl hexahydro benzoate (B.P.) 73°—78° C. | 70 |
| Furan | ,, | 1:2 | 100—205 | 555—740 | Mixtures of aldehydes and alcohols (tetrahydro furfuryl alcohol identified) | — |
| Tetramethylethylene | ,, | 1:2 | 130—140 | 600—775 | Mixture containing high boiling aldhehyde and alcohols | — |
| Allyl acetate | Cobalt (methyl formate = diluent) | 1:2 | 140—148 | 750—775 | $CH_3CO_2(CH_2)_4OH$ (B.P. 80° 2 mm.) | 39 |
| Methyl oleate | ,, | 1:2 | 140—145 | 600—750 | Mixed aldehyde esters | 72 |
| Vinyl cyclohexene | ,, | 1:2 | 120—134 | 475—720 | Mixed mono- and di-aldehydes | 65 |

### Example 13.

A mixture comprising 56.1 grams of butene-2, 100 cc. methyl formate, and 10 grams of reduced, fused alkali-free cobalt catalyst was heated in a silver-lined shaker tube for 2 hours at 120—175° C. under a $CO:2H_2$ pressure of 460—770 atmospheres gauge. On distillation the combined products of two such runs yielded 110.3 grams of α-methyl butyraldehyde (B.P. 54° C./200 mm.), corresponding to a conversion of 64%.

### Example 14.

A mixture containing 75 cc. of diethyl ether, 28 grams of ethylene and 10 grams of a reduced, fused, alkali-free cobalt catalyst containing 3% of copper was heated in a copper-lined shaker tube with a gas containing 2 volumes of hydrogen per volume of carbon monoxide under a pressure of 450—780 atmospheres at a temperature of 110°—120° C. for 1.8 hours. The resulting product was withdrawn from the reaction vessel, the ether was removed therefrom by fractional distillation and there was obtained a residue comprising propionaldehyde (B.P. 46°—48° C. and propionaldehyde trimer (B.P., 65° C./12.5 mm.; r.i. at 25° C. D. line=1.4140). The latter was depolymerised by distillation in the presence of a few drops of sulphuric acid. The total weight of propionaldehyde obtained was 42.8 grams, corresponding to a conversion of 73.8%.

### Example 15.

A mixture having the composition $4H_2:CO:C_3H_6$ was passed over metallic cobalt catalyst at 700 atmospheres gauge pressure at a temperature of 170° C. and a contact time of 0.8 minute. Distillation of the liquid product showed that 65% of the propylene had reacted, forming a product which was chiefly a mixture of normal and isobutyraldehydes. The relative amounts of *n*-butyraldehyde and isobutyraldehydes were 75% and 25% respectively. On repetition of the experiment employing the mixture $H_2:2CO:C_3H_6$ at 500 atmospheres gauge pressure a fraction containing butyraldehydes was obtained. The relative amounts of *n*-butyraldehyde and isobutyraldehyde in this fraction were 56% and 44% respectively.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of oxygen-containing organic compounds which comprises reacting an olefinic compound, carbon monoxide and hydrogen at a pressure exceeding 300 atmospheres gauge and at a temperature of 75° C. to 250° C. in the presence of a hydrogenation catalyst.

2. A process as claimed in claim 1 for the production of aldehydic compounds.

3. A process as claimed in claim 2 wherein the reaction temperature is maintained within the limits 100—200° C.

4. A process as claimed in claim 2 or 3 wherein the molar ratio $CO:H_2$ lies initially within the range 1:1.5 and 1:10.

5. A process as claimed in any of claims 1 to 4 wherein the hydrogenation catalyst is one containing nickel, cobalt, iron, copper or ruthenium.

6. A process as claimed in claim 5 wherein the catalyst is promoted with thoria or manganese.

7. A process as claimed in any of claims 1 to 6 wherein the catalyst is employed in a proportion amounting to 0.1—10.0% by weight of the total reaction mixture.

8. A process as claimed in any of claims 2 to 7 wherein the molar ratio $CO:H_2$: olefine lies within the range 1:2:1 to 1:4:1.

9. A process as claimed in any of claims 1 to 8 in which the reaction is conducted in the presence of a solvent which is inert to the reactants.

10. A process as claimed in any of claims 1 to 9 in which the reaction is conducted in the presence of water and unsaturated aldehydes are obtained.

11. A process as claimed in any of claims 1 to 10 wherein the solvent is cyclohexane, xylene, methyl formate or diethyl ether and saturated aldehydes are obtained.

12. A process as claimed in any of claims 1 to 11 wherein the olefinic compound contains two double bonds.

13. A process as claimed in any of claims 1 to 12 wherein condensation products of the aldehydes formed are reacted further *in situ* to give cyclic trimers.

14. A process as claimed in any of claims 1 to 12 wherein the hydrogenation is prolonged and the aldehydes first formed are thereby converted to alcohols.

15. A process as claimed in any of claims 1 to 12 wherein a temperature of at least 180° C. is employed and acetals are obtained.

16. A process as claimed in any of claims 1 to 15 wherein the reaction vessel is made of or lined with silver or copper.

17. A process as claimed in any of claims 1 to 16 wherein the reaction vessel is constructed of metals yielding small amounts of metallic carbonyls effective as catalysts.

18. A process as claimed in any of claims 1 to 17 wherein a tubular reaction

vessel is employed and the temperature and pressure vary throughout the length thereof.

19. A process as claimed in any of claims 1 to 18 wherein an inert gas or an excess of one of the reactants is employed as a diluent for the gaseous reactants.

20. A process for the production of oxygen-containing organic compounds substantially as described in any of the foregoing Examples.

21. Oxygen - containing compounds whenever produced by the process claimed in any of claims 1 to 20.

Dated the 4th day of June, 1946.
J. W. RIDSDALE,
Solicitor for the Applicants.

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