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3,215,743

PROCESS FOR OXIDIZING OLEFINS CONTAINING AT LEAST 3 CARBON ATOMS TO ALDEHYDES AND KETONES

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8 Claims. (Cl. 260—597)

The present invention relates to a process for oxidizing olefins containing at least 3 carbon atoms to aldehydes and ketones.

Commonly owned copending patent application Serial No. 747,115 filed July 8, 1958 (now abandoned) and 747,116 filed July 8, 1958 (now U.S. Patent 3,154,586 granted October 27, 1964) describe processes for oxidizing ethylene or other olefins, such as propylene, butylene, isobutylene or pentene to the corresponding aldehydes, ketones and acids by means of oxygen or gases containing oxygen in an acid to neutral medium in the presence of water, redox systems and noble metals or compounds of noble metals forming complex compounds with olefins.

When olefins containing at least 3 carbon atoms, for example propylene, butene or pentene, are treated according to the process of the aforesaid copending patent applications ketones are almost exclusively obtained (see *Angewandte Chemie*, 1959, vol. 71, page 179). For example, when propylene is oxidized in the aforesaid manner, only 1 part of propionaldehyde is obtained per 200 parts of acetone formed, and the oxidation of butene-1 yields only about 0.5% of butyraldehyde calculated on the methyl-ethylketone formed. With a fresh catalyst, the quantity of aldehyde formed in the first 2 to 3 hours is larger but it then drops to the aforesaid values given as examples.

Now we have found that the portion of aldehyde formed can be considerably enlarged as compared with ketone, by using a catalyst which contains, per liter of catalyst, more than about 0.5 mol of a noble metal salt, advantageously palladium chloride, in addition to a salt, advantageously the halide, of such metals as are capable of forming several stable valence stages. This is the more surprising since substantially no shift in the ratio of ketone to aldehyde has hitherto been observed when the amount of noble metal salt, for example palladium chloride, was varied within a wide range of, for example, 0.1 to 20 grams per liter of catalyst.

The amount of noble metal salt to be added according to the invention shall exceed 0.25 mol, which corresponds, for example, to 45 grams PdCl_2 , per liter of catalyst and shall be advantageously above 0.5 mol, which corresponds to about 90 grams PdCl_2 , per liter of catalyst. In the case of liquid catalysts, the upper limit is given by the solubility of the noble metal compound at the working temperature used. When a very large proportion of noble metal salt is used, the ratio of aldehyde to ketone may, however, become again unfavorable. The catalyst shall also contain a redox compound, for example a copper or iron salt, as described in the aforesaid specification. As compared with the formation of ketone, the formation of aldehyde increases with the amount of noble metal compound added and with the temperature. However, higher temperatures favor the formation of aldehyde only when the minimum quantity of noble metal compound to be added according

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to the invention is used. When the process is carried out in the presence of a liquid catalyst at a temperature above the boiling temperature of the solution, it is also necessary to increase the pressure; an elevated pressure may, however, also be advantageous at lower temperatures.

When propylene is reacted with oxygen in the liquid catalyst used in Example 2, the ratio of propionaldehyde formed to acetone formed is, for example, as follows:

At 20° C. = 1:7.2

At 85° C. = 1:4.3

At 100° C. = 1:3.5

At 120° C. and 1 atmosphere gage = 1:2.0

When butene-1 is reacted under similar conditions, a ratio of methylethylketone to butyraldehyde of 4.8:1 can already be attained at 100° C. By further elevating the temperature and, if necessary, the pressure, the ratio of aldehyde to ketone can be further changed in favor of aldehyde.

The catalyst used may be solid or liquid. If in catalysts containing halogen compounds losses in halogen occur, the lost proportion has to be replaced, for example, by the addition of hydrochloric acid.

The process may be carried out in a liquid or solid phase, for example, in the manner described in the aforesaid copending patent, applications or in commonly owned copending U.S. patent application Ser. No. 855,975 filed on November 30, 1959 (now U.S. 3,119,874 granted January 28, 1964), and under the conditions described therein. When the process is conducted continuously, compounds yielding anions, for example hydrogen chloride, are added in the course of the reaction. The process may be carried out at a temperature within the range of 20 to 200° C. or more, preferably at a temperature ranging from 50 to 170° C.

The following examples serve to illustrate the invention but they are not intended to limit it thereto.

EXAMPLE 1

A reaction tube in upright position was charged with 100 cc. of an aqueous catalyst containing 100 grams of PdCl_2 and 400 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per liter of liquid. 4 liters of propylene and 1 liter of oxygen were then introduced per hour into the catalyst through a frit and the acetone and propionaldehyde which formed were isolated by a water wash. At a temperature of 85° C., propionaldehyde and acetone were obtained in a ratio of 1:4.2; at 100° C. in a ratio of 1:3.6; at 120° C. and 1 atmosphere gage in a ratio of 1:2.9. In the last instance, the conversion of propylene to the sum of aldehyde + ketone amounted to 23%, calculated on the propylene which had been put through. The gases that had not been reacted could be returned to the process and re-used.

EXAMPLE 2

The apparatus of Example 1 was charged with 100 cc. of catalyst liquid containing, per liter, 160 grams of PdCl_2 and 320 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the process was carried out as described in Example 1. The ratio of propionaldehyde to acetone was 1:7.2 at 20° C.; 1:4.3 at 85° C.; 1:3.5 at 100° C.; 1:2.0 at 120° C. In the last instance, the conversion of propylene to the sum of acetone + propionaldehyde amounted to 31.6% calculated on the propylene put through.

EXAMPLE 3

The apparatus of Example 1 was charged with an aqueous catalyst solution containing, per liter, 220 grams of PdCl_2 and 440 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the process was carried out as described in Example 1. Propionaldehyde and acetone were obtained at 85° C. in a ratio of 1:4.0.

EXAMPLE 4

The apparatus of Example 1 was charged with 100 cc. of a catalyst containing, per liter, 160 grams of PdCl_2 and 320 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. A mixture of 4 liters/hour of butene-1 and 1 liter/hour of oxygen was introduced into the catalyst liquid. The ratio of butyraldehyde to methylethylketone was 1:11 at 20° C.; 1:6.7 at 85° C.; 1:4.8 at 100° C.

EXAMPLE 5

A long reaction tube 30 mm. in diameter and provided with a heating jacket was charged with 200 cc. of active carbon which was impregnated with a solution of 40 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and increasing amounts of PdCl_2 . Water which was constantly kept at 85° C. with the help of a thermostat was passed through the heating jacket. A mixture of 20 liters/hour of propylene and 40 liters/hour of air was conducted through an evaporator disposed before the reaction tube and then in a downward direction through the catalyst. Into the evaporator which was heated by means of an oil bath, 10 cc./hour of 0.1 N-hydrochloric acid were introduced dropwise at a uniform rate, evaporated and introduced into the catalyst together with the gas current. The reaction mixture leaving the reaction tube was freed from water in a cooler and samples were continuously taken in order to be analyzed by gas-chromatography. The carbonyl compounds, propionaldehyde and acetone, which had been formed were isolated from the reaction mixture by washing with water and finally a remainder of the said carbonyl compounds was absorbed with hydroxylamine.

The concentration of propionaldehyde in the reaction product increased as the content of PdCl_2 in the catalyst was increased, i.e., from 1.6% of propionaldehyde at a PdCl_2 content of 2 grams to 12.4% of propionaldehyde at a PdCl_2 content of 20 grams. The following table clearly shows the shift from ketone to aldehyde occurring in the reaction product in dependence on the PdCl_2 content of the catalyst.

Table

200 cc. active carbon charged with—		Heating temperature, ° C.	Percent propionaldehyde in the reaction product
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, grams	PdCl_2 , grams		
40	2	85	1.6
40	4	85	2.0
40	10	85	4.6
40	20	85	12.4

EXAMPLE 6

A mixture of 12 liters of propylene and 5 liters of oxygen was conducted per hour, as described in Example 5, at 95° C. together with 10 cc. of evaporated 0.1 N-hydrochloric acid over 200 cc. of silica gel which had been impregnated with a solution of 40 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 20 grams of PdCl_2 . After the water was separated from the reaction mixture, the composition of the latter was controlled for 700 working hours by gas-chromatographic analysis. The reaction mixture contained an average of 7.9% of acetone and 0.8% of propionaldehyde, i.e., more than 10% of aldehyde calculated on acetone. The bulk of the carbonyl compounds was condensed in a low cooling trap kept at -40 to -50° C. The exhaust gas could be recycled to the reaction after being regenerated.

EXAMPLE 7

A mixture of 7.5 liters of propylene and 30 liters of air was introduced per hour, at 85° C., into a catalyst solution of 50 grams of PdCl_2 and 200 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 500 cc. of water to which 10 cc. of concentrated hydrochloric acid had been added. The reaction mixture

was examined in a manner analogous to that described in the preceding examples. It contained 14% of propionaldehyde, calculated on acetone, in the first 24 working hours. The portion of aldehyde then gradually dropped by about 50% and maintained that value in a permanent test lasting 600 hours.

An experiment carried out with only 5 grams of PdCl_2 under otherwise the same reaction conditions yielded a reaction product containing only 1.2% of propionaldehyde calculated on acetone.

EXAMPLE 8

A heatable tube 10 mm. in diameter was charged with 30 cc. of silica gel which was impregnated with 10 cc. of a solution of 250 grams/liter of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and varying amounts of PdCl_2 per liter. The reaction temperature was about 90° C. 2 normal liters (N.T.P.) of propylene and 1 normal liter (N.T.P.) of oxygen were introduced per hour. The oxygen-containing compounds which had formed, particularly acetone and propionaldehyde, were isolated from the gas mixture leaving the reaction zone by washing with water.

Table

Concentration of PdCl_2 per liter	Temperature, ° C.	Proportion by volume of acetone to propionaldehyde in the reaction mixture after 5 hours of operation
30 g.-----	90	5:1
90 g.-----	90	3.7:1
180 g.-----	90	2:1

What we claim is:

1. In a process for the conversion of an olefinic hydrocarbon to a carbonyl compound selected from the group consisting of aldehydes and ketones by oxidation of an olefinic carbon atom of said olefinic hydrocarbon to a carbonyl group by contacting said hydrocarbon and oxygen with an acid to neutral aqueous catalyst solution of a salt of a noble metal selected from the group consisting of palladium, iridium, ruthenium, rhodium, and platinum, and as a redox system, a salt of the metal showing several valence states under the reaction conditions applied, the improvement of contacting an alpha olefin having at least 3 carbon atoms with a catalyst solution in which the concentration of said salt of a noble metal is greater than 0.25 mol per liter of catalyst solution, whereby the proportion of aldehydes to ketones in the reaction product is increased.

2. The process of claim 1 wherein said noble metal is palladium.

3. The process of claim 1 wherein said salt of a noble metal is a palladium chloride.

4. The process of claim 1 wherein the concentration of the salt of the noble metal in the catalyst solution is greater than 0.5 mol per liter of catalyst solution.

5. The process of claim 1 carried out at a temperature in the range between 50 and 170° C.

6. The process of claim 1 wherein said olefin is butene-1.

7. The process of claim 1 wherein said olefin is propylene.

8. In a process for the conversion of propylene to a carbonyl compound selected from the group consisting of propionaldehyde and acetone by oxidation of an olefinic carbon atom of said propylene to a carbonyl group by contacting said propylene and oxygen with an acid to neutral aqueous catalyst solution of palladous chloride, and as a redox system, cupric chloride, the improvement of contacting said propylene with a catalyst solution in which the concentration of said palladous chloride is at least 0.5 mol per liter of said catalyst solution at a temperature above 100° C. and under a pressure maintaining the catalyst solution in a liquid state, whereby the proportion

of propionaldehyde to acetone in the reaction product is increased.

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