

1

3,080,425

PROCESS FOR THE PRODUCTION OF ALDEHYDES AND KETONES COMPOUNDS

Jurgen Smidt, Munich-Solln, Walter Hafner, Munich, and Reinhard Jira, Munich-Pasing, Germany, assignors to Consortium für Elektrochemische Industrie G.m.b.H., Munich, Germany

No Drawing. Filed June 23, 1958, Ser. No. 744,011

Claims priority, application Germany June 28, 1957

9 Claims. (Cl. 260-586)

The present invention relates to a process for the production of carbonyl compounds by oxidation of olefinically unsaturated hydrocarbons, and more particularly relates to a process for the production of acetaldehyde from ethylene, as well as higher aldehydes and ketones from olefinic unsaturated hydrocarbons without altering the number of carbon atoms present in the molecule, by oxidation of such olefinically unsaturated hydrocarbons with the aid of an aqueous catalyst solution at relatively low temperatures.

In U.S. application S.N. 705,491, filed December 27, 1957, a process has been described in which olefines are oxidized to carbonyl compounds with oxygen in the presence of water and platinum metal compounds.

According to the present invention it was found that the oxidation of olefines which is catalyzed by compounds of the platinum metals can generally be carried out with oxidizing agents the oxidation potential of which is greater than that of the platinum metal compounds acting as the catalyst. As a result the field of application of the oxidation of olefines is considerably enlarged and a number of advantages are obtained. The process becomes more flexible in its individual applications and permits better adaption to the particularities of the starting materials employed.

In carrying out the process according to the invention the olefinically unsaturated hydrocarbons or mixtures containing such hydrocarbons are brought into intimate contact with aqueous solutions containing the platinum metal compounds and the oxidizing agents. The process can be carried out to produce good yields at temperatures of above 0° C. to about 200° C., preferably between 50° and 150° C. Above 200° C. side reactions such as, for example, further oxidation of the carbonyl compounds produced become disturbingly noticeable. Within the preferred range of temperatures the selection of the optimum temperature depends upon the composition of the catalyst solution and the type of oxidizing agent employed.

The compounds of the platinum metals, particularly those of palladium and rhodium, are catalytically active. The type of the non-metallic component of such compounds is only of secondary importance as long as extremely strong complex formers, such as cyanide ions, or precipitating agents, such as sulfide ions, are not concerned. The halides, sulfates, phosphates and corresponding complexes of the platinum metal can, for example, be employed.

The function of the oxidizing agent is to compensate or hinder the reduction of the platinum metal compound by the olefinically unsaturated hydrocarbons. The oxidation potential of such oxidizing agent therefore must be above that of the platinum metal compound acting as the catalyst. The oxidation potential can be determined in a known manner by electrical measurements. As a preliminary criterion the tabulated values of normal potentials can be employed.

2

NORMAL POTENTIALS OF OXIDIZING AGENTS

[Ea in volt]

	ClO ₃ ⁻ /Cl ⁻ -----	1.45
	Cr ₂ O ₇ ²⁻ /Cr ³⁺ -----	1.36
5	BrO ₃ ⁻ /Br ⁻ -----	1.44
	Cu ²⁺ /CuCl ₂ ⁻ -----	0.46
	Fe ³⁺ /Fe ²⁺ -----	0.77
	Hg ₂ ²⁺ /Hg ⁺ -----	0.91
	IO ₃ ⁻ /I ⁻ -----	1.09
10	O ₂ /H ₂ O -----	1.23
	O ₃ /O ₂ -----	2.07
	PbO ₂ /Pb ²⁺ -----	1.47
	MnO ₂ /Mn ²⁺ -----	1.28
	IO ₆ H ₄ ⁻ /I ⁻ -----	1.40

15 The selection of the suited oxidizing agent depends upon the desired manner of carrying out the reaction. In discontinuous processes, which are usable particularly for the production of higher carbonyl compounds, persulfates, oxygen acids of halogens and respectively their salts, chromates and other oxometallates can be employed.

20 Also, salts of multivalent metals such as have been described in S.N. 705,491 can also be employed if they possess the respective oxidation potential. In the absence of oxygen these salts are converted to a lower and inactive oxidation state during the reaction so that when the process is to be carried out continuously a special reaction step for the oxidation of the metal salts must be employed.

25 The oxidizing agents, insofar as they are soluble are used together with the platinum metal compounds in aqueous solution. The quantity of platinum metal compound should be relatively low, for example, about 2 to 20 g. per liter of solution. The oxidizing agents are employed in high concentration. When salts of multivalent metals are employed, molar ratios of platinum metal to multivalent metal of 1:1 to 1:100 are preferred. The reaction is carried out in an acid to neutral solution. A pH of 0 to 2 is preferred.

30 The presence of halide ions retards the reduction of the catalyst solution. As a consequence, the reaction can be regulated by the addition of halides, particularly the addition of chlorides.

35 The process according to the invention involves a reaction between phases of only limited miscibility. As a consequence, all measures which provide for intensive intimate contact of the phases or increase the miscibility of the phases promote the reaction. Intensive contact can be attained by mechanical measures such as stirring, shaking, vibrating, spraying and the like and chemical measures which favor the formation of large surfaces. In order to increase the miscibility, blending agents such as acetic acid or dioxane can be added. The solubility of gaseous reactants can be increased by employing super-atmospheric pressures. The process according to the invention can be carried out at any desired pressure, preferably, however, a pressure within the range of 1 to 50 atmospheres is employed.

40 The time during which the olefines and the carbonyl compounds formed are in contact with the aqueous catalyst solution can amount from a few seconds to several hours. The time of contact depends upon the reactivity of the olefine, the composition of the catalyst solution, the pressure and temperature, as well as the type of oxidizing agent employed. The lower olefines react relatively rapidly, while longer reaction times are required for higher olefines. Palladium compounds act very quickly

whereas the compounds of the other platinum metals are considerably slower in their action. The influence of the presence of halogen ions has already been mentioned. Increases in pressure and temperature accelerate the reaction. An upper limit for the time of contact is provided in the case of easily oxidizable and acid sensitive carbonyl compounds, especially when higher temperatures are employed and when strong oxidizing agents are employed. The permissible periods of contact can easily be determined for each individual case by determining the yields obtained.

Olefinically unsaturated hydrocarbons are generally suited as starting materials. The reaction does not occur only in the case of strongly sterically hindered compounds such as tetraphenyl ethylene.

There also are no special requirements with regard to the purity of the hydrocarbons employed as starting materials. Only acetylene, hydrogen sulfide and its derivatives lower the activity of the catalyst solution and decrease the conversion.

The process according to the invention can be carried out in all apparatus for reacting gases, liquids or solids with each other, such as, for example, trickle or spray towers, filled columns, stirring vessels and the like. Naturally, the portions of such apparatus coming into contact with the strong oxidizing acid solutions must be of corrosion resistant material. Suitable corrosion resistant materials, for example, are enamel, glass, porcelain, stoneware, synthetic resins, rubber, titanium, tantalum and Hastelloy.

The carbonyl compounds produced can be recovered in various ways. Easily volatilized compounds, insofar as they are carried out with the non-converted gas stream, can be separated out by condensation or scrubbing. The compounds retained in the catalyst solution can be recovered by distillation. Difficultly volatile compounds can be recovered by liquid-liquid extraction, separation or filtration. By-products, such as organic acids, are only produced in small quantities and easily can be separated. The yield of carbonyl compounds on an average is 90% and over.

The present invention therefore renders it possible to produce important carbonyl compounds from easily obtainable starting materials by a simple adaptable process.

The following examples will serve to illustrate a number of embodiments of the process according to the invention.

Example 1

5.4 g. of palladium black were dissolved in a mixture of 30 cc. of concentrated nitric acid and 25 g. of concentrated sulfuric acid and the solution boiled down until a white fog was produced. 93 g. of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and sufficient water were added to the residue to provide 500 cc. of solution. The solution was shaken at 95° C. at atmospheric pressure with ethylene. 8.7 g. of acetaldehyde were produced in 10 minutes. The yield amounted to 97% on the ethylene converted.

Example 2

10.7 g. of palladium were dissolved in aqua regia and the solution boiled down to dryness. 10 cc. of concentrated HCl were added twice to the residue and each time the mixture boiled down completely. The brown crusts produced were dissolved by adding 5 cc. of concentrated HCl in 500 cc. of water and heating. A number of solutions were prepared in this manner and the oxidizing agents indicated in the following table added to such solution together with sufficient water to produce 1 liter of solution. Each catalyst solution was then shaken with ethylene at 50° C. under atmospheric pressure. The following table shows the yields of acetaldehyde produced.

	Grams oxidizing agent added	Reaction time in minutes	Grams acetaldehyde formed
5	29.4 $\text{K}_2\text{Cr}_2\text{O}_7 + 50\text{H}_2\text{SO}_4$	10	12.0
	27 $\text{K}_2\text{S}_2\text{O}_8$	6	7.1
	185 $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O} + 40\text{H}_2\text{SO}_4$	40	17.6
	68.2 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	30	11.0
	40 $\text{Cu}(\text{C}_2\text{H}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$	4	6.0
	33.4 KBrO_3	17	25.0
	71.7 $\text{PbO}_2 + 100\text{C}_2\text{H}_5\text{CO}_2\text{H}$	6	15.1

The yield of acetaldehyde based on ethylene converted was between 90 and 98%.

Example 3

23 g. of KIO_4 were added to a palladium chloride solution prepared as in Example 2 and sufficient water added thereto to produce 1 liter. The resulting solution was then shaken at 50° C. under atmospheric pressure with a mixture of 1- and 2-butene. 25 g. of methyl ethyl ketone were formed in 12 minutes. The yield was 91% with reference to the quantity of butene mixture converted.

Example 4

185 g. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and 40 g. of concentrated H_2SO_4 were added to 62.5 cc. of a palladium chloride solution prepared as in Example 2 and sufficient water added to produce 1 liter of solution. The solution was shaken with ethylene at 50° C. under 5 atmospheres gauge pressure. 14.5 g. of acetaldehyde were produced in 10 minutes. The yield was 92% with reference to the ethylene converted.

Example 5

600 cc. of an aqueous solution containing 3.56 g. of PdCl_2 and 100 g. of $\text{Fe}_2(\text{SO}_4)_3$ per liter were vigorously shaken with 0.2 mol of each of the olefines indicated in the following table. The reaction products were recovered by steam distillation. The following table shows the quantity of carbonyl compounds produced.

	Starting Olefine	Reaction Temp., ° C.	Carbonyl Compound produced	Grams of product produced per hour
	Pentene-1.....	20	n-Propyl-methyl-ketone.....	6.3
	Hexene-1.....	20	n-Butyl-methyl-ketone.....	5.1
45	Heptene-1.....	50	n-Amyl-methyl-ketone.....	5.1
	Octene-1.....	50	n-Hexyl-methyl-ketone.....	3.8
	Nonene-1.....	70	n-Heptyl-methyl-ketone.....	2.3
	Decene-1.....	70	n-Octyl-methyl-ketone.....	1.9
	Pentene-2.....	30	n-Propyl-methyl-ketone.....	3.7
	Cyclopentene.....	30	Cyclopentanone.....	3.3
	Cyclohexene.....	30	Cyclohexanone.....	4.2
	Indene.....	50	β -Indanone.....	3.0
50	Allylbenzene.....	40	Benzyl-methyl-ketone.....	7.2
	Styrene.....	60	Acetophenone.....	5.1
	Butadiene-1.3.....	50	Crotonaldehyde.....	4.9
	Pentadiene-1.4.....	20	Pentene-2-al-1.....	8.3

The yield of carbonyl compound produced with reference to olefine converted mostly lies over 90%.

Example 6

An aqueous solution containing 11.7 g. H_2PtCl_6 and 142 g. $\text{Fe}_2(\text{SO}_4)_3$ per liter was sprayed at a temperature of 140° C. into a spray tower containing propene maintained at a pressure of 50 atmospheres. The solution running out of the tower was passed to a distillation column where the pressure was relieved and the acetone produced separated off. The solution from which the reaction product had been removed was again sprayed into the tower. The velocity of the solution recycled was adjusted so that the time it remained in the reaction tower did not exceed 5 minutes. Under these conditions the yield of acetone obtained was about 90% with reference to the propylene converted.

Very nearly the same results were obtained when the chloroplatinic acid in the solution was replaced by equimolar quantities of K_2PtCl_6 or CuPtBr_6 .

Example 7

9.4 g. rhodium-(III)-oxyhydrate with a metal content

5

of 54.7% were dissolved under warming in 250 cc. 1-normal hydrochloric acid; then 300 g. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ were added and filled up to 1 liter. The solution was then reacted with ethylene in a shaking autoclave of titanium at a temperature of 60° C. and a pressure of 40 atmospheres. After three hours 20.9 g. of acetaldehyde had been obtained.

Example 8

2.9 g. of finely divided palladium were dissolved in concentrated nitric acid at room temperature and then evaporated to dryness. The residue was dissolved in cold water, then added to 281 g. $\text{Fe}_2(\text{SO}_4)_3$ and 100 g. H_2SO_4 were added and filled up to 1 liter. The solution was then shaken with ethylene at a pressure of 10 atmospheres and a temperature of 95° C. After 30 minutes 7.8 g. acetaldehyde had been obtained, the yield being 96%.

Example 9

3.9 g. of palladium chloride were dissolved in water adding a small quantity of hydrochloric acid, heated and then mixed with concentrated sodium hydroxide solution. The precipitated palladium oxyhydrate was filtered, washed with hot water and then dissolved in glacial acetic acid. After that the solution was again precipitated with sodium hydroxide solution, filtered and washed with hot water until the filtrate was completely free of chlorine ions. The residue was dissolved in 200 cc. glacial acetic acid, mixed with 281 g. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and 100 g. H_2SO_4 and filled up with water to 1 liter. This solution was reacted with ethylene according to Example 1. After 2.5 hours 10.5 g. acetaldehyde had been formed.

Example 10

2 g. of finely divided palladium were dissolved in nitric acid and mixed with 50 g. ortho-phosphoric acid and then evaporated until the solution had the consistency of syrup, whereby nitric oxides and nitric acid were removed completely. The residue was dissolved in water, mixed with 281 g. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and filled up with water to 1 liter. This solution was then reacted with ethylene according to Example 1. After 5 minutes 1.3 g. acetaldehyde had been formed.

Example 11

1.34 g. of technical palladium were dissolved in 20 cc. concentrated hydrobromic acid, adding bromine, and then evaporated to dryness. The residue was dissolved under warming in 33 cc. 1-n hydrobromic acid. After the addition of 112 g. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ the solution was filled up with water to 500 cc. The reaction with ethylene took place according to Example 1. After 1 hour 8.2 g. acetaldehyde had been formed.

Example 12

An internally gummied spray tower with an inside diameter of 7.5 cm. and 5 m. height, filled with Raschig rings, was used as reaction vessel. In this tower ethylene was irrigated with a solution containing 1.3 g. palladium chloride and 260 g. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ per liter at a rate of 300 liters per hour employing a temperature of 90° and a pressure of 15 atmospheres. The solution running out of the tower was passed to a column where the pressure was relieved and the acetaldehyde separated off. There was a yield of 300 g. acetaldehyde per hour.

Example 13

RuO_4 was treated on the water bath with concentrated hydrochloric acid, the hydrochloric acid evaporated and the residue dissolved in water, whereby a solution containing 22 m-mol RuCl_3 and 19 m-mol HCl per liter was obtained. 200 cc. of this solution were mixed with 2.13 g. ferric-(III)-chloride and reacted with propylene in a shaking autoclave at a temperature of

6

120° C. and a pressure of 50 atmospheres. After 2 hours 0.5 g. of acetone had been produced.

Example 14

1.2 g. $\text{Ir}(\text{OH})_4$ were treated under irradiation with a chlorine stream for 15 minutes at a temperature of 240° C. The reaction product consisting approximately of 75% iridium-(IV)-chloride and 25% iridium-(III)-chloride was dissolved in 200 cc. water, mixed with 3.78 g. FeCl_3 and reacted with propylene according to Example 13. After 4 hours yield of 112 g. acetone had been obtained.

Example 15

9.4 g. rhodium-(III)-oxyhydrate with a metal content of 54.7% were dissolved under warming in 250 cc. 1 n-hydrochloric acid, mixed with 54 g. potassium persulfate and filled up with water to 500 cc. This solution was then reacted with ethylene according to Example 1. After 15 hours 6.2 g. acetaldehyde had been formed. There was a yield of 95% based on the reacted ethylene.

We claim:

1. A process for the production of a carbonyl compound selected from the group consisting of aldehydes and ketones which comprises contacting an olefinically unsaturated hydrocarbon with an aqueous solution of a catalytically active inorganic salt of a metal of the platinum group at a temperature from above 0° C. to about 200° C. in the presence of at least one multivalent metal salt having an oxidation potential higher than that of the platinum metal salt in such solution and recovering the carbonyl compound thus produced.

2. The process of claim 1 in which said multivalent metal salt is ferric salt.

3. The process of claim 1 in which said multivalent metal salt is a cupric salt.

4. The process of claim 1 in which said solution contains a mixture of ferric and cupric salts.

5. The process of claim 1 in which said salt of a metal of the platinum group is a palladium salt.

6. The process of claim 1 in which said salt of a metal of the platinum group is a rhodium salt.

7. A process for the production of a carbonyl compound selected from the group consisting of aldehydes and ketones which comprises contacting an olefinically unsaturated hydrocarbon with an aqueous solution of a catalytically active inorganic salt of palladium at a temperature from above 0° C. to about 200° C. in the presence of at least one multivalent metal salt having an oxidation potential higher than that of the palladium salt in such solution, the ratio of the palladium salt to the multivalent metal salt being such as to provide a ratio of palladium to multivalent metal between 1:1 and 1:100 and recovering the carbonyl compound thus produced.

8. The process of claim 7 in which said aqueous solution contains 2 to 20 grams of the palladium salt per liter.

9. The process of claim 7 in which said aqueous solution contains chlorine ions.

References Cited in the file of this patent

UNITED STATES PATENTS

1,999,620	Van Peski et al. -----	Apr. 30, 1945
2,523,686	Engel -----	Sept. 26, 1950
2,690,457	Hackmann -----	Sept. 28, 1954

FOREIGN PATENTS

767,409	Great Britain -----	Feb. 6, 1957
713,791	Germany -----	Nov. 14, 1941
891,209	France -----	Nov. 29, 1943

OTHER REFERENCES

- Phillips: Amer. Chem. Jour., vol. 16, pp. 255-77 (pp. 265-72 relied upon), 1894.
 Chatt: Chem. Abstracts, vol. 48, p. 5067 (1954).
 (Copies of above in Library.)