

PROCESS FOR THE HYDROXYCARBONYLATION OF BUTADIENE

The present invention relates to the hydroxycarbonylation of butadiene and/or of its derivatives, into pentenoic acids, by reaction of
5 carbon monoxide and water.

One of the possible routes of access to adipic acid, which is one of the two basic constituents of nylon 6.6 polymers, is the double carbonylation of butadiene or of its derivatives.

10 Although it may be envisaged to perform the two hydroxycarbonylations leading from butadiene to adipic acid in a single step, in practice it turns out that the two reactions must be carried out successively, if it is desired to obtain sufficiently
15 high selectivities to be able to envisage an economically viable industrial process.

Patent US-A-3 509 209 describes the hydroxycarbonylation of various olefins, including butadiene, by carbon monoxide and water, in the
20 presence of hydrochloric or hydrobromic acid and a palladium-containing catalyst, at a temperature of 15°C to 300°C and at a pressure of 1 to 1000 bar and preferably of 10 to 200 bar.

Under the conditions described, it is
25 observed that the yields of pentenoic acids are very low and that, in fact, very often the product obtained is valerolactone.

Patent FR-A-2 529 885 has proposed a process

for the preparation of beta,gamma-unsaturated acids such as pentenoic acids, by carbonylation of a conjugated diene (more particularly butadiene) in the presence of water, a halogenhydracid, a palladium-based catalyst and a quaternary onium salt of an element chosen from nitrogen, phosphorus and arsenic.

This process gives good results, but it requires the use of a relatively large amount of a quaternary onium salt, which compound is expensive and whose presence tends to complicate the treatment of the mixtures at the end of the reaction.

It has now been found that the hydroxycarbonylation of butadiene and its derivatives may be performed with a very good selectivity towards products whose value may be upgraded, that is to say particularly towards pentenoic acids, without, moreover, working in the presence of a quaternary onium salt.

More precisely, the present invention consists of a process for the hydroxycarbonylation of butadiene and of its derivatives by carbon monoxide and water, at a pressure greater than atmospheric pressure and in the presence of a palladium catalyst which is soluble in the reaction medium, characterized in that:

- the process is performed in the presence of crotyl chloride, in an amount of at least two mol per mole of palladium,

- the palladium is, at least partly, in the

form of a crotyl pi-complex,

- the water present in the reaction medium represents an amount less than or equal to 20% by weight relative to the weight of the reaction mixture.

5 Butadiene derivative is understood, in the present text, to refer in particular to allylic butenols, for instance 3-buten-2-ol, 2-buten-1-ol and their mixtures and addition compounds of hydrogen chloride with butadiene (chlorobutenes), the main one
10 of which is crotyl chloride. In the present process, butadiene, one or more of its derivatives or the mixtures of butadiene with one or more of its derivatives may be used. Butadiene or mixtures containing a majority of butadiene nevertheless
15 represent the preferred substrates for use.

The crotyl-palladium pi-complex catalyst may be introduced into the reaction medium or may be formed in situ from Pd halides, more particularly the chloride, from Pd carboxylates, in particular the
20 acetate, or alternatively from finely divided palladium metal.

The amount of pi-crotyl-palladium catalyst used in the process may vary within a wide range. From 10^{-5} mol to 0.2 mol of Pd per mole of butadiene or of
25 butadiene derivative employed in the reaction and preferably from 10^{-4} mol to 0.1 mol per mole is generally used.

Besides the pi-crotyl-palladium catalyst,

palladium in another, less active, form (for example Pd metal or Pd chloride) may also be found in the reaction medium in a variable amount. However, in an industrial process, it is preferable for all or
5 practically all of the palladium to be in an active form which is soluble in the medium, for instance pi-crotyl-palladium, possibly with palladium chloride.

The crotyl-palladium pi-complex may be prepared, for example, by reacting a palladium salt,
10 for instance palladium chloride, with crotyl chloride in a solvent which may consist of a water/methanol mixture. The mixture is stirred, generally at room temperature, advantageously under a gentle stream of carbon monoxide. The pi-crotyl-palladium complex
15 precipitates and, after an optional degassing step, the mixture is poured into water and then extracted using a suitable organic solvent, such as chloroform for example. The complex is subsequently isolated from the organic solution by evaporation of the solvent.

20 The crotyl chloride promoter may be introduced into the reaction mixture or may be formed in situ, from butadiene and/or from 2-buten-1-ol and hydrochloric acid.

It preferably represents, in moles per mole,
25 from 5 to 10 times the amount of palladium, although it may be present in greater proportions, since it may constitute all or some of the substrate to be hydroxycarbonylated.

Overall, it is preferable to have a Cl/Pd molar ratio in the reaction medium of less than or equal to 100 and preferably of less than or equal to 20, because high ratios have an adverse effect on the reaction kinetics.

As indicated above, the water concentration in the reaction mixture should be maintained at a value equal to or less than 20% by weight relative to the weight of the said mixture. This is because the water concentration has an unfavourable effect on the reaction kinetics. This water concentration will preferably be maintained at a value equal to or less than 8% weight for weight and even more preferably at a value equal to or less than 5%.

As water is a reactant which is essential for the hydroxycarbonylation reaction, one advantageous variant of the process of the invention consists in injecting this water progressively as the reaction proceeds, which allows its concentration in the reaction mixture to be maintained at a very low value, while allowing the reaction to occur.

Although the presence of a third solvent is not excluded, the reaction is generally carried out without any solvent other than the reactants themselves or the reaction products. It may also be favourable to introduce a pentenoic acid and more particularly 3-pentenoic acid from the start of the hydroxycarbonylation reaction, in order to minimize

side reactions.

Within the context of an industrial implementation of the process, recycling of the catalyst, the promoter and the unreacted butadiene may lead to the introduction of larger or smaller amounts of other compounds into the reaction medium, in particular of by-products formed during the hydroxycarbonylation reaction. Thus, the reaction mixture may, for example, contain butenes, gamma-valerolactone, valeric acid, adipic acid, 2-methylglutaric acid, 2-ethylsuccinic acid, 2-methylbutanoic acid and 2-methylbutenoic acids. Bearing in mind the requirements of a possible continuous implementation of the process, the amounts of these compounds present may reach up to 90% by weight of the reaction mixture employed in the hydroxycarbonylation reaction.

The butadiene concentration is an important parameter of the reaction, in particular as regards the stability of the palladium catalyst, that is to say essentially its maintenance in solution in the reaction mixture. It has thus been observed that it is not favourable to have less than 0.2% by weight of butadiene relative to the total weight of the reaction mixture. When the process is performed discontinuously, conversion of the butadiene or of its derivatives will preferably be limited so that the reaction mixture contains at least 0.5% by weight of the said butadiene

or of its derivatives.

The butadiene concentration will also preferably be maintained at a value equal to or less than 50% of the reaction mixture on a weight for weight basis, and even more preferably at a value less than or equal to 30%, when the process is performed discontinuously, and at a value less than or equal to 10% when the process is performed continuously.

Whereas the palladium catalyst tends to precipitate in a large proportion in the form of insoluble palladium metal when the hydroxycarbonylation of butadiene is performed under conditions different from those of the present process, it is observed, on the contrary, that with the conditions claimed the catalyst retains a noteworthy stability.

In the industrial context, it is very advantageous to convey only liquid phases in the apparatus and thus as far as is possible to avoid the presence of solids in suspension. It is this in particular which the present process makes possible.

The hydroxycarbonylation reaction may be carried out at a temperature which is generally between 60°C and 230°C and preferably between 90°C and 200°C, and at a pressure at the reaction temperature of 50 to 500 bar and preferably of 100 to 300 bar.

The partial pressure of carbon monoxide, measured at 25°C, is from 25 bar to 440 bar and preferably from 55 bar to 240 bar.

As has been indicated, the process of the invention may be implemented continuously or discontinuously. Depending on the implementation chosen, it will therefore be necessary to adapt the various operating conditions defined above.

The examples which follow illustrate the invention.

EXAMPLE 1.

1) Preparation of the crotyl-Pd chloride pi-complex.

5.04 g of PdCl_2 , 3.37 g of NaCl , 50 cm^3 of methanol, 15 cm^3 of water, 8.03 g of crotyl chloride and a further 20 cm^3 of methanol are successively charged into a 150 cm^3 glass round-bottomed flask.

The heterogeneous mixture is stirred and progressively becomes dark brown and cloudy. The solution is subsequently treated, while stirring, with a gentle stream of carbon monoxide (at bubble rate) for one hour. The mixture becomes clear and a yellow precipitate appears. The stirring and the stream of CO are stopped and the solution is left to stand for one hour and is then poured into 300 cm^3 of water and extracted with 5 times 50 cm^3 of chloroform. The resulting straw-yellow organic phase is washed with 2 times 100 cm^3 of water, dried over disodium sulphate overnight and the solvent is then evaporated off. 3.35 g of a pale yellow solid are thus recovered, which product has a purity of greater than 94% (assay by Nuclear Magnetic Resonance: NMR).

2) Hydroxycarbonylation of butadiene.

The following reactants are successively charged into a 50 cm³ glass flask:

- pi-crotyl-Pd chloride: 0.9 mmol
- 5 - crotyl chloride: 6.2 mmol
- H₂O: 100 mmol
- 3-pentenoic acid: 20 g (200 mmol)
- butadiene: 100 mmol

The butadiene is introduced last, by
10 condensation (cold wall at -78°C) from a gate.

The flask is placed in a 125 cm³ autoclave; the autoclave is placed in an oven incorporating agitation by shaking, connected to a system for the supply of gas at high pressure, and a pressure of
15 100 bar of CO is established at room temperature.

The temperature is subsequently brought to 140°C with agitation over a period of 25 min. At this temperature, the pressure in the autoclave is brought to 200 bar by the introduction of CO and it is
20 maintained constant at this value by means of a CO tank under pressure for 30 min.

The agitation is then stopped, the autoclave is cooled and degassed and the gases and the solution obtained are analysed by gas chromatography (GC).

25 The following results were obtained:

- extent of conversion of butadiene (ECBD): 92%
- yield (Yd) of 3-pentenoic acid (P3)
relative to the butadiene converted: 89.5%

	- Yd of adipic acid (A1):	0.1%
	- Yd of 2-methylglutaric acid (A2):	4.1%
	- Yd of 2-ethylsuccinic acid (A3):	1.8%
	- Yd of gamma-valerolactone (VAL):	0.7%
5	- Yd of 2-pentenoic acid (P2):	0.3%
	- Yd of butenes (C4):	0.6%
	- Yd of methylbutenoic acids and methylbutanoic acid (MB):	2.4%

At the end of the test, all of the palladium
10 charged remains in solution.

The production efficiency of the test is
500 g P3/litre of reactor/hour.

EXAMPLE 2

Part 2) of Example 1 is repeated with the
15 same charges except for the amount of water, which is
50 mmol instead of 100 mmol.

The temperature and pressure conditions are
the same as for Example 1.

The same yields are obtained for the various
20 products formed, but the production efficiency of the
test is 1200 g P3/litre of reactor/hour.

EXAMPLE 3

Part 2) of Example 1 is repeated with the
following charges:

25	- Pd acetate:	0.9 mmol
	- crotyl chloride:	7.2 mmol
	- H ₂ O:	100 mmol
	- 3-pentenoic acid:	20 g (200 mmol)

- butadiene: 100 mmol

The apparatus and the experimental procedure are the same as in Example 1.

The operating conditions are: 140°C; 200 bar
5 at this temperature; 30 min at this temperature and pressure.

The following results were obtained:

	- EC of butadiene:	87%
	- Yd of 3-pentenoic acid (P3):	91%
10	- Yd of adipic acid (A1):	0.1%
	- Yd of 2-methylglutaric acid (A2):	3%
	- Yd of 2-ethylsuccinic acid (A3):	2%
	- Yd of gamma-valerolactone (VAL):	0.8%
	- Yd of 2-pentenoic acid (P2):	0.2%
15	- Yd of butenes (C4):	0.3%
	- Yd of methylbutenoic acids and methylbutanoic acid (MB):	2%

At the end of the test, 97% of the palladium charged remains in solution.

20 The production efficiency of the test is 500 g P3/litre of reactor/hour.

EXAMPLES 4 TO 8

Part 2) of Example 1 is repeated with the following charges:

25	- pi-crotyl-Pd chloride (prepared in Example 1):	0.9 mmol
	- crotyl chloride:	6.2 mmol
	- H ₂ O:	100 mmol

- 3-pentenoic acid: 20 g (200 mmol)
- butadiene: 100 mmol

The apparatus and the experimental procedure are the same as in Example 1.

5 The operating conditions are: 140°C; 200 bar at this temperature; 25 min at this temperature and pressure.

A duration of 25 min is chosen so as to have an EC of butadiene of approximately 80%. After a first
10 hydroxycarbonylation operation, the agitation is stopped, the autoclave is cooled and degassed and the homogeneous solution obtained is placed under reduced pressure, in order to distil off the 3-pentenoic acid formed (between 5 and 7 g).

15 The distillation residue is still homogeneous and it is re-used in the glass flask, with new charges of crotyl chloride (6.2 mmol), water (100 mmol) and butadiene (100 mmol).

5 successive tests of the
20 hydroxycarbonylation of butadiene are thus performed under the same operating conditions.

The distillates obtained and the final distillation residue are analysed by GC.

The following results were obtained (over the
25 set of 5 tests):

- | | |
|--------------------------------|-----|
| - EC of butadiene: | 80% |
| - Yd of 3-pentenoic acid (P3): | 93% |
| - Yd of adipic acid (A1): | 0% |

- Yd of 2-methylglutaric acid (A2): 2.6%
- Yd of 2-ethylsuccinic acid (A3): 0.9%
- Yd of gamma-valerolactone (VAL): 0.8%
- Yd of 2-pentenoic acid (P2): 0%
- 5 - Yd of methylbutenoic acids and
methylbutanoic acid (MB): 1.7%

At the end of the test, all of the palladium charged remains in solution.

The production efficiency of the test is
10 415 g P3/litre of reactor/hour.

EXAMPLES 9 and 10

Part 2) of Example 1 is repeated with the following charges:

- pi-crotyl-Pd chloride: 0.9 mmol
- 15 - crotyl chloride: 7.1 mmol
- H₂O: 120 mmol
- 3-pentenoic acid: 20 g (200 mmol)
- butadiene: 100 mmol

The reactants are charged directly into the
20 autoclave (made of nickel-molybdenum alloy of tradename Hastelloy B2) and the experimental procedure is the same as in Example 1.

The operating conditions are: 140°C; 200 bar
at this temperature; 20 min at this temperature and
25 pressure.

The following results were obtained:

- EC of butadiene: 81%
- Yd of 3-pentenoic acid (P3): 92%

	- Yd of adipic acid (A1):	0.1%
	- Yd of 2-methylglutaric acid (A2):	3.6%
	- Yd of 2-ethylsuccinic acid (A3):	2.2%
	- Yd of gamma-valerolactone (VAL):	1.8%
5	- Yd of 2-pentenoic acid (P2):	0.1%
	- Yd of butenes (C4):	0.1%
	- Yd of methylbutenoic acids and methylbutanoic acid (MB):	2.4%

At the end of the test, all of the palladium
10 charged remains in solution.

The final butadiene concentration is 2% by
weight of the reaction mixture.

The production efficiency is 800 g P3/litre
of reactor/hour.

15 Example 9 is repeated with the same charges
and the same operating conditions, but it is maintained
for 40 min at the reaction temperature and pressure
instead of 20 min (Example 10).

The yields obtained are the same as in
20 Example 9, but the final butadiene concentration is
0.35% by weight in the reaction mixture.

It is observed that 20% of the catalyst
charged has precipitated in the form of Pd metal.

EXAMPLE 11

25 Part 2) of Example 1 is repeated with the
following charges:

- pi-crotyl-Pd chloride: 0.9 mmol
- crotyl chloride: 112 mmol

- H₂O: 100 mmol
- 3-pentenoic acid: 20 g (200 mmol)

The apparatus and the experimental procedure are the same as in Example 1.

5 The operating conditions are: 140°C; 200 bar at this temperature; 40 min at this temperature and pressure.

The following results were obtained:

	- EC of crotyl chloride:	90%
10	- Yd of 3-pentenoic acid (P3):	26%
	- Yd of adipic acid (A1):	0.1%
	- Yd of 2-methylglutaric acid (A2):	0.1%
	- Yd of 2-ethylsuccinic acid (A3):	6.0%
	- Yd of gamma-valerolactone (VAL):	17.0%
15	- Yd of 2-pentenoic acid (P2):	0.2%
	- Yd of methylbutenoic acids and methylbutanoic acid (MB):	2.0%

The production efficiency is 130 g (P3/litre of reactor/hour).

20 COMPARATIVE TEST 1 (with a high water concentration)

Part 2) of Example 1 is repeated with the following charges:

	- pi-crotyl-Pd chloride:	0.9 mmol
	- crotyl chloride:	7.1 mmol
25	- H ₂ O:	500 mmol
	- 3-pentenoic acid:	15 g (150 mmol)
	- butadiene:	100 mmol

The apparatus and the experimental procedure

are the same as in Example 1.

The operating conditions are: 140°C; 200 bar at this temperature; 103 min at this temperature and pressure.

5 The following results were obtained:

	- EC of butadiene:	72%
	- Yd of 3-pentenoic acid (P3):	79%
	- Yd of adipic acid (A1):	0.4%
	- Yd of 2-methylglutaric acid (A2):	2%
10	- Yd of 2-ethylsuccinic acid (A3):	0.3%
	- Yd of gamma-valerolactone (VAL):	13%
	- Yd of butenes (C4):	1%
	- Yd of methylbutenoic acids and methylbutanoic acid (MB):	5%

15 The production efficiency is 87 g P3/litre of reactor/hour.

At the end of the test, although the butadiene concentration is still 2%, it is observed that approximately 25% of the catalyst charged has
20 precipitated in the form of Pd metal.

Furthermore, the yield of 3-pentenoic acid is only 79% and the production efficiency 87 g P3/l/h.

EXAMPLE 12

25 Part 2) of Example 1 is repeated with the following charges:

- pi-crotyl-Pd chloride:	0.9 mmol
- crotyl chloride:	7.1 mmol

- H_2O : 100 mmol
- 2-methylglutaric acid 15 g (103 mmol)
- 2-ethylsuccinic acid: 5 g (34 mmol)
- butadiene: 100 mmol

5 The apparatus and the experimental procedure are the same as in Example 1.

The operating conditions are: 140°C; 200 bar at this temperature; 70 min at this temperature and pressure.

10 The following results were obtained:

- EC of butadiene: 78%
- Yd of 3-pentenoic acid (P3): 95%
- Yd of gamma-valerolactone (VAL): 0.6%
- Yd of butenes (C4): 0.8%
- 15 - Yd of methylbutenoic acids and
methylbutanoic acid (MB): 4%

The diacids formed, representing very low amounts relative to the amounts employed at the start of the test, were not assayed.

20 At the end of the test, all of the palladium charged remains in solution.

The production efficiency is 164 g P3/litre of reactor/hour.

CLAIMS

1. Process for the hydroxycarbonylation of butadiene or of one of its derivatives by carbon monoxide and water, at a pressure greater than atmospheric pressure and in the presence of a palladium catalyst which is soluble in the reaction medium, characterized in that:

- the process is performed in the presence of crotyl chloride, in an amount of at least two mol per mole of palladium,

- the palladium is, at least partly, in the form of a crotyl pi-complex,

- the water present in the reaction medium represents an amount less than or equal to 20% by weight relative to the weight of the reaction mixture.

2. Process according to Claim 1, characterized in that in that the total pressure at the reaction temperature is from 50 bar to 500 bar and preferably from 100 bar to 300 bar.

3. Process according to either of Claims 1 and 2, characterized in that the partial pressure of carbon monoxide, measured at 25°C, is from 25 bar to 440 bar and preferably from 55 bar to 240 bar.

4. Process according to one of Claims 1 to 3, characterized in that the amount of palladium represents from 10^{-5} mol to 0.2 mol per mole of butadiene employed and preferably from 10^{-4} mol to 0.1 mol per mole.



5. Process according to one of Claims 1 to 4, characterized in that the crotyl chloride represents, in moles, from 5 to 10 times the molar amount of palladium in the reaction medium.

5 6. Process according to one of Claims 1 to 5, characterized in that the butadiene concentration is at least 0.2% by weight relative to the weight of the reaction medium and preferably at least 0.5%.

10 7. Process according to one of Claims 1 to 6, characterized in that the butadiene concentration is less than or equal to 50% by weight relative to the weight of the reaction medium and preferably less than or equal to 30% when the process is implemented discontinuously.

15 8. Process according to one of Claims 1 to 6, characterized in that the butadiene concentration is less than or equal to 10% by weight relative to the weight of the reaction medium when the process is implemented continuously.

20 9. Process according to one of Claims 1 to 8, characterized in that the hydroxycarbonylation reaction is carried out in 3-pentenoic acid.

25 10. Process according to one of Claims 1 to 9, characterized in that the hydroxycarbonylation reaction is carried out at a temperature of 60°C to 230°C and preferably of 90°C to 200°C.

11. Process according to one of Claims 1 to 10, characterized in that the crotyl chloride is



formed in_situ from the butadiene present and hydrochloric acid.

12. Process according to one of Claims 1 to 11, characterized in that the crotyl-palladium pi-complex is formed in situ from the butadiene present and a palladium salt which is soluble in the reaction medium.

13. Process according to one of Claims 1 to 12, characterized in that the water concentration in the reaction mixture is maintained at a value less than or equal to 8% and preferably less than or equal to 5% by weight relative to the weight of the said reaction mixture.

14. Process according to one of Claims 1 to 13, characterized in that the overall Cl/Pd molar ratio is less than or equal to 100 and preferably less than or equal to 20.