

PROCESS FOR THE HYDROXYCARBONYLATION OF BUTADIENE

The present invention relates to the hydroxycarbonylation of butadiene, by reaction with carbon monoxide and water, in order to prepare pentenoic acids.

5 One of the possible routes of access to adipic acid, which is one of the two basic constituents of nylon 6-6, lies in the double carbonylation of butadiene.

 Although it is possible to envisage performing the two hydroxycarbonylation reactions leading from butadiene to
10 adipic acid in a single step, in practice it turns out that these two reactions must be performed successively, at least in part, if it is desired to obtain selectivities which are sufficiently high to allow an industrial process which is economically viable.

15 US-A-3,759,551 describes a process for the conversion of a compound containing at least one ethylenic double bond into a carboxylic acid, by reaction with carbon monoxide and water, in the presence of an iridium compound and an iodine-containing promoter, at a temperature of 50°C
20 to 330°C and under a partial pressure of carbon monoxide of about 0.3 to 210 bar.

 In the process described, it would appear that any iridium compound can be used and various types of iodine-containing compounds are mentioned; the iodine:iridium
25 molar ratio may vary within a very wide range, from 1:1 to 2,500:1 and preferably from 3:1 to 300:1.

 The reaction medium may contain any solvent



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compatible with the catalytic system. Preferred solvents are monocarboxylic acids having from 2 to 20 carbon atoms, such as acetic acid, propionic acid, hexanoic acid, decanoic acid, dodecanoic acid, naphthoic acid, oleic acid and
5 trans-9-octadecenoic acid.

The Examples of US-A-3,759,531 show that the process as defined leads predominantly to branched carboxylic acids. Thus the hydroxycarbonylation of propylene mainly gives isobutyric acid (Example 1) whereas the hydroxycarbonylation
10 of 1-hexene mainly gives branched C₇ acids (Example 19).

In US-A-3,816,489, by the same inventors as US-A-3,759,551 and which follows directly therefrom, it is proposed to use an iodine:iridium molar ratio of 3:1 to 100:1 so as to attempt to obtain predominantly a linear carboxylic
15 acid. When applied to monoolefins such as 1-hexene, 1-pentene, 2-pentene and 1-dodecene, this technique appears to lead to the desired result. No Example is performed with a diene.

If, however, the process according to US-A-3,759,551
20 is carried out in order to hydroxycarbonylate a diene such as butadiene, it is observed that the selectivity towards pentenoic acids, the intended products, is very low or else zero and that the corresponding saturated acids, that is to say valeric acid and methylbutyric acid, are essentially
25 obtained.

EP-A-405,433 relates to the hydroxycarbonylation of butadiene into pentenoic acids, in the presence of a rhodium catalyst and a bromide or iodide promoter, in a carboxylic acid solvent. This process uses a catalyst based on rhodium,

which is a particularly expensive metal.

The problem of the hydroxycarbonylation of butadiene into pentenoic acids has thus not been solved in an economically satisfactory manner by the techniques described
5 in the prior art.

The present invention proposes a solution to this problem.

The present invention provides a process for the hydroxycarbonylation of butadiene, by reaction with carbon
10 monoxide and water, at a temperature above 30°C, under a partial pressure of carbon monoxide, measured at 25°C, of equal to or greater than 0.5 bar, in the presence of an iridium-based catalyst and an iodine-containing or bromine-containing promoter, in a solvent medium, wherein the
15 iodine or bromine:iridium molar ratio is less than or equal to 20:1 and wherein the concentration by weight of water in the reaction mixture is less than or equal to 8%.

The concentration by weight of water in the reaction mixture is preferably from 0.00001% to 5%.

20 Even more preferably, the concentration by weight of water in the reaction mixture is from 0.01% to 2%.

An advantageous variant of the process of the invention consists in injecting water progressively as the reaction proceeds, thereby allowing its concentration in the
25 reaction mixture to be maintained at a very low value, while at the same time allowing the hydroxycarbonylation reaction to take place.

The lower limit of the water concentration is thus given as a guide, since it may be very low at any given

moment, in particular in the hypothesis envisaged above of a continuous injection of water, which is then rapidly converted.

The substrate used, butadiene, may contain a minor amount of derived compounds, for example allylic butenols such as 3-buten-2-ol, 2-buten-1-ol and mixtures thereof.

Preferably, the butadiene represents at least 80% by weight of the butadiene/butadiene derivatives mixture and, even more preferably, at least 90%.

The concentration of butadiene in the mixture is also an important parameter to take into account when carrying out the process of the invention. It is preferably maintained at a value less or equal to 16% by weight relative to the total weight of the reaction mixture.

The concentration of butadiene may be instantaneously very low, in particular in the case of continuous injection of butadiene, which is then converted very rapidly. There is thus no critical lower limit for this concentration, which depends in particular on the mode of introduction of the butadiene.

Preferably, the concentration of butadiene in the reaction mixture is less than or equal to 11% on a weight for weight basis and, even more preferably, less than or equal to 5.5% on a weight for weight basis.

For the iridium catalyst necessary in the present process, various sources of iridium may be used.

Examples of such sources of iridium which may be mentioned are:

- Ir metal; IrO_2 , Ir_2O_3 ;

- IrCl_3 ; $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$;
 - IrBr_3 ; $\text{IrBr}_3 \cdot 3\text{H}_2\text{O}$;
 - iridium iodides;
 - iridium carboxylates, in particular Ir acetate or
- 5 Ir pentenoate;
- $\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;
 - $\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;
 - $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;
 - $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;
 - 10 - $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$;
 - $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;
 - $\text{Ir}(\text{acac})(\text{CO})_2$; and
 - $[\text{IrCl}(\text{cod})]_2$;

(acac - acetylacetonate; cod = 1,5-cyclooctadiene).

15 The amount of catalyst to be used may vary within a wide range.

In general, an amount, expressed as moles of iridium metal per litre of reaction mixture, of from 10^{-4} to 10^{-1} leads to satisfactory results. Lower amounts may be used but it is

20 observed, however, that the reaction rate is low. Larger amounts have no drawbacks other than from the economic point of view.

The concentration of iridium in the reaction mixture is preferably from 5×10^{-4} to 5×10^{-2} mol/litre.

25 In the context of the process, the expression iodine-containing or bromine-containing promoter is understood to refer to hydrogen iodide, hydrogen bromide and organoiodine and organobromine compounds capable of generating hydrogen iodide and hydrogen bromide respectively

under the reaction conditions; these organoiodine and organobromine compounds are more particularly alkyl iodides and alkyl bromides having from 1 to 10 carbon atoms, among which methyl iodide and methyl bromide are preferred.

5 Among the promoters, iodine-containing promoters are generally preferred.

 The iodine or bromine:iridium molar ratio is preferably from 1:1 to 10:1.

 More preferably, the iodine or bromine:iridium molar
10 ratio is from 1:1 to 5:1.

 The lower limit indicated for the iodine or bromine:iridium molar ratio is not a critical feature for the reaction. This ratio may be less than 1:1. However, in such a case there are economic drawbacks, since some of the
15 iridium is not activated and has almost no catalytic role.

 Another characteristic of the present process lies in the use of a solvent which is liquid under the conditions of the hydroxycarbonylation reaction of the butadiene.

 This solvent may be very varied in nature.

20 Carboxylic acids, aliphatic hydrocarbons, cycloaliphatic hydrocarbons, aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, chlorinated cycloaliphatic hydrocarbons, chlorinated aromatic hydrocarbons, aliphatic ethers, aromatic ethers, mixed ethers or mixtures of several of these solvents
25 may be in particular chosen.

 The carboxylic acids which may be used as solvents in the process of the invention are, in particular, monoacids or diacids such as aliphatic acids, which are saturated or unsaturated, and aromatic acids, having a maximum of 20

carbon atoms, insofar as they are liquid under the operating conditions. Examples of such carboxylic acids are acetic acid, propionic acid, butanoic acid, valeric acid, methylbutanoic acid, adipic acid, methylglutaric acid, ethylsuccinic acid, dimethylsuccinic acid, pentenoic acids, benzoic acid, phenylacetic acid or mixtures of several of these acids. It may be advantageous to use carboxylic acids which are formed in the reaction for the hydroxycarbonylation of butadiene, in particular pentenoic acids, methyl-
5 2-butenic acids, valeric acid, methylbutanoic acid, adipic acid, methylglutaric acid, ethylsuccinic acid and dimethylsuccinic acid, especially in the case of the recycling of the reaction products and of the catalyst.

3-Pentenoic acid or mixtures of 3-pentenoic acid with 2-pentenoic acid and/or 4-pentenoic acid and/or other
15 reaction by-products are more particularly used.

Examples of the hydrocarbons, chlorinated hydrocarbons and ethers which may be used are benzene, toluene, xylenes, chlorobenzenes, dichloromethane, dichloroethane, hexane, cyclohexane and diphenyl ether.
20

In the context of an industrial use of the process, recyclings of the catalyst, of the promoter and of the unreacted butadiene may lead to the introduction into the reaction medium of larger or smaller amounts of other compounds, in particular by-products formed during the hydroxycarbonylation reaction, which are different from the carboxylic acids mentioned above. Thus, there may also be
25 butenes and gamma-valerolactone in the reaction mixture. Within the context of the invention, these compounds will be

considered as forming part of the solvent system.

The hydroxycarbonylation reaction may, for example, generally be carried out at a temperature of from 60°C to 230°C, preferably from 90°C to 200°C.

5 The partial pressure of carbon monoxide, measured at 25°C, is generally from 0.5 bar to 300 bar. It is preferably from 2 bar to 200 bar and, even more preferably, from 5 bar to 150 bar.

 As has been mentioned, the process of the invention
10 may be carried out in a continuous or batchwise manner. According to the implementation chosen, it will thus be necessary to adapt the various operating conditions defined above.

 It is known, in particular from EP-A-511,126 and
15 EP-A-536,064, to hydroxycarbonylate pentenoic acids into adipic acid, in the presence of an iridium-based catalyst and an iodine-containing or bromine-containing promoter. By adaptation of the operating conditions to those described for this second carbonylation, it is possible to use the final
20 reaction mixture, after it has been made to undergo optional treatments, for the preparation of adipic acid.

The Examples which follow illustrate the invention.

EXAMPLE 1

The following are loaded into a 125 ml autoclave:

25	- [IrCl(cod)],	0.42 mmol of Ir
	- HI (aqueous 57% solution)	0.84 mmol
	- butadiene	2.56 g (47.4 mmol)
	- water	0.88 g (48.9 mmol)
	- dichloromethane	66.25 g

The autoclave is closed and connected to a carbon monoxide supply circuit. The pressure is brought to 60 bar of CO and the autoclave is heated to 160°C.

At this temperature, the pressure is adjusted to 100 bar by carbon monoxide and the test is continued for 4 h under these conditions.

At the end of the test, the autoclave is cooled and the reaction mixture is assayed by gas chromatography. The final reaction mixture is homogeneous and has a light orange colour. It contains no tarry compounds.

The yields (RY) obtained correspond to the number of moles of compound formed per 100 mol of butadiene employed.

The following were obtained:

- RY of 3-pentenoic acid: 25%
- RY of valeric acid: 6%
- RY of methylbutanoic acid: 2%
- RY of methylbutenoic acids: 1%
- RY of butenes: 9%

EXAMPLE 2

Working as in Example 1, a test was performed in 3-pentenoic acid as solvent, at 140°C and under a pressure of 50 bar.

The HI:Ir molar ratio is 2.5:1; the initial water concentration is 1.8% weight/weight.

After maintaining the temperature for 4 h, cooling the reaction mixture and assaying (homogeneous, orange-coloured final reaction mixture, with no presence of tarry compounds), the following were obtained:

- RY of 3-pentenoic acid: 45%



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- RY of valeric acid: 2%
- RY of methylbutanoic acid: 1%
- RY of gamma-valerolactone: 4%
- RY of diacids containing 6 carbon atoms: 19%

5 EXAMPLE 3

Working as in Example 1, a test was performed in 3-pentenoic acid as solvent, at 140°C and under a pressure of 200 bar.

The HI:Ir molar ratio is 2.5:1; the initial water
10 concentration is 1.8% weight/weight.

After maintaining the temperature for 4 h, cooling of the reaction mixture and assaying (homogeneous, orange-coloured final reaction mixture, with no presence of tarry compounds), the following were obtained:

- 15 - RY of 3-pentenoic acid: 40%
- RY of valeric acid: 2%
- RY of methylbutanoic acid: 2%
- RY of gamma-valerolactone: 5%
- RY of diacids containing 6 carbon atoms: 22%

20 COMPARATIVE TEST A

This comparative test is performed according to Example 10 of US-A-3,759,551.

The following are loaded into a glass bulb placed in a 125 ml autoclave:

- 25 - $(\text{NH}_4)_2\text{IrCl}_6$ 0.0478 g
(0.108 mmol of Ir)
- HI (aqueous 57% solution) 2.74 g (12.2 mmol)
- butadiene 5.78 g (107 mmol)
- water 0.65 g (36 mmol)

- acetic acid 20 cm³ (21.8 g)

The HI:Ir molar ratio is 113:1; the initial water concentration is 9.5% weight/weight.

After 17 h at 165°C under 42 bar of carbon monoxide,
5 the final reaction mixture is dark brown with a large amount of tarry deposit. 2.1 g of these tars are isolated. The liquid part is assayed by gas chromatography.

The following were obtained:

- RY of C₅ acids: 0.47%

10

including:

- RY of 3-pentenoic acid: 0.05%

The amount of pentenoic acid formed is very low; the other C₅ acids are essentially valeric acid and methylbutanoic acid.



CLAIMS

1. Process for the hydroxycarbonylation of butadiene, by reaction with carbon monoxide and water, at a temperature above 30°C, under a partial pressure of carbon monoxide, measured at 25°C, of equal to or greater than 0.5 bar, in the presence of an iridium-based catalyst and an iodine-containing or bromine-containing promoter, in a solvent medium, wherein the iodine or bromine:iridium molar ratio is less than or equal to 20:1 and wherein the concentration by weight of water in the reaction mixture is less than or equal to 8%.
2. Process according to Claim 1 wherein the concentration by weight of water in the reaction mixture is from 0.00001% to 5%.
3. Process according to Claim 2 wherein the concentration is from 0.01% to 2%.
4. Process according to any one of Claims 1 to 3 wherein the concentration of butadiene in the reaction mixture is maintained at a value of less than or equal to 16% by weight relative to the total weight of the reaction mixture.
5. Process according to any one of Claims 1 to 4 wherein the concentration of butadiene in the reaction mixture is less than or equal to 11% on a weight for weight basis.



6. Process according to Claim 5 wherein the concentration is less than or equal to 5.5% on a weight for weight basis.

7. Process according to any one of Claims 1 to 6 wherein the iridium catalyst is chosen from:

- Ir metal; IrO_2 ; Ir_2O_3 ;
- IrCl_3 ; $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$;
- IrBr_3 ; $\text{IrBr}_3 \cdot 3\text{H}_2\text{O}$;
- iridium iodides;
- 10 - iridium carboxylates;
- $\text{Ir}_2(\text{CO})_4\text{Cl}_2$; $\text{Ir}_2(\text{CO})_4\text{I}_2$;
- $\text{Ir}_2(\text{CO})_8$; $\text{Ir}_4(\text{CO})_{12}$;
- $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$;
- $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$;
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- $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$;
- $\text{Ir}(\text{acac})(\text{CO})_2$; and
- $[\text{IrCl}(\text{cod})]_2$.

8. Process according to Claim 7 wherein the iridium catalyst is Ir acetate or Ir pentenoate.

9. Process according to any one of Claims 1 to 8 wherein the amount of catalyst, expressed as moles of iridium metal per litre of reaction mixture, is from 10^{-4} to 10^{-1} mol/litre.

25 10. Process according to Claim 9 wherein the amount of catalyst is from 5×10^{-4} to 5×10^{-2} mol/litre.



11. Process according to any one of Claims 1 to 10 wherein the iodine-containing or bromine-containing promoter is chosen from hydrogen iodide, hydrogen bromide and alkyl iodides and alkyl bromides having from 1 to 10 carbon atoms and which are capable of generating hydrogen iodide and hydrogen bromide respectively under the reaction conditions.

12. Process according to any one of Claims 1 to 11 wherein the iodine or bromine:iridium molar ratio is from 1:1 to 10:1.

13. Process according to Claim 12 wherein the ratio is from 1:1 to 5:1.

14. Process according to any one of Claims 1 to 13 wherein the solvent, which is liquid under the reaction conditions, is chosen from carboxylic acids, aliphatic hydrocarbons, cycloaliphatic hydrocarbons, aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, chlorinated cycloaliphatic hydrocarbons, chlorinated aromatic hydrocarbons, aliphatic ethers, aromatic ethers, mixed ethers, or mixtures thereof.

15. Process according to any one of Claims 1 to 14 wherein the reaction is carried out at a temperature of from 60°C to 230°C.

16. Process according to Claim 15 wherein the temperature is from 90°C to 200°C.

17. Process according to any one of Claims 1 to 16 wherein the reaction is carried out under a partial pressure of carbon monoxide, measured at 25°C, of 0.5 bar to 300 bar.



18. Process according to Claim 17 wherein the reaction is carried out under a partial pressure of carbon monoxide of 2 bar to 200 bar.

19. Process according to Claim 18 wherein the
5 reaction is carried out under a partial pressure of 5 bar to 150 bar.

20. A pentenoic acid obtained by a process as defined in any one of Claims 1 to 19.

ABSTRACT

PROCESS FOR THE HYDROXYCARBONYLATION OF BUTADIENE

Process for the hydroxycarbonylation of butadiene,
by reaction with carbon monoxide and water, at a temperature
5 above 30°C, under a partial pressure of carbon monoxide,
measured at 25°C, of equal to or greater than 0.5 bar, in the
presence of an iridium-based catalyst and an
iodine-containing or bromine-containing promoter, in a
solvent medium, wherein the iodine or bromine:iridium molar
10 ratio is less than or equal to 20:1 and wherein the
concentration by weight of water in the reaction mixture is
less than or equal to 8%.

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 Although it is possible to envisage performing the two hydroxycarbonylation reactions leading from butadiene to
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20 to 330°C and under a partial pressure of carbon monoxide of about 0.3 to 210 bar.

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