

The present invention relates to a process for the preparation of adipic acid by hydrocarboxylation of pentenic acids, that is to say by reaction of water and carbon monoxide with at least one pentenic acid in the presence of a catalyst based rhodium and on at least one iodine-containing promoter.

European Patent Application No. 188 209 proposes a process for the preparation of linear dicarboxylic acids, in particular adipic acid, by reaction of unsaturated monocarboxylic acids, in particular 3-pentenoic acid, carbon monoxide and water in the presence of a rhodium-based catalyst and an iodine-containing promoter, the reaction being carried out in a solvent such as methylene chloride at a temperature of 100 to 240°C and at a total pressure between 14 and 240 atm; a temperature between 150 and 180°C and a total pressure between 24 and 40 atmospheres are considered preferable. The partial pressure of carbon monoxide is usually between 10 and 35 atm and preferably between 10 and 17 atm. The choice of solvent is indicated as being critical within the context of the process in question.

It is affirmed that non-polar solvents such as cyclohexane and toluene are undesirable on account of their tendency for directly favouring the formation of branched products and indirectly favouring that of saturated monocarboxylic acids.

European Patent Application No. 0 274 076 proposes a process for the preparation of linear carboxylic acids by hydroxycarboxylation of unsaturated esters or of alkenes having terminal unsaturation containing from 4 to 16 carbon atoms, in the presence of a rhodium-based catalyst and an iodine-containing promoter. The reaction is carried out in a solvent chosen either from methylene chloride, 1,2-dichloroethane or aromatic solvents, and an aliphatic or aromatic acid of pKa between 4.2 and 5.2 is present as reaction accelerator. The partial pressure of carbon monoxide is between 10 and 200 and preferably between 13 and 20 atm. However, starting from pentenic esters, the formation of methyl monoadipate is observed

essentially.

It has now been found that it is possible to obtain adipic acid selectively by hydrocarboxylation of pentenic acids in the presence of a rhodium-based catalyst and an iodine-containing promoter in a solvent chosen from the group consisting of saturated aliphatic or cycloaliphatic hydrocarbons, aromatic hydrocarbons and their chlorinated derivatives.

The subject of the present invention is thus a process for the preparation of adipic acid by reaction of water and carbon monoxide with at least one pentenic acid in the presence of a catalyst based on rhodium and of at least one iodine-containing promoter, at a temperature of between 100 and 240°C, at a pressure higher than atmospheric pressure, characterized in that

a) the reaction is performed in at least one solvent chosen from the group consisting of saturated aliphatic or cycloaliphatic hydrocarbons, aromatic hydrocarbons and chlorinated cycloaliphatic or aromatic hydrocarbons, and in that

b) the partial pressure of carbon monoxide, measured at 25°C, is lower than 12 bars.

The present invention also relates to a process as described above, but characterized in that the reaction is performed in a chlorinated aliphatic hydrocarbon and in that the partial pressure of carbon monoxide, measured at 25°C, is lower than or equal to 8 bars.

Pentenic acid is understood, within the context of the present invention, to refer to 2-pentenoic acid, 3-pentenoic acid, 4-pentenoic acid and their mixtures.

4-Pentenoic acid leads to good results but is not readily available.

3-Pentenoic acid, taken alone or as a mixture with its isomers, is more particularly suitable on account of its accessibility and the satisfactory results to which it leads within the context of the present process.

The process according to the present invention requires the presence of a rhodium-based catalyst. Any

source of rhodium may be used.

By way of examples of rhodium sources which may be suitable for use in the present process, there may be mentioned:

- 5 Rh metal; Rh_2O_3 ;
RhCl₃; $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$;
RhBr₃; $\text{RhBr}_3 \cdot 3\text{H}_2\text{O}$;
RhI₃; $\text{Rh}(\text{NO}_3)_3$; $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$;
Rh₂(CO)₄Cl₂; Rh₂(CO)₄Br₂; Rh₂(CO)₄I₂;
10 Rh(CO)Cl[P(C₆H₅)₃]₂
Rh[P(C₆H₅)₃]₂(CO)I
Rh[P(C₆H₅)₃]₃Br
Rh₄(CO)₁₂; Rh₆(CO)₁₆; Rh(CO)₂(acac);
Rh(Cod)(acac)₂; Rh(acac)₃;
15 Rh₂(Cod)₂Cl₂ · Rh₂(CO₂CH₃)₄;
HRh(CO)[P(C₆H₅)₃]₃;
(Cod = 1,5-cyclooctadiene; acac: acetylacetonate)
The following are more particularly suitable for
use in the present process:
20 HRh(CO)[P(C₆H₅)₃]₃;
Rh(CO)Cl[P(C₆H₅)₃]₂;
Rh₂(Cod)₂Cl₂;
Rh₂(CO)₄Cl₂;
RhI₃; RhCl₃ · 3H₂O; Rh(acac)₃;
25 Rh(Cod)(acac)₂; Rh₂(CO₂CH₃)₄; Rh₄(CO)₁₂;
and Rh₆(CO)₁₆.

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

30 In general, an amount expressed in moles of rhodium metal per litre of reaction medium between 10⁻³ and 10⁻¹ leads to satisfactory results. Lower amounts may be used; it is observed, however, that the rate of reaction is low. Higher amounts have no disadvantages other than from the economic viewpoint.

35 The rhodium concentration is preferably between 5.10⁻³ and 10⁻² (inclusive) mol/l.

Iodine-containing promoter is understood, within the context of the present process, to refer to HI and organoiodo compounds capable of generating of HI under

the reaction conditions, and in particular C₁-C₁₀ alkyl iodides, methyl iodide being more particularly recommended.

5 The amount of iodine-containing promoter to be used is generally such that the I/Rh molar ratio is higher than or equal to 0.1. It is not desirable for this ratio to exceed 20. The I/Rh molar ratio is preferably between 1 and 4 (inclusive).

10 The presence of water is essential for carrying out the process according to the present invention. The amount of water to be used is generally such that the water/pentenic acid(s) molar ratio is between 1 and 10 (inclusive).

15 A lower amount has the disadvantage of limiting the conversion. A higher amount is not desirable on account of the loss of catalytic activity observed.

20 According to one of the essential characteristics of the present invention, the reaction is performed in at least one solvent chosen from the group consisting of saturated aliphatic or cycloaliphatic hydrocarbons, aromatic hydrocarbons and their chlorinated derivatives.

25 The precise nature of the solvent chosen from the abovementioned group is not critical within the context of the present process, as long as the latter is in the liquid state under the reaction conditions.

By way of example of such solvents there may be mentioned: benzene, toluene, chlorobenzene, methylene chloride, hexane and cyclohexane.

30 Toluene and chlorobenzene are particularly suitable for use in the process according to the invention.

35 The amount of solvent present in the reaction medium may vary within a wide range, for example from 10 to 99 (inclusive) % by volume of the reaction medium. This amount is preferably between 30 and 90 (inclusive) % by volume.

According to another essential characteristic of the present process, the partial pressure of carbon monoxide, measured at 25°C, is lower than 12 bars.

When the partial pressure of carbon monoxide, measured at 25°C, is higher than this value, selectivity towards linear diacids among the diesters (degree of linearity) falls considerably.

5 A minimum partial pressure of carbon monoxide of 0.5 bar (measured at 25°C) is recommended.

The partial pressure of carbon monoxide, measured at 25°C, is preferably lower than or equal to 8 bars.

10 Carbon monoxide which is substantially pure or of technical grade, as found commercially, may be used.

As indicated at the start of the present specification, the reaction temperature is between 100 and 240°C. For good implementation of the present invention, the temperature is between 160 and 190°C (inclusive).

15 The reaction is carried out at a pressure higher than atmospheric pressure and generally in the liquid phase.

The total pressure may vary within a certain range which will depend upon the experimental procedure selected, on the partial pressure of carbon monoxide and of those of the constituents of the reaction medium at the reaction temperature chosen and, where appropriate, on the autogenous pressure of the pentenic acid(s) present.

25 The reaction medium contains at least one solvent chosen from the abovementioned group, water, one or more sources of rhodium, one or more iodine-containing promoters and, where appropriate, all or some of the pentenic acid(s) employed and of the reaction products.

30 At the end of the reaction or of the time allotted to the latter, the adipic acid is separated out by any suitable means, for example by crystallization.

The examples below illustrate the present invention.

35 Example 1 :

The following are introduced into a 125 cm³ stainless steel autoclave (HASTELLOY B2), purged beforehand with argon:

160 mg (0.65 mmol) of rhodium in the form of
[RhCl(COD)]₂

0.7 g (5 mmol) of CH₃I

2 g (110 mmol) of water

5 5 g (50 mmol) of 3-pentenoic acid

50 cm³ of toluene

The autoclave is hermetically sealed, placed in
an oven incorporating agitation and connected to the
supply of gas under pressure. While cold, 2 bars of CO
are introduced and the mixture is heated at 190°C over 30
minutes. When this temperature is reached, the pressure
is adjusted to 20 bars.

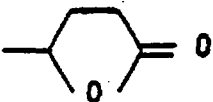
After a reaction time of 20 minutes, the absorp-
tion of CO has stopped; the autoclave is then cooled and
degassed.

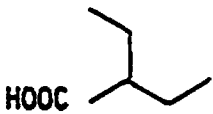
The reaction solution is analysed by gas chroma-
tography and by high performance liquid chromatography.

The amounts of products formed (molar yield
relative to the 3-pentenoic acid charged) are as follows:

20 valeric acid (Pa):  COOH = 3 %

2-pentenoic acid (P2):  COOH = 8 %

4-methylbutyrolactone (M4L):  = 8 %

ethylsuccinic acid (A3):  COOH = 5 %

methylglutaric acid (A2):  COOH = 27 %

25 adipic acid (A1): HOOC  COOH = 47 %

The degree of linearity (L) is 60 %.

The extent of conversion of the 3-pentenoic acid (EC) is 100 %.

Example 2 to 5; Control Tests (a) to (d):

5 A first series of tests is performed, in the autoclave and according to the experimental procedure described for Example 1, at 175°C and by modifying the partial pressure of carbon monoxide and/or the nature of the solvent used.

10 The specific conditions and the results obtained, all conditions being otherwise equal, are collated in Table (I) below, in which the conventions used are the same as in Example 1 and t represents the time at the reaction temperature.

TABLE I

Ref.	Solvent	P(CO) bar	t min	EC %	A1 %	L %	Pa %
2	Toluene	3	120	32	10	62	< 1
3	"	11	20	100	45	53	3
a	"	18	20	100	36	43	3
b	"	71	20	100	36	24	2
4	Chloro- benzene	4	30	100	52	70	5
c	"	22	20	100	31	35	2
5	Methylene chloride	8	20	100	55	61	2
d	"	25	20	100	38	44	1

These results demonstrate the critical influence of a low partial pressure of CO on the degree of linearity (L).

Example 6:

Example 5 is repeated in the autoclave and according to the experimental procedure described above, with the exception that the charge contains 50 mmol of 4-pentenoic acid in place of the 3-pentenoic acid.

After reaction for 30 min, all conditions being otherwise equal, the results obtained are as follows:

10 • EC = 100 %
 • Al = 69 %
 • L = 85 %
 • Pa = 1 %

Example 7:

Example 5 is repeated in the autoclave and according to the experimental procedure described above, with the exception that the charge contains 50 mmol of 2-pentenoic acid in place of the 3-pentenoic acid.

After reaction for 16 h, all conditions being otherwise equal, the results obtained are as follows:

20 • EC = 62 %
 • Al = 36 %
 • L = 60 %
 • Pa = 26 %

Example 8:

Example 4 is repeated in the autoclave and according to the experimental procedure described above, modifying only the temperature (150°C).

After reaction for 60 min, the results obtained are as follows:

30 • EC = 100 %
 • Al = 42 %
 • L = 46 %



CLAIMS

1. Process for the preparation of adipic acid by reaction of water and carbon monoxide with at least one pentenic acid in the presence of a catalyst based on rhodium and of at least one iodine-containing promoter, at a temperature of between 100 and 240°C, at a pressure higher than atmospheric pressure, characterized in that
 - a) the reaction is performed in at least one solvent chosen from the group consisting of saturated aliphatic or cycloaliphatic hydrocarbons, aromatic hydrocarbons and chlorinated cycloaliphatic or aromatic hydrocarbons,
 - b) the partial pressure of carbon monoxide, measured at 25°C, is lower than 12 bars.
2. Process for the preparation of adipic acid by reaction of water and carbon monoxide with at least one pentenic acid, in the presence of a rhodium-based catalyst and of at least one iodine-containing promoter, at a temperature of between 100 and 240°C, at a pressure higher than atmospheric pressure, characterized in that
 - a) the reaction is performed in a chlorinated aliphatic hydrocarbon,
 - b) the partial pressure of carbon monoxide, measured at 25°C, is lower than or equal to 8 bars.
3. Process according to Claim 1, characterized in that the solvent is chosen from toluene and chlorobenzene.
4. Process according to Claim 2, characterized in that the solvent is methylene chloride.
5. Process according to Claim 1 to 4, characterized in that the solvent represents at least 10 % by volume of the liquid reaction mixture.
6. Process according to Claim 5, characterized in that the solvent represents from 30 to 90 (inclusive) % by volume of the liquid reaction mixture.
7. Process according to any one of the preceeding Claims, characterized in that the rhodium concentration in the reaction mixture is between 10^{-3} and 10^{-1} mol/l (inclusive).



8. Process according to any one of the preceeding Claims, characterized in that the I/Rh molar ratio is higher than or equal to 0.1.
9. Process according to any one of the preceeding
5 Claims, characterized in that the I/Rh molar ratio is lower than or equal to 20.
10. Process according to any one of the preceeding Claims, characterized in that the molar ratio water/pentenic acid(s) is between 1 and 10 (inclusive).
- 10 11. Process according to any one of the preceeding Claims, characterized in that the reaction temperature is between 160 and 190°C.
12. Process according to one of Claims 1 and 3 to 11, characterized in that the partial pressure of carbon
15 monoxide, measured at 25°C, is lower than or equal to 8 bars.