

PROCESS FOR PREPARING ADIPIC ACID
BY HYDROCARBOXYLATION OF PENTENOIC ACIDS

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

A process is proposed, in European Patent Application No. 188,209, for preparing linear dicarboxylic acids, in particular adipic acid, by reaction of unsaturated monocarboxylic acids, in particular penten-3-oic acid, carbon monoxide and water, in the presence of a rhodium-based catalyst and of an iodinated promoter, the reaction being carried out in a solvent such as methylene chloride at a temperature of 100 to 240°C and under a total pressure of between 14 and 240 atm; a temperature of between 150 and 180°C and a total pressure of between 24 and 40 atmospheres are regarded as preferable. The carbon monoxide partial pressure is generally between 10 and 35 atmospheres and preferably between 10 and 17 atmospheres. The choice of solvent is shown to be critical within the scope of the process in question and it is even judged that solvents such as acetic acid are undesirable due to the low degrees of linearity obtained in their presence.

Likewise, it is maintained that nonpolar

solvents such as cyclohexane and toluene are also undesirable, due to their propensity to directly promote the formation of branched products and indirectly that of saturated monocarboxylic acids.

5 A process is proposed, in European Patent Application No. 0,274,076, for preparing linear carboxylic acids by hydroxycarboxylation of unsaturated esters or of alkenes containing end unsaturation comprising from 4 to 16 carbon atoms in the presence of
10 a rhodium-based catalyst and of an iodinated promoter. The reaction is carried out in a solvent chosen without distinction from methylene chloride, 1,2-dichloroethane and aromatic solvents, and an aliphatic or aromatic acid with a pKa of between 4.2 and 5.2 is present as
15 the reaction accelerator. The carbon monoxide partial pressure is between 10 and 200 atmosphere and preferably between 13 and 20 atmospheres.

 However, when starting from pentenoic esters, the formation of methyl monoadipate is essentially
20 observed.

 Patent EP-A-0,477,112 describes the preparation of adipic acid by hydrocarboxylation of pentenoic acids in the presence of rhodium and of an iodinated promoter in a solvent chosen from carboxylic
25 acids.

 All these processes of the prior art are used in a solvent of one type or another.

 It has now been found that it is possible to

selectively obtain adipic acid by hydrocarboxylation of pentenoic acids in the presence of a rhodium-based catalyst and of an iodinated promoter without using a third solvent, that is to say, using solely one or a
5 number of pentenoic acids.

The subject of the present invention is thus a process for preparing adipic acid by reaction of water and carbon monoxide with at least one pentenoic acid, in the presence of a rhodium-based catalyst and
10 of at least one iodinated promoter, at a temperature between 100 and 240°C, at a pressure greater than atmospheric pressure, characterised in that

- a) the reaction is implemented in the absence of a third solvent
- 15 b) and the carbon monoxide partial pressure, measured at 25°C, is less than or equal to 20 bar.

Pentenoic acid is understood to mean, within the scope of the present invention, penten-2-oic acid, penten-3-oic acid or penten-4-oic acid and their
20 mixtures.

Penten-4-oic acid leads to good results but is still not readily available.

Penten-3-oic acid, taken in isolation or as a mixture with its isomers, is more particularly
25 suitable, considering its accessibility and the satisfactory results which it gives within the scope of the present process.

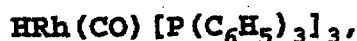
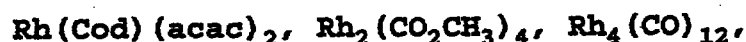
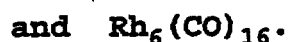
The pentenoic acids used may, of course, contain minor amounts of by-products formed during their preparation, such as, for example, valeric acid, methylbutyrolactones, adipic acid, methylglutaric acid
 5 and ethylsuccinic acid.

The process according to the present invention requires the presence of a rhodium-based catalyst. Any rhodium source is capable of being used.

As examples of rhodium sources capable of
 10 being suitable for use in the present process, there may be mentioned:

Rh metal, Rh_2O_3 ,
 RhCl_3 , $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$,
 RhBr_3 , $\text{RhBr}_3 \cdot 3\text{H}_2\text{O}$,
 15 RhI_3 , $\text{Rh}(\text{NO}_3)_3$, $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$,
 $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, $\text{Rh}_2(\text{CO})_4\text{Br}_2$, $\text{Rh}_2(\text{CO})_4\text{I}_2$,
 $\text{Rh}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$,
 $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{I}$,
 $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Br}$,
 20 $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}(\text{CO})_2(\text{acac})$,
 $\text{Rh}(\text{Cod})(\text{acac})_2$, $\text{Rh}(\text{acac})_3$,
 $\text{Rh}_2(\text{Cod})_2\text{Cl}_2$, $\text{Rh}_2(\text{CO}_2\text{CH}_3)_4$,
 $\text{HRh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$,
 (Cod = 1,5-cyclooctadiene, acac =
 25 acetylacetonate).

More particularly suitable for use in the present process are:



The quantity of rhodium to be used can vary within wide limits.

10 In general, a quantity, expressed in mole of metallic rhodium per litre of reaction mixture, of between 10^{-4} and 10^{-1} leads to satisfactory results. Lower quantities can be used; however, the reaction velocity is observed to be low. Higher quantities have
15 disadvantages only at an economic level.

Preferably, the concentration of rhodium is between $5 \cdot 10^{-4}$ and 10^{-2} (inclusive) mol/l.

Iodinated promoter is understood to mean, within the scope of the present process, HI and the
20 organoiodine compounds capable of generating HI under the reaction conditions and, in particular, the C_1 - C_{10} alkyl iodides, methyl iodide being more particularly recommended.

The quantity of iodinated promoter to be used
25 is in general such that the I/Rh molar ratio is greater than or equal to 0.1. It is not desirable for this ratio to exceed 20. Preferably, the I/Rh molar ratio is between 1 and 4 (inclusive).

The presence of water is vital to the running of the process according to the present invention. In general, the quantity of water to be used is such that the water/pentenic acid(s) molar ratio is between 0.01 and 10 (inclusive).

A lower quantity has the disadvantage of excessively limiting the conversion. A higher quantity is not desirable due to the loss of catalytic activity observed.

According to an essential characteristic of the present process, the carbon monoxide partial pressure, measured at 25°C, is less than or equal to 20 bar.

When the carbon monoxide partial pressure, measured at 25°C, is greater than this value, the selectivity towards linear and/or branched diacids is very low and the formation of significant quantities of 4-methylbutyrolactone, an undesirable compound, is recorded.

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

Preferably, the carbon monoxide partial pressure, measured at 25°C, is less than or equal to 10 bar.

It is possible to use carbon monoxide which is substantially pure or of technical quality, such as is commercially available.

As shown above, 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).

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

The total pressure can vary within certain limits which will depend on the procedure retained, on the carbon monoxide partial pressure and on those of the constituents of the reaction mixture at the chosen reaction temperature and, if appropriate, on the autogenous pressure of the pentenoic acid(s) present.

The reaction mixture contains water, one or more rhodium sources, one or more iodinated promoters and, if appropriate, all or part of the pentenoic acid(s) involved, and reaction products.

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

The examples below illustrate the present invention.

EXAMPLE 1

The following are introduced into a glass flask purged beforehand with argon:

- 1.31 mmol of rhodium in the form of $[\text{RhCl}(\text{Cod})]_2$
- 0.35 g (2.5 mmol) of CH_3I
- 2.29 g (127 mmol) of water

55.2 g (552 mmol) of penten-3-oic acid.

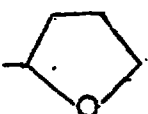
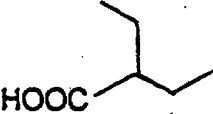
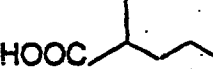
The flask is placed in a 125-ml autoclave.

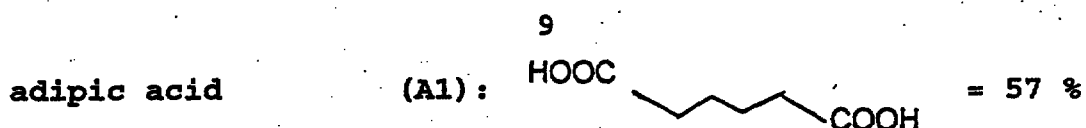
The autoclave is hermetically closed, placed in an oven equipped with agitation and connected to the supply of pressurised gas. 2 bar of CO are admitted while cold and the mixture is heated to 175°C over 20 minutes. When this temperature is reached, the pressure is adjusted to 8 bar.

After a period of reaction of 90 minutes, CO absorption has ceased; the autoclave is then cooled and degassed.

The reaction solution is analysed by gas phase chromatography and by high pressure liquid chromatography.

The quantities of products formed (molar yield in relation to converted penten-3-oic acid) are as follows:

valeric acid	(Pa):		COOH	= 0 %
penten-4-oic acid	(P4):		COOH	= 9.5 %
20 penten-2-oic acid	(P2):		COOH	= 7.5 %
4-methylbutyrolactone (M4L):			= O	= 16 %
ethylsuccinic acid (A3):			COOH	= 0 %
methylglutaric acid (A2):			COOH	= 16 %



The degree of linearity (L) is 77 %.

The degree of conversion of penten-3-oic acid (DC) is 47 %.

5 The productivity, expressed in grams of adipic acid produced per hour and per litre of reaction mixture (calculated over 30 min of CO absorption) is 1100 g/h.l.

COMPARATIVE TEST 1

10 Example 1 is repeated under the same conditions but with the following charges:

- 1.31 mmol of rhodium in the form of $[\text{RhCl}(\text{Cod})]_2$
- 0.35 g (2.5 mmol) of CH_3I
- 15 - 2.29 g (127 mmol) of water
- 4.88 g (48.8 mmol) of penten-3-oic acid
- 43.2 g of acetic acid.

The following results are obtained:

- DC of P3: 100 %
- 20 - degree of linearity: 73 %
- yield of adipic acid: 62 %
- productivity: 130 g/h.l

EXAMPLE 2

25 Example 1 is repeated according to its procedure, under the following conditions:

- temperature: 175°C
- CO pressure: 20 bar

- duration of temperature: 180 min

and the following charges:

- 0.192 mmol of rhodium in the form of $[\text{RhCl}(\text{Cod})]_2$
- 5 - 0.105 g (0.468 mmol) of HI in the form of a 57 % solution in water
- 2.31 g (128 mmol) of water
- 53.63 g (536 mmol) of penten-3-oic acid.

The following results are obtained:

- 10 - DC of P3: 41 %
- degree of linearity: 55 %
- yield of adipic acid: 42 %
- productivity: 170 g/h.l

EXAMPLE 3

15 Example 1 is repeated according to its procedure, under the following conditions:

- temperature: 175°C
- CO pressure: 8 bar
- duration of temperature: 205 min.

20 and the following charges:

- 0.192 mmol) of rhodium in the form of $[\text{RhCl}(\text{Cod})]_2$
- 0.105 g (0.468 mmol) of HI in the form of a 57 % solution in water
- 25 - 2.31 g (128 mmol) of water
- 53.76 g (538 mmol) of penten-3-oic acid.

The following results are obtained:

- DC of P3: 38 %

- degree of linearity: 63 %
- yield of adipic acid: 49 %
- productivity: 150 g/h.l

CLAIMS

1. Process for preparing adipic acid by reaction of water and carbon monoxide with at least one pentenoic acid, in the presence of a rhodium-based catalyst and of at least one iodinated promoter, at a temperature between 100 and 240°C, at a pressure greater than atmospheric pressure, characterised in that
- a) the reaction is implemented in the absence of a third solvent
- b) and the carbon monoxide partial pressure, measured at 25°C, is less than or equal to 20 bar.
2. Process according to claim 1, characterised in that the rhodium concentration in the reaction mixture is between 10^{-4} and 10^{-1} mol/l (inclusive).
3. Process according to either of claims 1 or 2, characterised in that the I/Rh molar ratio is greater than or equal to 0.1.
4. Process according to one of claims 1 to 3, characterised in that the I/Rh molar ratio is less than or equal to 20.
5. Process according to one of claims 1 to 4, characterised in that the water/pentenoic acid(s) molar ratio is between 0.01 and 10 (inclusive).
6. Process according to one of claims 1 to 5, characterised in that the reaction temperature is



between 160 and 190°C.

7. Process according to one of claims 1 to 6, characterised in that the carbon monoxide partial pressure, measured at 25°C, is less than or equal to 10 bar.

8. Process according to one of claims 1 to 7, characterised in that the pentenoic acid used is penten-3-oic acid alone or as a mixture with penten-4-oic acid and/or penten-2-oic acid.