

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 rhodium-based catalyst and at least one iodinated 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 iodinated 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 to be critical in the context of the process in question, and it is even considered that solvents such as acetic acid are undesirable on account of the low degrees of linearity obtained in their presence.

Similarly, it is affirmed that non-polar solvents such as cyclohexane and toluene are, themselves, also undesirable on account of their propensity to promote directly the formation of branched products and indirectly 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 and containing from 4 to 16 carbon atoms, in the presence of a rhodium-based catalyst and an iodinated promoter. The reaction is carried out in a solvent which is chosen from either 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 an accelerator for the

reaction. The partial pressure of carbon monoxide is between 10 and 200 and preferably between 13 and 20 atm.

However, the formation of methyl mono adipate is essentially observed starting from pentenic esters.

5 It has now been found that it is possible to obtain selectively adipic acid by hydrocarboxylation of pentenic acids in the presence of a rhodium-based catalyst and an iodinated promoter in a solvent chosen from carboxylic acids.

10 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 rhodium-based catalyst and at least one iodinated promoter, at a temperature between 100 and 15 240°C, under a pressure greater than atmospheric pressure, characterized in that

a) the reaction is carried out in a saturated aliphatic or an aromatic carboxylic acid containing a maximum of 20 carbon atoms, and in that

20 b) the partial pressure of carbon monoxide measured at 25°C is less than or equal to 20 bar.

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

25 4-Pentenoic acid leads to good results, but is not readily available.

3-Penteneoic acid, taken individually or mixed with its isomers, is more particularly suitable, when its accessibility and the satisfactory results to which it leads in the context of the present process are taken into account.

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

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

Rh metal; Rh_2O_3 ;
 RhCl_3 ; $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$;

RhBr₃; RhBr₃·3H₂O;
RhI₃; Rh(NO₃)₃; Rh(NO₃)₃·2H₂O;
Rh₂(CO)₄Cl₂; Rh₂(CO)₄Br₂; Rh₂(CO)₄I₂;
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;
Rh₂(Cod)₂Cl₂·Rh₂(CO₂CH₃)₄;

HRh(CO)[P(C₆H₅)₃]₃;
(Cod = 1,5-cyclooctadiene; acac: acetylacetonate)
More particularly suitable for implementation of
the present process are:

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;
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.

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

The concentration of rhodium is preferably
between 5·10⁻³ and 10⁻² mol/l (inclusive).

Iodinated promoter, in the context of the present
process, is understood to refer to HI and the organo-
iodine compounds capable of generating HI under the
reaction conditions and, in particular, C₁-C₁₀ alkyl
iodides, methyl iodide being more particularly
recommended.

The amount of iodinated promoter to be used is
generally 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. The I/Rh molar ratio is preferably between 1 and 4 (inclusive).

5 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).

10 A smaller amount has the disadvantage of limiting the conversion. A larger amount is not desirable on account of the loss of catalytic activity observed.

According to one of the essential characteristics of the present invention, the reaction is carried out in a saturated aliphatic or an aromatic carboxylic acid containing a maximum of 20 carbon atoms.

15 The precise nature of the carboxylic acid is not critical in the context of the present process, inasmuch as this acid is in the liquid state under the reaction conditions.

20 By way of examples of carboxylic acids which may be suitable for implementation of the process according to the invention, there may be mentioned:

acetic acid, propionic acid, butyric acid, valeric acid, adipic acid, benzoic acid and phenylacetic acid.

25 Use is preferably made of a C₁-C₄ aliphatic carboxylic acid. Acetic acid is more particularly suitable for implementation of the present invention.

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

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

When the partial pressure of carbon monoxide measured at 25°C is greater than this value, the selectivity towards linear and/or branched diacids is very low

and the formation of large amounts of 4-methylbutyrolactone, which is an undesirable compound, is noted.

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

5 The partial pressure of carbon monoxide measured at 25°C is preferably less than or equal to 10 bar.

Substantially pure or technical grade carbon monoxide, as found on the market, may be used.

10 As indicated at the beginning 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 under a pressure greater than atmospheric pressure and, generally, in the liquid phase.

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

25 The reaction mixture contains the saturated aliphatic or aromatic carboxylic acid, water, one or more sources of rhodium, one or more iodinated promoters and, where appropriate, all or part of the pentenic acid or acids employed and 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 appropriate means, for example by crystallization and/or distillation of the carboxylic acid.

The examples below illustrate the present invention.

Example 1:

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

325 mg (1.32 mmol) of rhodium in the form of
[RhCl(COD)]₂

0.64 g (4.5 mmol) of CH₃I

2 g (110 mmol) of water

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

50 cm³ of acetic acid

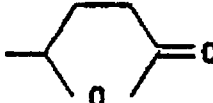
The autoclave is hermetically closed and placed
in an oven incorporating agitation and connected to the
supply of gas under pressure. 2 bar of CO are introduced
10 while cold and the mixture is heated [lacuna] 175°C over
20 minutes. When this temperature is reached, the
pressure is adjusted to 8 bar.

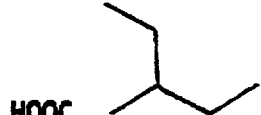
After a reaction time of 20 minutes, the absorp-
tion of CO has ceased; the autoclave is then cooled and
15 degassed.

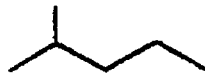
The reaction solution is analysed by gas chroma-
tography and by high performance liquid chromatography.

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

20 valeric acid (Pa):  COOH = 1 %
4-pentenoic acid (P4):  COOH = 2.2 %
3-pentenoic acid (P3):  COOH = 13 %
2-pentenoic acid (P2):  COOH = 8.8 %

4-methylbutyrolactone (4ML):  = 8 %

25 ethylsuccinic acid (A3):  COOH = 3 %

methylglutaric acid (A2):  COOH = 23 %

adipic acid (A1): HOOC  COOH = 54 %

The degree of linearity (L) is 67 %

The degree of conversion of 3-pentenoic acid (DC) is 87 %.

5 Example 2; control tests (a) to (c):

10 A first series of tests is performed in an autoclave and according to the experimental procedure described for Example 1, by modifying only the partial pressure of carbon monoxide. This pressure (at 175°C) is equal to the difference between the total pressure (P_T) and the autogenous pressure of the order of 4 bar.

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

TABLE I

Ref.	P_T bar	t min.	DC %	A1 %	L %	4ML %
1	8	20	87	54	67	8
2	15	10	100	35	42	10
a	28	20	100	22	27	16
b	60	15	100	18	24	21
c	100	20	100	19	27	27

25 These results demonstrate the determining role of a low partial pressure of CO on the degree of linearity (L) and on the amount of lactone formed (4ML).

Examples 3 to 5; control tests (d) to (f):

A second series of tests analogous to the above test are performed in an autoclave and according to the

experimental procedure described above, except that the charge contains 50 mmol of 4-pentenoic acid in place of the 3-pentenoic acid.

5 The specific conditions and the results obtained, all other conditions being equal, are featured in Table II below:

TABLE II

Ref.	P _r bar	t min.	DC %	Al %	L %	4ML %
3	8	20	100	72	78	7
4	12	10	100	65	73	10
5	15	20	100	42	51	15
d	28	15	100	48	59	17
e	50	20	100	43	53	17
f	100	20	100	40	56	29

15 Example 6; control tests (g) and (h):

20 A third series of tests analogous to the first series is performed in an autoclave and according to the experimental procedure described above, except that the charge contains 50 mmol of 4-pentenoic acid in place of the 3-pentenoic acid and an amount of methyl iodide divided by two.

The specific conditions and the results obtained, all other conditions being equal, are featured in Table III below:

TABLE III

Ref.	P _r bar	t min.	DC %	Al %	L %	4ML %
6	8	20	100	71	80	8
g	50	20	100	43	60	26
h	100	35	100	36	58	36

Examples 7 and 8 control tests (i) and (j):

A fourth series of tests is performed in an autoclave and according to the experimental procedure described for Examples 1 and 2, using 50 mmol of 2-pentenoic acid in place of the 3-pentenoic acid.

The specific conditions and the results obtained, all other conditions being equal, are featured in Table IV below:

TABLE IV

Ref.	P _r bar	t min.	DC %	Al %	L %	4ML %
7	8	40	35	23.5	55	4
8	12	90	77	27	49	7
i	28	100	98	17	30	6.5
j	50	120	97	16	28	7

In this series of tests the presence of large amounts (~ 35-45 %) of valeric acid is noted; in all of the above series this saturated acid, when it is present, only represents ~ 0.5 to 2 %.

Example 9:

A test is performed, in an autoclave and according to the experimental procedure described above, on a charge consisting of:

- 25 mmol of 3-pentenoic acid
- 110 mmol of water
- 1.32 mmol of rhodium in the form of $[\text{RhCl}(\text{COD})]_2$
- 5 - 2.6 mmol of methyl iodide and
- 50 cm³ of acetic acid

The results obtained after reaction for 30 minutes at 175°C under a total pressure of 8 bar are as follows:

- 10 · DC = 100 %
- Al = 58 %
- L = 67 %
- 4ML = 6 %

Example 10:

- 15 Example 9 above is repeated, except that the charge contains 100 mmol of 3-pentenoic acid.

The results obtained after reaction for 80 minutes, all other conditions being equal, are as follows:

- 20 · DC = 99 %
- Al = 58 %
 - L = 68 %
 - 4ML = 6 %

Examples 11 to 15:

- 25 A fifth series of tests is performed, in an autoclave and according to the experimental procedure described above, on a charge containing:

- 1.32 mmol of rhodium in the form of $[\text{RhCl}(\text{COD})]_2$
- 30 - 2.5 mmol of CH_3I
- 110 mmol of water
- 50 mmol of 3-pentenoic acid
- 50 cm³ of acetic acid

- 35 The specific conditions and the results obtained are featured in Table V below:

TABLE V

Ref.	T °C	P _T bar	P(CO) bar	t min.	DC %	Al %	L %	4ML %
11	145	8	5	70	100	34	37	5
12	160	8	4	30	100	49	54	5
13	175	8	3	40	100	62	71	6.5
14	190	9	3	20	97	62	76	9.5
15	210	16	6	120	97	35	59	28

In Example 11, an induction period of the order of 40 min. is observed before absorption.

In Example 12, an induction period of the order of 20 min. is observed before absorption.

Examples 16 to 23:

A sixth series of tests is performed under the conditions of Example 13, by varying the amount of [RhCl(COD)]₂ and/or that of CH₃I charged.

The specific conditions and the results obtained are featured in Table VI below:

(* In Example 18 the amount of water charged is only 10 mmol).

TABLE VI

Ref.	Rh mmol	CH ₃ I mmol	I/Rh	t min.	DC %	Al %	L %	4ML %
16	2.6	4.5	2	40	99	65	78	5.6
17	2.6	2.2	1	60	100	65	77	9.5
1	1.32	4.5	3.5	20	87	46.5	67	7
18*	1.32	4.5	3.5	120	37	48	68	12
13	1.32	2.25	2	40	100	62	71	6.5
19	1.32	1.30	1	180	97	57	73	11.5
20	1.32	0.6	0.5	(24h)	80	32	78	29.5
21	0.65	1.3	2	90	100	55.5	65	8
22	0.33	2.45	7.4	60	99	38	52	17
23	0.33	0.6	2	210	88	43	59	8



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 rhodium-based catalyst
5 and at least one iodinated promoter, at a temperature between 100 and 240°C, under a pressure greater than atmospheric pressure, characterized in that
 - a) the reaction is carried out in a saturated aliphatic or an aromatic carboxylic acid containing a
10 maximum of 20 carbon atoms, and in that
 - b) the partial pressure of carbon monoxide measured at 25°C is less than or equal to 20 bar.
2. Process according to claim 1 characterized in that the carboxylic acid is acetic acid.
- 15 3. Process according to claim 1 or 2 characterized in that the carboxylic acid represents at least 10 % by volume of the liquid reaction mixture.
4. Process according to claim 3 characterized in that the carboxylic acid represents from 30 to 90 %
20 (inclusive) by volume of the liquid reaction mixture.
5. Process according to any one of the preceding claims, characterized in that the concentration of rhodium in the reaction mixture is between 10^{-3} and 10^{-1} mol/l (inclusive).
- 25 6. Process according to any one of the preceding claims, characterized in that the I/Rh molar ratio is greater than or equal to 0.1.
7. Process according to any one of the preceding claims, characterized in that the I/Rh molar ratio is
30 less than or equal to 20.
8. Process according to any one of the preceding claims, characterized in that the water/pentenic acid(s) molar ratio is between 1 and 10 (inclusive).
9. Process according to any one of the preceding
35 claims, characterized in that the reaction temperature is between 160 and 190°C.
10. Process according to any one of the preceding claims characterized in that the partial pressure of carbon monoxide measured at 25°C is less than or equal to

10 bar.

