

The present invention relates to a process for preparing adipic acid by hydrocarboxylation of pentenic acids, that is to say by reaction of water and carbon monoxide with at least one pentenic acid.

5 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,
10 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
15 total pressure of between 24 and 40 atmospheres are regarded as preferable.

The choice of the solvent and the water content of the reaction mixture are critical in the context of the process in question, which constitutes constraints
20 which are difficult to accept on an industrial scale.

American Patent No. 3,579,552 teaches the use of a rhodium-based catalyst and of an iodinated promoter in the hydrocarboxylation reactions of olefins and of some of their derivatives. However, the proportion of linear
25 acid remains insufficient.

American Patent No. 3,579,552 teaches the use of an iridium-based catalyst and of an iodinated promoter in the hydrocarboxylation reactions of olefins and of some of their derivatives. However, the activity of such a
30 system remains insufficient.

In such a context, it would obviously be desirable to be able to have available a catalytic system which simultaneously has an improved activity and an improved selectivity towards adipic acid and which makes
35 it possible to be at least partially freed from the constraints mentioned above.

The subject of the present invention is thus a process for preparing adipic acid by hydrocarboxylation of at least one pentenic acid in the presence of rhodium

or a rhodium compound and an iodinated promoter, characterized in that the reaction is also performed in the presence of at least one cocatalyst chosen from the group consisting of iridium, ruthenium, osmium and their compounds.

Pentenic acid is understood to mean, in the context of the present invention, penten-2-oic acid, penten-3-oic acid or penten-4-oic acid and their 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 suitable, considering its accessibility and the satisfactory results which it gives within the scope of the present process.

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 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 , $\text{RhBr}_3 \cdot 3\text{H}_2\text{O}$,
 RhI_3 , $\text{Rh}(\text{NO}_3)_3$, $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$,
 $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, $\text{Rh}_2(\text{CO})_4\text{Br}_2$, $\text{Rh}_2(\text{CO})_4\text{I}_2$,
 $\text{Rh}(\text{CO})\text{Cl}[\text{P}(\text{C}_6\text{H}_5)_3]_2$,
 $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{I}$,
 $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Br}$,
 $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Rh}(\text{CO})_2(\text{acac})$,
 $\text{Rh}(\text{Cod})(\text{acac})_2$, $\text{Rh}(\text{acac})_3$,
 $\text{Rh}_2(\text{Cod})_2\text{Cl}_2$, $\text{Rh}_2(\text{CO}_2\text{CH}_3)_4$,
 $\text{HRh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$,
(Cod = 1,5-cyclooctadiene, acac = acetyl-acetate).

More particularly suitable for use in the present process are:

$\text{Rh}_2(\text{Cod})_2\text{Cl}_2$,

$\text{Rh}_2(\text{CO})_4\text{Cl}_2$,
 RhI_3 , $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Rh}(\text{acac})_3$,
 $\text{Rh}(\text{Cod})(\text{acac})_2$, $\text{Rh}_2(\text{CO}_2\text{CH}_3)_4$, $\text{Rh}_4(\text{CO})_{12}$,
and $\text{Rh}_6(\text{CO})_{16}$.

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

 In general, a quantity, expressed in mole of metallic rhodium per litre of reaction mixture, of between 10^{-3} and 10^{-1} leads to satisfactory results. Lower
10 quantities can be used; however, the reaction velocity is observed to be low. Higher quantities have disadvantages only at an economic level.

 Preferably, the rhodium concentration is between $5 \cdot 10^{-3}$ and 10^{-2} (inclusive) mol/l.

15 Iodinated promoter is understood to mean, within the scope of the present process, HI and the 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.

20 It will be noticed that compounds such as RhI_3 can be both a useful source of rhodium and constitute all or part of the iodinated promoter.

 The quantity of iodinated promoter to be used is in general such that the I/Rh mole ratio is greater than
25 or equal to 0.1. It is not desirable for this ratio to exceed 20. Preferably, the I/Rh mole 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
30 general, the quantity of water to be used is such that the water/pentenic acid(s) mole ratio is between 1 and 10 (inclusive).

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

 The process according to the present invention also requires the presence of at least one cocatalyst chosen from the group consisting of iridium, ruthenium, osmium and their compounds.

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

- metallic Ir, IrO_2 , Ir_2O_3 ,
- 5 - IrCl_3 , $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$,
- IrBr_3 , $\text{IrBr}_3 \cdot 3\text{H}_2\text{O}$,
- IrI_3 ,
- $\text{Ir}_2(\text{CO})_4\text{Cl}_2$, $\text{Ir}_2(\text{CO})_4\text{I}_2$,
- $\text{Ir}_2(\text{CO})_8$, $\text{Ir}_4(\text{CO})_{12}$,
- 10 - $\text{Ir}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{I}$,
- $\text{Ir}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}$,
- $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{I}$,
- $\text{HIr}[\text{P}(\text{C}_6\text{H}_5)_3]_3(\text{CO})$,
- $\text{Ir}(\text{acac})(\text{CO})_2$,
- 15 - $[\text{IrCl}(\text{Cod})_2]$,
- (cod = 1,5-cyclooctadiene, acac = acetyl-acetate).

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

- metallic Ru, RuO_2 , RuO_4 ,
- RuCl_3 , $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, RuBr_3 , RuI_3 , $\text{Ru}(\text{OAc})_3$, RuCl_4 ,
- $\text{Ru}(\text{CO})_5$, $\text{Ru}(\text{CO})_{12}$, $[\text{Ru}(\text{CO})_3\text{Br}_2]_2$, $\text{Ru}(\text{CO})_4\text{I}_2$,
- $\text{Ru}(\text{acac})_3$, $\text{RuCl}(\eta\text{-C}_3\text{H}_5)$.

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

- metallic Os, OsO , Os_2O_3 , OsO_2 , OsOF_4 ,
- OsCl_3 , OsBr_3 , $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$,
- 30 OsCl_4 ,
- $\text{Os}_3(\text{CO})_{12}$.

Among the iridium sources, the following are more particularly suitable for use in the present process:

- IrCl_3 , $\text{IrCl}(\text{Cod})_2$, $\text{Ir}_4(\text{CO})_{12}$.

Among the ruthenium sources, the following are more particularly suitable for use in the present process:

- $\text{RuO}_2 \cdot \text{H}_2\text{O}$,
- $\text{RuCl}_3 \cdot \text{H}_2\text{O}$, $\text{RuCl}_2(\text{Cod})$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$.

Among the osmium sources, the following are more particularly suitable for use in the present process:

OsCl_3 , $\text{Os}_3(\text{CO})_{12}$.

The cocatalyst is advantageously chosen from
5 iridium and its compounds.

The mole ratio of the cocatalyst expressed as metal M relative to the rhodium can vary within wide limits, for example between 0.05 and 50 inclusive.

The M/Rh ratio is preferably between 0.1 and 5
10 inclusive.

The process according to the present invention is advantageously carried out in the liquid phase. Of course, the reaction mixture can contain a solvent or a diluent. As examples of solvents or diluents capable of
15 being used in the context of the present process, there may be mentioned: aromatic or saturated aliphatic carboxylic acids containing a maximum of 20 carbon atoms and chlorinated or nonchlorinated aromatic or saturated aliphatic hydrocarbons, which are liquid under the
20 reaction conditions.

According to an advantageous variant of the present process, recourse is made to a saturated C_1 - C_6 aliphatic carboxylic acid and preferably to acetic acid.

According to another advantageous variant of the
25 present process, recourse is made to a chlorinated saturated aliphatic hydrocarbon and preferably to methylene chloride.

The quantity of solvent or diluent, when such a solvent or diluent is present in the reaction mixture,
30 can reach 99 % by volume of the said mixture. For good implementation of the invention, this quantity will be greater than or equal to 10 %, and preferably between 30 and 90 %, by volume (inclusive).

The reaction temperature is generally between 100
35 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. The total pressure can vary

within wide limits, for example between 2 and 150 bar. In general, good results are observed for pressures between 5 and 50 bar.

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

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 extraction and/or
10 crystallization.

The examples below illustrate the present invention.

EXAMPLES

EXAMPLE 1:

15 0.1 mmol of rhodium, in the form of $[\text{RhCl}(\text{Cod})]_2$, 0.1 mmol of iridium, in the form of IrCl_3 , 20 mmol of penten-3-oic acid, 35 mmol of water, 0.57 mmol of HI, in the form of a 57 % by weight aqueous solution, and 10 ml of acetic acid are introduced successively into a glass
20 flask.

The flask is then placed in a stainless steel (Hastelloy B2) autoclave, with a capacity of 125 cm³, which has been purged beforehand with argon.

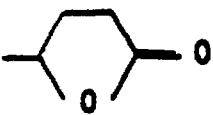
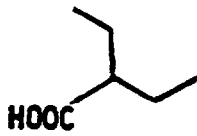
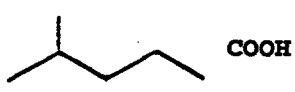
The autoclave is hermetically closed, placed in
25 an oven with agitation and connected to a supply of pressurized gas.

2 bar of CO are admitted while cold into the autoclave and the mixture is brought to 175°C over 25 minutes. The pressure in the autoclave is then 4 bar.
30 The latter is adjusted to 10 bar.

After reacting for 30 minutes at the reaction temperature, CO absorption has ceased; the autoclave is then cooled and degassed.

The reaction mass is analysed by gas phase
35 chromatography and by high performance liquid chromatography.

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

valeric acid	(Pa)	:		< 1 %
penten-2-oic acid	(P2)	:		= 6 %
4-methylbutyrolactone	(M4L)	:		= 18 %
ethylsuccinic acid	(A3)	:		= 5.7 %
5 methylglutaric acid	(A2)	:		= 14.7 %
adipic acid	(A1)	:		= 48 %

The degree of linearity (L) is 76 %.

The degree of conversion of penten-3-oic acid (DC) is 100 %.

10 EXAMPLES 2 and 3 : Control Tests (a) and (b):

A first series of tests is carried out in the autoclave and according to the procedure each described for Example 1, only the nature of the cocatalyst being modified.

15 The specific conditions and the results obtained are collated in Table I below:

TABLE I

Ref.	Cocatalyst	DC (%)	Yd (%)		L (%)
			M4L	A1	
1	IrCl ₃	100	18	48	76
2	RuCl ₃	97	40	38	65
3	OsCl ₃	95	38	32	64
a	-	100	42	26	55
b(*)	IrCl ₃	83	86	1.2	ε

(*) test carried out in the absence of rhodium;
reaction time 120 min.

EXAMPLES 4 to 8:

5 A second series of tests is carried out, in the
autoclave and according to the procedure each described in
Example 1, on a charge containing, on each occasion, various
ruthenium compounds as cocatalyst whose nature appears in
Table II below. Moreover, the results mentioned in this
table are obtained under the same conditions and t
10 represents the reaction time thereof.

TABLE II

Ref.	Cocatalyst	t (min)	DC (%)	Yd (%)		L (%)
				M4L	A1	
4	RuCl ₃ ·H ₂ O	60	89	23	45	66
5	RuCl ₂ (Cod)	300	93	29	44	70
6	Ru ₃ (CO) ₁₂	90	70	24	47	70
7	Ru(acac) ₃	60	67	25	42	66
8	RuO ₂ ·H ₂ O	90	81	21	44	62

EXAMPLE 9:

20 A test is carried out, in the autoclave and
according to the procedure each described for Example 1, on
a charge containing 0.1 mmol of rhodium, in the form of
RhI₃, 0.1 mmol of iridium, in the form of IrCl₃, 20 mmol of
penten-3-oic acid, 35 mmol of water and 10 mmol of acetic
acid.

25 After reacting for 35 minutes at 175°C under 10 bar
of total pressure, the results obtained are as follows:

DC(%) = 100
A1(%) = 64
M4L(%) = 14
30 L(%) = 86

EXAMPLES 10 to 17:

A third series of tests is carried out on a charge

identical to that used in Example 9, the reaction temperature (T) and/or the total pressure (P) at the reaction temperature being modified. The specific conditions and the results obtained are collated in Table III below:

5

TABLE III

Ref.	T (°C)	P (bar)	t (min)	DC (%)	Yd (%)		L (%)
					M4L	A1	
10	175	5	45	100	10	67	82
11	"	8	35	100	9	67	81
9	"	10	35	100	14	64	86
12	"	25	30	100	10	63	76
13	"	47	30	99	10	66	80
14	"	100	60	83	10	53	65
15	190	15	30	100	10	65	78
16	160	10	65	99	9	65	79
17	140	10	105	59	6	48	58

EXAMPLE 18:

Example 9 above is reproduced, IrCl₃ being replaced by the same quantity of [IrCl(Cod)]₂.

All conditions, moreover, being the same, substantially the same results are obtained.

EXAMPLE 19:

Example 9 above is reproduced, IrCl₃ being replaced by the same quantity of Ir₄(CO)₁₂.

All conditions, moreover, being the same, substantially the same results are obtained.

EXAMPLE 20:

Example 9 above is reproduced, RhI₃ being replaced by an equivalent quantity of [RhCl(Cod)]₂, and 0.3 mmol of HI being added to the charge.

All conditions, moreover, being the same,

substantially the same results are obtained.

EXAMPLES 21 to 26; Control Test c:

5 A fourth series of tests is carried out on a charge analogous to that used in Example 9, apart from the fact that the quantity of IrCl_3 and/or the nature of the pentenic acid charged differs. The specific conditions and the results obtained at 175°C under a total pressure of 10 bar are collated in Table IV below:

TABLE IV

10	Ref.	Ir/Rh	Pentenic acid	t (min)	DC (%)	Yd (%)		L (%)
						M4L	A1	
	21	0.5	penten-3-oic	90	100	17	58	76
	22	1	"	60	100	12	62	83
	23	2	"	50	100	17	54.5	85
	24	5	"	50	100	39	28	90
15	25	1	penten-4-oic	30	100	10	69	81
	26	1	penten-2-oic	75	92	12.5	50	82
	c	0	penten-2-oic	120	8	11	23	45

EXAMPLES 27 to 29:

20 A fifth series of tests is carried out on a charge analogous to that of Example 9, the concentration of water in the reaction mixture being varied while keeping the total volume (water + acetic acid) constant and equal to 12.5 ml.

The specific conditions and the results obtained are collated in Table V below:

TABLE V

Ref.	H ₂ O (g/l)	t (min)	DC (%)	Yd (%)		L (%)
				M4L	A1	
27	29	40	100	12	67	81
9	47	35	100	14	64	86
28	147	50	90	19	48	65
29	290	70	61	19	27	46

EXAMPLES 30 to 32:

A sixth series of tests is carried out, in the autoclave and according to the procedure each described for Example 1, on a charge containing 0.1 mmol of iridium, in the form of IrCl₃, 20 mmol of penten-3-oic acid, 39 mmol of water, 10 ml of solvent, the exact nature of which appears in Table VI below, and 0.1 mmol of rhodium, in the form of [RhCl(Cod)]₃ (Examples 30 and 31) or in the form of RhI₃ (Example 32). In Examples 30 and 31, the charge additionally contains 0.3 mmol of HI. The results obtained at 175°C and the specific conditions are collated in Table VI below:

TABLE VI

Ref.	Nature of the solvent	P (bar)	t (min)	DC (%)	Yd (%)		L (%)
					M4L	A1	
30	Toluene	10	60	70	6	21	75
31	Methylene chloride	30	60	81	6	50	75
32	Valeric acid	28	100	95	7	56	70



CLAIMS

1. Process for preparing adipic acid by hydro-carboxylation of at least one pentenic acid in the presence of rhodium or a rhodium compound and an iodinated promoter,
5 characterized in that the reaction is also performed in the presence of at least one cocatalyst chosen from the group consisting of iridium, ruthenium, osmium and their compounds.
2. Process according to claim 1, characterized in that
10 the mole ratio of the cocatalyst expressed as metal M relative to the rhodium is between 0.05 and 50 inclusive.
3. Process according to claim 1 or 2, characterized in that the cocatalyst is chosen from iridium and its compounds.
- 15 4. Process according to any one of the preceding claims, characterized in that the rhodium concentration is between 10^{-3} and 10^{-1} mol/l.
5. Process according to any one of the preceding claims, characterized in that the I/Rh mole ratio is greater
20 than or equal to 0.1, and preferably less than or equal to 20.
6. Process according to any one of the preceding claims, characterized in that the water/pentenic acid(s) mole ratio is between 1 and 10.
- 25 7. Process according to any one of the preceding claims, characterized in that the reaction is performed in the presence of a saturated C_1-C_6 carboxylic acid.
8. Process according to claim 7, characterized in that the saturated carboxylic acid is acetic acid.
- 30 9. Process according to any one of claims 1 to 6, characterized in that the reaction is performed in the presence of methylene chloride.
10. Process according to any one of the preceding claims, characterized in that the M/Rh ratio is between 0.1
35 and 5 inclusive.
11. Process according to any one of the preceding claims, characterized in that the I/Rh ratio is between 1 and 4 inclusive.
12. Process according to any one of the preceding



claims, characterized in that the reaction temperature is between 100 and 240°C, and preferably between 160 and 190°C, inclusive.

13. Process according to any one of the preceding
5 claims, characterized in that the pressure is between 2 and 150 bar, and preferably between 5 and 50 bar, inclusive.