

PROCESS FOR THE HYDROLYSIS OF AN ALKYL DICARBOXYLATE

The present invention relates to the hydrolysis of a lower alkyl dicarboxylate, that is to say with alkyl having 1 to 4 carbon atoms, to a
5 dicarboxylic acid.

Very generally, the hydrolysis of esters is carried out in homogeneous medium either using an acid or using a base.

The use of a base leads to the formation of
10 metal salts with the obvious disadvantages that that implies.

The acidic hydrolysis of adipates presents the problem of the two-phase nature of the medium, due to the very low miscibility of water and the adipate.
15 This is why it has been recommended to use mixtures of solvents (see, for example, Journal of Indian Chemical Society, 48(9), pages 811-12), which markedly complicates the subsequent separation and purification of the adipic acid obtained. Additionally, the use of a
20 liquid acid leads to significant problems of corrosion of the equipment.

It has also been recommended to carry out the hydrolysis of adipates in heterogeneous medium on acidic resins.

25 Thus, an article published in Synthetic Communications, 19, pages 627-631 (1989) describes the hydrolysis of dimethyl adipate in an aqueous suspension

of Dowex-50 resin at reflux. This type of suspension reaction does not solve the problem of displacement of the equilibrium of the reaction by removal of the methanol formed.

5 Patent EP-A-0,056,489 proposes a solution to this problem, consisting of a continuous process of hydrolysis by water of alkyl adipates containing 1 to 4 carbon atoms, at high temperature and in the presence of strongly acidic ion-exchange resins; the main
10 characteristic of this process consists in withdrawing part of the water/adipate reaction mixture on several plates of the column, below the region of delivery of this mixture into the column, the part thus removed is then passed onto a strongly acidic ion exchanger and is
15 then recycled. Adipic acid is thus obtained at the bottom of the column whereas alcohol/water mixtures are removed at the column head.

 This process requires the addition of a number of circuits appended to the column in order for
20 the hydrolysis reaction proper to be carried out and its implementation is thus complex.

 The present invention proposes to solve the problem of the production of dicarboxylic acid by hydrolysis of alkyl dicarboxylates in which the alkyls
25 contain 1 to 4 carbon atoms by the use of a simplified, but very efficient, process in which the acidic resin used corresponds to a series of carefully selected characteristics.

This process makes it possible to carry out both the hydrolysis of the dicarboxylate and the separation of the alcohol formed.

More specifically, the invention consists of a process for the preparation of a carboxylic acid by hydrolysis in the liquid phase of a C₁-C₄ alkyl aliphatic dicarboxylate, characterised in that a mixture of the said alkyl dicarboxylate and water is subjected to a reactive distillation by introduction of the said mixture into the middle part of a column containing a gel-type resin containing sulphonic acid groups, maintained in place using a support and having the following characteristics:

- a skeleton based on styrene and divinylnbenzene, the level of divinylnbenzene by weight with respect to the total weight of the said skeleton being between 1 % and 12 % and preferably between 2 % and 5 %, - an exchange capacity of 3 to 6.5 milliequivalents H⁺/gram of dry resin, and by continuous distillation of the alcohol formed by the hydrolysis reaction.

In the context of the present process, a gel-type resin containing sulphonic acid groups and having the following characteristics will preferably be used:

- a skeleton based on styrene and divinylnbenzene, the level of divinylnbenzene

by weight with respect to the total weight of the said skeleton being between 1 % and 12 % and preferably between 2 % and 5 %,

- an exchange capacity of 5 to

5 6.5 milliequivalents H^+ /gram of dry resin,

- a mean particle size of between 100 and

2000 micrometres and preferably between 200 and 1200 micrometres.

Generally, the column which can be used
10 comprises a lower section in which the resin is arranged and where hydrolysis is carried out and an upper section, optionally containing a conventional packing, in which purification of the methanol is carried out.

15 The gel-type resins containing sulphonic acid groups are resins known in themselves.

There will be chosen from the commercial resins/gels those which correspond to the characteristics shown above.

20 The resin/gel can be used in the column according to varying techniques. It can be maintained in a metal, textile, ceramic or plastic structure ensuring an efficient liquid/solid and liquid/vapour exchange, the structure containing the resin being
25 arranged in the column.

It can also be deposited or coated on such a structure.

The resin/gel can also be placed on

capacitive plates.

These uses are not limiting.

The C_1 to C_4 alkyl aliphatic dicarboxylates which can be hydrolysed in the process of the invention are essentially the C_1 to C_4 alkyl esters of aliphatic dicarboxylic acids having 3 to 6 carbon atoms, such as, for example, the methyl, ethyl or n-propyl esters of succinic, ethylsuccinic, glutaric, methylglutaric, adipic, 2-hexenedioic or 3-hexenedioic acid.

Among these esters, dimethyl adipate, dimethyl methylglutarate, dimethyl ethylsuccinate and the dimethyl hexenedioates are the most important and dimethyl adipate is the compound whose hydrolysis is even more particularly important.

These esters and more specifically dimethyl adipate can be used in isolation or in a mixture of a number of them.

In that which follows, it will be a matter, for convenience, of the hydrolysis of dimethyl adipate but this will be transposable to another alkyl dicarboxylate as defined above.

Dimethyl adipate and water are introduced into the column in the middle part of the latter, above the section where the resin/gel is situated.

The amount of water is such that the water/dimethyl adipate molar ratio is at least equal to 2.

Preferably, the amount of water will be in

excess with respect to the stoichiometric amount, that is to say that the water/dimethyl adipate molar ratio will be greater than 2, generally of between 5 and 60.

The dimethyl adipate and water can be
5 introduced separately or as a mixture.

Hydrolysis of dimethyl adipate is carried out on the resin/gel and there is recovered, on the one hand, at the upper end of the column, the methanol formed and, on the other hand, at the lower end of the
10 column, the adipic acid, the excess water, the possible nonhydrolysed monomethyl adipate and the possible amount of nonhydrolysed dimethyl adipate.

The temperature in the column is generally between 80°C and 150°C in the part where the hydrolysis
15 reaction is carried out and preferentially between 90°C and 130°C.

The adipic acid prepared by the process according to the invention is separated from the water and other minor compounds which it may contain by the
20 usual separation methods used in chemistry, for example by crystallisation, especially by crystallisation under vacuum.

The mother liquors generally contain between 2 % and 10 % of adipic acid and the various impurities
25 or by-products of the reaction can advantageously be recycled to the hydrolysis column.

In the illustrative examples of the invention which follow, the productivity of the hydrolysis will

be expressed in kg of adipic acid per kg of dry resin/gel per hour.

EXAMPLES

5 The equipment used for the various examples and comparative tests consists of a column with an internal diameter of 4 cm, composed of two sections:

- a lower section with a length of 45 cm in which the resin is arranged, hereafter called the reactive section,
- 10 - an upper section with a length of 150 cm, containing a standard packing making the water/methanol separation possible.

This column is equipped with a distillation flask at its base, with a condenser at the head and
15 with a reflux device; feeding is carried out at the top of the reactive section by virtue of two pumps: one for water, the other for dimethyl adipate.

The methanol formed is obtained at the column head whereas the water/adipic acid mixture is drawn off
20 at the foot.

The resin is arranged in the reactive section of the column according to two types of packaging.

1) Packaging a)

The resin is placed inside four pods whose
25 walls consist of a metal gauze having a mesh of approximately 500 μm , less than the diameter of the beads of the resin.

These pods, 45 cm long, are closed at their

ends. They are maintained side by side by a metal fabric, in order to ensure the cohesion of the assembly and to promote liquid/vapour exchanges, as well as the redistribution of the liquid towards the pods containing the resin.

The amount of resin thus represents 26 % of the volume of the reactive section of the column. The number of theoretical stages of this section is 4. Each theoretical stage contains 36.25 g of wet resin (containing 65 or 50 % water according to the resin used).

2) Packaging b)

The resin is arranged inside a sandwich consisting of two layers of metal gauze having a mesh of approximately 500 μm . This sandwich, containing a thin resin layer, was folded "accordion-style" with an amplitude of the folds such that it can pack the whole of the cross-section of the column section.

Each sandwich thus folded has a height of 15 cm. Three are therefore necessary to pack the 45 cm of the reactive section of the column. Each sandwich, inside the column, is directed perpendicularly with respect to the preceding one, in order to avoid preferentially passing through outside the regions laden with resin.

The amount of resin thus represents 32 % of the volume of the reactive section of the column. The number of theoretical stages of this section is 4. Each

theoretical stage contains 45 g of wet resin
(containing 65 % or 50 % water according to the resin
used).

These two types of packaging of the resin
5 constitute a reactive packing making it possible to
catalyse a reaction and to promote liquid/vapour
exchanges in order to carry out a separation by
distillation.

EXAMPLES 1 AND 2

10 These two examples are carried out with a
resin/gel A containing sulphonic acid groups, which is
provided in the form of beads with a diameter of
1000 μm and which has a level of divinylbenzene by
weight with respect to the total weight of the skeleton
15 based on styrene and divinylbenzene (or degree of
crosslinking) of 4 %, an exchange capacity of
5.4 milliequivalents (meq) H^+/g and a moisture content
of approximately 65 %.

These 2 examples are carried out with the
20 type a) resin packaging described above:

The feed flow rates are the following:

- dimethyl adipate (DMA) : 188 g/h

(Example 1)

100 g/h

(Example 2)

25 - water

295 g/h

(Example 1)

155 g/h

(Example 2)

The working pressure is equal to atmospheric pressure.

5 In continuous operation, the temperature at the column head is 65°C (that is to say, the boiling temperature of pure methanol at atmospheric pressure). The temperature at the foot is 101°C.

Analyses by HPLC (high performance liquid chromatography) make it possible to calculate the degree of conversion (DC) of the DMA, the yield (RY) of adipic acid (AA) expressed in mol % with respect to the DMA charged and the productivity of the reaction expressed in kg of AA per kg of dry resin per hour.

15 These results, as well as various pieces of information, are collated in the table below.

EXAMPLE 3 AND COMPARATIVE TEST 1

These two tests are carried out:

- one (Example 3) with the resin/gel described for Examples 1 and 2 (resin A)
- the other (Comparative Test 1) with a macroporous resin B having a polystyrene/divinylbenzene skeleton and containing sulphonic acid groups which does not correspond to all the claimed characteristics: degree of crosslinking of 16 %, exchange capacity of 5.4 meq H⁺/g of dry resin, beads with a diameter of 1000 μm

and a moisture content of approximately 50 %, these two resins being used with the type b) packaging described above.

The conditions of use of these tests are the same as for Examples 1 and 2, with the exception of the feed flow rates which are the following:

- DMA: 152 g/h
- water: 295 g/h

The results obtained, as well as various pieces of information, are collated in the table below:

COMPARATIVE TEST 2

This test was carried out with resin A, in an amount equal to that used in Example 3, but by arranging it in the distillation flask and not in the column. There is thus no reactive distillation as in the process of the invention, but the use of a continuous stirred reactor, surmounted by a column for removing the methanol formed.

The feed flow rates and the operating conditions are those of Example 3.

The results obtained, as well as various pieces of information, are collated in the table below.

EXAMPLE 4

This example was carried out with resin A, arranged according to the type b) packaging described above.

In order to obtain a higher AA yield than in the above examples, the column used contains a 99 cm

reactive section with, in practice, 9 theoretical stages.

The feed flow rates and the operating conditions are those of Example 3.

5 The results obtained, as well as various pieces of information, are collated in the table below.

COMPARATIVE TEST 3

10 This test was carried out with resin B, arranged according to the type b) packaging described above.

In order to obtain a higher AA yield than in the above examples, the column used contains a 340 cm reactive section with 30 theoretical stages.

15 The feed flow rates and the operating conditions are those of Example 3.

The results obtained, as well as various pieces of information, are collated in the table below.

Tests	Resin	Flow rate in g/h	% by volume/volume of resin in the reaction section	DC (DMA)	RY (AA)	Productivity kg AA/kg dry resin/h
Example 1	A	H ₂ O : 295 DMA : 188	26	99.0 %	80.4 %	2.486
Example 2	A	H ₂ O : 155 DMA : 100	26	99.97 %	93 %	1.543
Example 3	A	H ₂ O : 295 DMA : 152	32	99.95 %	92.7 %	1.886
Example 4	A	H ₂ O : 295 DMA : 152	32	99.95 %	97 %	0.877
Comparative Test 1	B	H ₂ O : 295 DMA : 152	32	96.5 %	61 %	1.249
Comparative Test 2	A	H ₂ O : 295 DMA : 152	-	97.1 %	82.6 %	1.677
Comparative Test 3	B	H ₂ O : 295 DMA : 152	32	99.95 %	97 %	0.179

CLAIMS

1. Process for the preparation of a carboxylic acid by hydrolysis in the liquid phase of a C₁-C₄ alkyl aliphatic dicarboxylate, characterised in that a mixture of the said alkyl dicarboxylate and water is subjected to a reactive distillation by introduction of the said mixture into the middle part of a column containing a gel-type resin containing sulphonic acid groups, maintained in place using a support and having the following characteristics:
- a skeleton based on styrene and divinylbenzene, the level of divinylbenzene by weight with respect to the total weight of the said skeleton being between 1 % and 12 % and preferably between 2 % and 5 %,
 - an exchange capacity of 3 to 6.5 milliequivalents H⁺/gram of dry resin, and by continuous distillation of the alcohol formed by the hydrolysis reaction.
2. Process according to claim 1, characterised in that a gel-type resin containing sulphonic acid groups and having the following characteristics is used:
- a skeleton based on styrene and divinylbenzene, the level of divinylbenzene by weight with respect to the total weight of the said skeleton being between 1 % and 12 % and preferably between 2 % and 5 %,



- an exchange capacity of 5 to 6.5 milliequivalents H^+ /gram of dry resin,
- a mean particle size of between 100 and 2000 micrometres and preferably between 200 and 1200 micrometres.

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3. Process according to either of claims 1 and 2, characterised in that the C_1 to C_4 alkyl aliphatic dicarboxylates are C_1 to C_4 alkyl esters of aliphatic dicarboxylic acids having 3 to 6 carbon atoms such as the methyl, ethyl or n-propyl esters of succinic, ethylsuccinic, glutaric, methylglutaric, adipic, 2-hexenedioic or 3-hexenedioic acid and their mixtures:

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4. Process according to either of claims 1 and 2, characterised in that the C_1 to C_4 alkyl aliphatic dicarboxylate is chosen from dimethyl adipate, dimethyl methylglutarate, dimethyl ethylsuccinate, the dimethyl hexenedioates and their mixtures and is preferably dimethyl adipate.

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5. Process according to one of claims 1 to 4, characterised in that dimethyl adipate and water are introduced into the column in the middle part of the latter, above the section where the resin/gel is situated, the amount of water being such that the water/dimethyl adipate molar ratio is at least equal to 2, preferably greater than 2 and generally between 5 and 60.

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6. Process according to one of claims 1 to



5, characterised in that hydrolysis of dimethyl adipate is carried out on the resin/gel and in that there is recovered, on the one hand, at the upper end of the column, the methanol formed and, on the other hand, at the lower end of the column, the adipic acid, the excess water, the possible nonhydrolysed monomethyl adipate and the possible amount of nonhydrolysed dimethyl adipate.

7. Process according to one of claims 1 to 6, characterised in that the temperature in the column is between 80°C and 150°C in the part where the hydrolysis reaction is carried out and more preferentially between 90°C and 130°C.