

- 1 -

PROCESS FOR THE SEPARATION OF A KETOXIME
OR ALDOXIME FROM AN AMIDE

5

This invention relates to a process for the separation of a ketoxime or aldoxime from a ketoxime- or aldoxime-containing amide mixture, for instance such a mixture obtained from a Beckman rearrangement
10 reaction.

BACKGROUND OF THE INVENTION

Such a process has been disclosed in GB-A-1286427, which describes a process in which an oxime-
15 containing lactam mixture is treated with sulphur dioxide. For this process, at least 1 mol of sulphur dioxide is added per mol of oxime. The excess sulphur dioxide is subsequently removed and, through distillation, of caprolactam the latter is obtained in
20 pure form.

The disadvantage of such a process lies in the introduction of a foreign substance into the process, which must ultimately be removed from the process at a later stage.

25 Moreover, oximes, such as ketoxime or aldoxime, function as chain terminators in the polymerization of amides, for instance in the polymerization of caprolactam to nylon-6, which is disadvantageous. It is therefore important to seek to
30 obtain the desired amide product in the purest form possible.

GENERAL DESCRIPTION OF THE INVENTION

The object of this invention is to separate
35 the ketoxime or aldoxime from the amide in a simple and direct process technique.

This object is accomplished by this invention by separation of the ketoxime or aldoxime by means of distillation.

- 2 -

This is an extremely surprising result, since GB-A-1286427 states that separation of an oxime from a lactam is either impossible or much too expensive to be realized by means of simple, straightforward physical separation techniques. It is also surprising since the ketoxime or aldoxime is not stable thermally. Undesired by products are expected to be formed upon distillation, for example octahydrophenaxine (OHP). OHP is disadvantageous to the ultimate quality of the caprolactam.

It is generally known that amides, in particular lactams (for instance, ϵ -caprolactam), may be produced by means of a Beckmann rearrangement of ketoximes or aldoximes, for instance cyclohexanone oxime. This rearrangement takes place with the aid of a solid acid or neutral catalyst. Such a rearrangement may be conducted in either the gas phase or in the liquid phase.

As examples of a solid acid or neutral catalyst, use may be made of boric acid on a support, such as for instance silica or alumina and crystalline silicas, for instance silicalite I (a silicon-rich MFI) and silicalite II (a silicon-rich MEL); alternatively, an acid ion exchanger or (mixed) metal oxides can be used.

An advantage of this catalysis approach to the process is that no ammonium sulphate is formed as byproduct, as is the typical case in a Beckmann rearrangement through treatment of the ketoxime or aldoxime with the aid of strong acids such as sulfuric acid. The desired amide must then be recovered via neutralization of the reaction mixture, usually by use of ammonia water. However, this gives rise to the formation of a large amount of ammonium sulphate as byproduct.

However, in Beckmann rearrangements conducted in either the liquid phase or in the gas phase, only

- 3 -

incomplete conversion of the ketoxime or aldoxime may take place, so that along with the desired amide, a certain amount of unreacted ketoxime or aldoxime leaves the reactor. On the other hand, it is most desirable
5 that the ketoxime or aldoxime be fully removed from the oxime-containing mixture in view of disruptions in the further downstream processing of the amide. Therefore, it is of importance to obtain a high purity of the desired amide.

10 Examples of ketoximes or aldoximes in ketoxime- or aldoxime-containing amide mixtures that can be obtained from a Beckmann rearrangement include unsaturated and saturated, substituted or unsubstituted aliphatic ketoximes or aldoximes or cyclic ketoximes
15 with 2-12 carbon atoms, for instance acetone oxime, acetaldoxime, benzaldoxime, propanaldoxime, butanaldoxime, butanone oxime, 1-butene oxime, cyclopropanone oxime, cyclohexanone oxime, cyclooctanone oxime, cyclododecanone oxime,
20 cyclopentenone oxime, cyclododecenone oxime, 2-phenyl cyclohexanone oxime, cyclohexenone oxime.

The distillation techniques employed in the practice of this invention include both steam distillation and distillation under reduced pressure.
25 The temperature at which the distillation can be effected is between 80°C and 180°C. Preferably, the temperature is between 100°C and 160°C.

The distillate containing the ketoxime or aldoxime can then be returned to the reactor for
30 another or continuing rearrangement operation.

The distillation can be carried out in two stages, which stages may in turn be subdivided into theoretical trays, the pressure drop being less than 200 Pa per theoretical tray. Said pressure drop of less
35 than 200 Pa relates to a measurement under standard conditions, namely the reaction of a cis-trans decalin mixture (50% cis and 50% trans) under total reflux at a

pressure of 50 mbar and a vapour rate of 5.2 m/s.

In the distillation according to the invention various evaporators can be used, for instance a falling-film evaporator. As packing material for the distillation column any packing is suitable which gives a pressure drop of less than 200 Pa per theoretical tray. Such a packing materials are generally commercially available, for instance Intalox^R metal packing (described in Chemical Engineering Progress, March 1979, pp. 86-91), Sulzer BX^R (see Chemie Ingenieur Technik, volume 37, page 322, 1965) and Sulzer Mellapak^R (see Chemical Engineering Progress, November 1977, pp. 71-77). Preferably, a packing material is used with which the said pressure drop is less than 100 Pa per theoretical tray, for instance the above-mentioned Mellapak^R of Sulzer. The required number of theoretical trays in the rectification column is usually from 1-15, preferably between 5-12, and more preferably between 8-12. The caprolactam-oxime mixture to be purified can be fed to the top of the column or to the column itself. As a rule, a reflux ratio between 3 and 8 is used. The purity of the bottom product obtained according to the invention is usually > 99%.

The rectification column is preferably operated at a bottom pressure of 500-3000 Pa and preferably at a bottom temperature of between 120 and 160°C.

EXAMPLES OF THE INVENTION

The invention will now be elucidated with reference to certain exemplary embodiments, without however being limited thereto.

Example I

A mixture consisting of 700 g of water, 4.57 g of cyclohexanone oxime and 16 g of caprolactam was supplied to a 1-liter vessel. The vessel temperature

- 5 -

was raised to 100°C, after which steam was passed through the mixture. Gaseous stream was cooled and in total, six distillate fractions were collected. In each fraction and in each sample of the residue, taken at the same points of time, the cyclohexanone oxime content and the caprolactam content were determined by means of gas chromatography in an HP gas chromatograph with a CP wax 52 CB column. Detection took place with the aid of an FID detector. The results are presented in Table I.

Table I

	fraction + cumulative weight	oxime in distillate, cumulative in g	oxime in residue, in g	lactam in distillate, cumulative in g	lactam in residue, in g
15	fraction 1 28.7 g	0.53	4.04	0.0035	16.10
	fraction 2 175 g	1.95	2.62	0.029	15.93
20	fraction 3 265 g	3.03	1.53	0.08	15.86
	fraction 4 420 g	3.90	0.66	0.15	15.82
25	fraction 5 950 g	4.52	0.05	1.54	14.31
	fraction 6 1000 g	4.57	0.003	3.3	12.67

From this table it can be seen that there are minimum losses of lactam in the overhead distillate and substantial recovery of nearly pure lactam in the distillate bottoms, coupled with substantial removal of the undesired oximes.

Example II

- A vacuum distillation set-up consisted of a 30 cm column (Widmer[®]) with 10-15 theoretical trays.
- 5 The reflux ratio was 5. The reflux ratio is defined as reflux flow relative to product flow. At the top of the column the pressure was 5 mm Hg, at a temperature of 130°C. At the bottom of the column the temperature was 151°C. The composition of the starting material
- 10 obtained upon the Beckmann rearrangement was as follows:
- 40 g of caprolactam flakes and 10 g of cyclohexanone oxime, twice recrystallized from toluene, so that >99% pure cyclohexanone oxime was obtained.
- 15 This starting material was transferred one time only to the bottom of the column. The distilled fractions obtained as overhead product of the column were gas chromatographically analyzed as described in example I. Upon completion of the distillation the
- 20 residue obtained from the bottom of the column was also analyzed. The results are presented in Table II. The distilled fractions were returned to the vessel in which the Beckmann rearrangement took place. A large portion of the oxime was found in the piping due to
- 25 condensation and solidification and as such was not included in the various distillate fractions.

- 7 -

Table II

		% oxime	g of oxime	g of lactam
5	distillate fraction I 4.01 g	30.4	1.22	2.79
	distillate fraction 2 2.10 g	58	1.22	0.88
10	distillate fraction 3 3.26 g	11.6	0.38	2.88
	residue 32 g	-	<100 ppm	32
15	remainder in off-gas and piping	86.4	6.91	1.09

C L A I M S

1. Process for the separation of a ketoxime or
5 aldoxime from a ketoxime- or aldoxime-containing
amide mixture, characterized in that the ketoxime
or aldoxime is distilled off from the amide
mixture. 2.
Process according to claim 1, characterized in
10 that the distillation is conducted under reduced
pressure.
3. Process according to claim 1, characterized in
that the distillation is steam distillation.
4. Process according to any one of claims 1-3,
15 characterized in that the distillation is
conducted at a temperature between 80°C and 180°C.
5. Process according to claim 4, characterized in
that the distillation is conducted at a
temperature between 100°C and 160°C.
- 20 6. Process according to any one of claims 1-5,
characterized in that the distillation is
conducted in a column with 1-15 theoretical trays.
7. Process according to claim 6, characterized in
that the distillation is conducted in a column
25 with 5-15 theoretical trays.
8. Process according to claim 7, characterized in
that the pressure drop per theoretical tray is
less than 200 Pa.
9. Process according to any one of claims 1-8,
30 characterized in that ketoxime or aldoxime
obtained by the distillation is recycled to a
reactor for preparation of the corresponding
amide.
10. Process according to any one of claims 1-9,
35 characterized in that the distillation is



WO 98/02416

PCT/NL97/00395

- 9 -

conducted in two stages.

11. Process as described in the introductory description and illustrated in the examples.

9806203-7
1805



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07D 201/16	A1	(11) International Publication Number: WO-98/02416 (43) International Publication Date: 22 January 1998 (22.01.98)
(21) International Application Number: PCT/NL97/00395 (22) International Filing Date: 8 July 1997 (08.07.97) (30) Priority Data: 1003564 11 July 1996 (11.07.96) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (73) Inventors/Applicants (for US only): ERENTZEN, Yvonne, Helene [NL/NL]; Averbodestraat 44, NL-5921 ES Venlo (NL). HAASEN, Nicolaas, Franciscus [NL/NL]; Lintjeshoog 20, NL-6141 MB Limbriicht (NL). WOLTERS, Hepaticus, Franciscus, Wilhelmus [NL/NL]; Olmstraat 4, NL-6101 BT Echt (NL). (74) Agent: GEERTS, Johanna, Adriana, Maria; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.
(54) Title: PROCESS FOR THE SEPARATION OF A KETOXIME OR ALDOXIME FROM AN AMIDE		
(57) Abstract The invention relates to a process for the separation of a ketoxime or aldoxime from a ketoxime- or aldoxime-containing amide mixture in which the ketoxime or aldoxime is separated from the amide mixture by means of distillation. This has proved to be a very simple and direct method for separating the ketoxime and/or aldoxime from the desired amide.		