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One step synthesis of ε-caprolactam from cyclohexanone and hydroxylamine catalyzed by SO3H-functioned ionic liquids

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Abstract. One step synthesis of ε-caprolactam from cyclohexanone and hydroxylamine used acidic ionic liquids [HSO3-b-N(CH3)3]HSO4 as reaction medium and catalyst were investigated. Reaction conditions were investigated to obtain the optimum conditions. The results indicate that the yield of CPO is 35.9% and the yield of CPL is 20.4% under optimal reaction conditions.

Introduction

ε -caprolactam(CPL) is an important monomer for the production of nylon-6 synthetic fibers and resins [1,2,3]. Most of the current ε -caprolactam production methods involve the conversion of cyclohexanone with hydroxylamine (in its sulfate or phosphate form) into cyclohexanone oxime(CPO), followed by Beckmann rearrangement by the action of fuming sulfuric acid, and then treatment with ammonia giving ε -caprolactam. However, this process suffers from many problems such as the formation of large quantities of low-value ammonium sulfate, the corrosion of equipment and environmental pollution caused by the use of fuming sulfuric acid [4, 5]. The use of room temperature ionic liquids as environmentally friendly media for catalytic processes is widely recognized and accepted [6, 7]. The Beckmann rearrangement was found to be efficiently progressed using ionic liquids in the presence of PCl5, PCl3, P2O5 or Lewis acid as catalyst [8, 9, 10, 11, 12, 13, 14]. One step synthesis brings about multistep synthetic processes in ways which are both environmentally friendly and economical. The term "one step" indicates to that two or more reactions with distinct mechanisms occur sequentially in a single reaction vessel.

In this paper, we first report a simple and efficient process for one step synthesis ofε-caprolactam from cyclohexanone and hydroxylamine used acidic ionic liquids [HSO3-b-N(CH3)3]HSO4 as a reaction medium and catalyst, and the excellent conversion and selectivity were obtained.

Experimental

Reagents and instrument

All reagents and solvents used were analytical grade and were obtained commercially. Gas chromatography was performed on BEIFEN 3420A equipped with a OV-17 (φ 0.25mm × 30m×0.25μm) column and FID.

Typical reaction procedure

The one step synthesis of ε-caprolactam was carried out in liquid-phase at a certain set temperature in a 50 ml three-necked, round-bottomed flask reactor equipped with a reflux condenser and a magnetic stirrer.The reactor was immersed in an oil bath. A typical reaction run was as follows: 9.9g NaNO4, 4.4 g NaOH, 9.8 ml H3PO4(85%),25 ml H2O were added into a three-necked flask to preparation of phosphoric acid buffer solution, a mount of IL and 0.63 ml cyclohexanone were added in the buffer solution. The obtained mixture was heated to the reaction temperature and stirred for 2 h . The resulting mixture was extracted by dichloromethane. The extract liquid was analyzed by using an BEIFEN 3420A gas chromatography.

Results and discussion

Effect of the reaction temperature on one step synthesis of CPL from cyclohexanone and hydroxylamine

Table.1 Effect of reaction temperature on one step synthesis of CPL from cyclohexanone and hydroxylamine

T（℃）	X（%）	S_{CPO}（%）	Y_{CPO}（%）	S_{CPL}（%）	Y_{CPL}（%）
50	78.6	97.1	76.3	--	--
80	82.2	99.6	81.9	--	--
90	83.1	99.7	82.9	0.31	0.20
110	91.9	93.1	85.5	6.91	6.30
130	85.3	94.0	80.2	5.95	5.08

Reaction conditions: n(cyclohexanone): n (hydroxylamine sulphate): n（IL）=1:1:3,t=2h.
X: conversion of cyclohexanone; S_{CPO}, S_{CPL}: selectivity of cyclohexanone oxime andε-caprolactam;
Y_{CPO},Y_{CPL}: the yield of cyclohexanone oxime andε-caprolactam;

Table.1 shows the effect of the reaction temperature on one step synthesis of CPL from cyclohexanone and hydroxylamine. When the reaction temperature is 50℃ and 80℃, there is no CPL. The conversion of cyclohexanone, the yield of CPO and CPL increase initially and then decreases with the increase of temperature. The conversion of cyclohexanone reaches the highest (91.9%) when the temperature rises to 110℃, while the yield of CPO increases to 85.5% and the yield of CPL increases to 6.30%. The oximate reaction of cyclohexanone with hydroxylamine is a liquid-phase heterogeneous reversible exothermic reaction, low temperature is beneficial to the improvement of the cyclohexanone conversion, but, cyclohexanone, which is in the form of small droplets in the water phase, can react with hydroxylamine in the reaction. Low temperature can reduce the mass transfer rate, so that the reaction rate reduced greatly.

In phosphate buffer solution, when reaction temperature is below 90℃, the rearrangement of CPO does not occur. When the temperature rises to 110℃, the yield ofε-caprolactam increase to 6.30%, while the conversion of cyclohexanone increase from 83.1% to 91.9%. Because, part of CPO, which is produced by oximation reaction, rearrange into CPL and then promote the oximation reaction of cyclohexanone. In the investigated temperature range and the reaction conditions, the optimum reaction temperature is 110℃.

Effect of the molar ratio of cyclohexanone and IL on one step synthesis of CPL from cyclohexanone and hydroxylamine

The effect of the molar ratio of cyclohexanone and IL on one step synthesis of CPL from cyclohexanone and hydroxylamine is studied in range from 1:0 to 1:12.

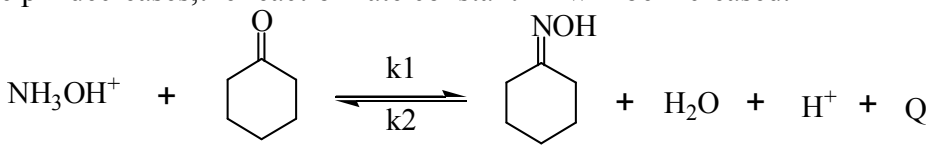
Table 2 Effect of the molar ratio of cyclohexanone and IL on one step synthesis of CPL from cyclohexanone and hydroxylamine

molar ratio	X（%）	S_{CPO}（%）	Y_{CPO}（%）	S_{CPL}（%）	Y_{CPL}（%）
1:0	91.9	93.1	85.7	6.7	6.19
1:3	91.9	93.1	85.5	6.9	6.38
1:4	83.6	92.0	76.9	8.0	6.74
1:5	83.2	89.2	74.2	10.8	9.01
1:6	81.7	89.5	73.1	10.5	8.59
1:7	74.3	80.7	60.0	19.3	14.3
1:8	74.2	81.3	60.8	18.6	13.4
1:10	58.5	76.4	46.7	19.3	11.8
1:12	18.6	49.5	9.2	50.5	9.40

Reaction conditions: n(cyclohexanone):n(hydroxylamine sulphate)=1:1,T=110℃,t=2h

The reaction equation of the oximation reaction of cyclohexanone with hydroxylamine is shown in Eq.1. The reaction rate constant k1, k2 is almost entirely depends on the pH and temperature. The effect of molar ratio of cyclohexanone and IL on one step synthesis of CPL is investigated at 110℃. As shown in Table.2, the conversion of cyclohexanone, the yield of CPO decreases gradually, whereas the yield of CPL first increases gradually and then decreases with the elevation of the IL.

With the elevation of the IL, the pH of buffer solution, the reaction rate constant k1 and the conversion of cyclohexanone decreased gradually. H. Egberink[15] studied the synthesis of oxime from cyclohexanone and hydroxylamine and the hydrolysis mechanism of oxime in aqueous solution system. It was found that when the pH decreased, it was more advantageous to CPO hydrolysis. Because most part of oxime was in the form of protonation of CPO in the aqueous solution system. So, when the pH decreases,the reaction rate constant k2 will be increased.



(1)

The ionic liquid, which is a type of quaternary ammonium salt sulfonic acid, has good solubility of ketone, oxime and amide. It plays a role of catalyst and solvent in the reaction process. Beckmann rearrangement of CPO to CPL is a acid catalytic reaction. The system acidity and the yield of CPL increases with the elevation of the IL. After the molar ratio of cyclohexanone and IL is 1:7, the yield of CPO decreases, reduces the reaction speed of Beckmann rearrangement, the yield of CPL begin to decrease. So that, under the investigated reaction conditions, the best molar ration of cyclohexanone to IL is 1:7.

The effect of phase transfer catalysis on one step synthesis of CPL from cyclohexanone and hydroxylamine

Table3 Effect of the Phase transfer catalysis on one step synthesis of CPL from cyclohexanone and hydroxylamine

Phase transfer catalysis	X（%）	S_{CPO} （%）	Y_{CPO} （%）	S_{CPL} （%）	Y_{CPL} （%）
--	74.3	80.7	60.0	19.3	14.3
TAB	57.4	62.5	35.9	35.6	20.4
CTAB	65.4	87.7	55.4	12.3	10.0

Reaction conditions: n(cyclohexanone):n(hydroxylamine sulphate):n（IL）=1:1:7,T=110℃,t=2h.

As shown in Table 3, the conversion of cyclohexanone and the yield of CPO decreased, whereas the yield of CPL increased with the addition of tetrabutyl ammonium bromide(TAB). The addition of TAB favors Beckmann rearrangement of CPO to CPL. However, the conversion of cyclohexanone, the yield of CPO and CPL decreased with cetyltrimethylammoniumbromide(CTAB) be added. This is because that cyclohexanone and CPO are oil soluble, hydroxylamine is water soluble, the poor solubility of reactants and intermediate, the reaction is not likely to happen. With the addition of phase transfer catalysis, the intermiscibility of cyclohexanone and CPO increase, the hydrolysis and Beckmann rearrangement reaction of cyclohexanone oxime can be further react. So the conversion of cyclohexanone, the yield of CPO decreased, the yield of CPL increased. The catalytic effect for using TAB is better than using CTAB. The yield of CPL increased to 20.4%, the reason is that the catalytic effect of approximate symmetry quaternary salt ions is better than the ions has a long chain substituent[16].

Conclusions

Acidic ionic liquids $[HSO_3\text{-b-}N(CH_3)_3]HSO_4$, as a reaction medium and catalyst, can be effective in one step synthesis of CPL from cyclohexanone and hydroxylamine. The effect of the reaction temperature, the molar ratio of cyclohexanone to IL and phase transfer catalysis on the reaction system were investigated. The optimized reaction conditions were: molar ratio of cyclohexanone and hydroxylamine and IL 1:1:7, the reaction temperature 110°C, reaction time 2h, tetrabutyl ammonium bromide as a phase transf er catalyst, the selectivity to CPO is 62.5%, the yield of CPO is 35.9%; the select iveity to CPL is 35.6% ,the yield of CPL is 20.4%.

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References

[1] Liquan Cheng: Fine chemical intermediates. (In Chinese). Vol. 35 (2005), p.17-23.

[2] Xueping Yang: Chemical Techno-Economics. (In Chinese). Vol. 23 (2005), p. 1-5.

[3] Lixin Yang, Yunfang Wei: Chemical Industry Engineering Progress.(In Chinese). Vol. 234 (2005), p. 96-99.

[4] Pengjia Jian , Youquan Deng: Tetrahedron Letters. Vol. 42 (2001), p. 403-405.

[5] Jiangkun Zhao, Hefang Wang: Journal of Chemical Engineering of Chinese Universities. (In Chinese). Vol.25(2011), p, 838-843.

[6] Ruxiong Li: Reseach and Application on Green Solvent-the Ionic Liquid. Beijing: Chemical Industry Press(2004). (In Chinese).

[7] Christian P M, Raymond A C, Nicholas C D,et al. J Am Chem Soc. Vol.124 (2002) ,P,12932-12933

[8] R.X. Ren, L.D. Zueva, Ou Wei: Tetrahedron Lett, Vol.42(2001), p, 8441~8443.

[9] Andris Zicmanis, Sarmite Katkevica, Peteris Mekss: Catalysis Communications Vol.10 (2009), p, 614–619.

[10] Wei Zhang, Wei Wu, Shuzhong Zhang: The Chinese Journal of Process Engineer- ing. (In Chinese). Vol.4.(2004),p, 261-264.

[11] Wei Zhang, Wei Wu, Shuzhong Zhang: Petrol Eum Processing And Petrochemi- cals. (In Chinese). Vol.35(2004), p, 47-50.

[12] Miguel Vilas, Emilia Tojo. A mild and efficient way to prepareε-caprolactam by using a novel salt related with ionic liquids. Tetrahedron Letters. Vol.51 (2010), p, 4125–4128.

[13] Guo Shu,Du Zhengyin,Zhang Shiguo,et al: Green Chem. Vol.8 (2006), p, 296-300.

[14] Qiang Guo, Xianghai Meng: Journal of Northeast Petroleum University. (In Chinese). Vol.36 (2012), p, 64-67.

[15] H. Egberink, C. Van Heerden:Analytica Chimica Acta. Vol. 118 (1980), Issue 2,p, 359–368.

[16] Dishun Zhao: Phase transfer catalysis: principles and applications. Chemical Industry Press (2007). (In Chinese). p, 35–35.