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Reactivity of hydroxylamine ionic liquid salts in the direct synthesis of caprolactam from cyclohexanone under mild conditions†

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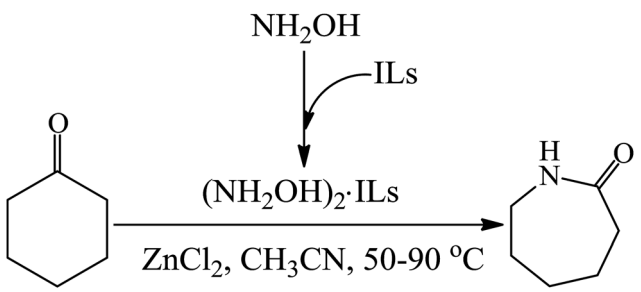
The reactivity of several sulfobutyl hydrosulfate hydroxylamine ionic liquid salts in the direct synthesis of caprolactam from cyclohexanone under mild conditions was investigated. The results showed that the cyclohexanone conversion was mainly affected by cation species in the molecules of the hydroxylamine ionic liquid salts, and hydroxylamine *N*,*N*,*N*-trimethyl-*N*-sulfobutyl hydrosulfate salt was a better choice for the direct synthesis of caprolactam. The optimum reaction condition was at 80 °C for 4 h, and the suitable molar ratio of cyclohexanone : hydroxylamine ionic liquid salt : $ZnCl_2$ was 2 : 1 : 3. Under the optimal reaction conditions, cyclohexanone was almost completely converted into caprolactam, corresponding to 99.1% cyclohexanone conversion and 92.0% caprolactam selectivity. Furthermore, the reaction medium acetonitrile, and the ionic liquid which was combined in the hydroxylamine salt, can be recovered after the reaction, achieving an eco-friendly route for the direct synthesis of caprolactam.

Introduction

Caprolactam (CPL) is an important precursor for nylon-6 fibers and plastics.[1,2] Traditionally, it is produced from cyclohexanone (CYC) by a double-step process (Scheme S1†) with the disadvantages of complex routes, serious corrosion problems and large amounts of by-products.[3,4] Recently direct routes to CPL from CYC has attracted rising interest. Among these one-step process, when air and ammonia was used as oxidant,[5–7] the maximum CYC conversion of 68% and CPL selectivity of 78% were achieved. And when H_2O_2 and NH_3 was used as oxidant,[8] the CYC conversion and CPL selectivity were 7.3% and 66%, respectively. These routes are very interesting consideration from an industrial point of view. However, the CYC conversion and CPL selectivity need to be further improved. More recently, hydroxylamine salts,[9–12] such as hydroxylamine sulfate (HAS) and hydroxylamine hydrochloride (HAL), were used to synthesis CPL from CYC, excellent results have been obtained.[13–16] The maximum CYC conversions and CPL selectivity were 100% and 99%, respectively.[17] Nevertheless, the using of these hydroxylamine inorganic acid salts will inevitably lead to problems of equipment corrosion and environmental pollution because the salts release strong acids.

To overcome the above-mentioned problems, we have previously employed a ionic liquid (1-sulfobutyl-3-methyl imidazole hydrosulfate ($[HSO_3$-*b*-mim$]\cdot HSO_4$)) as an alternative to conventional inorganic acids in hydroxylamine stabilization, and therefore a novel hydroxylamine 1-sulfobutyl-3-methyl imidazole hydrosulfate salt ($(NH_2OH)_2\cdot[HSO_3$-*b*-mim$]\cdot HSO_4$) had been obtained and used in the one-step, solvent-free synthesis of CPL from CYC with satisfactory CYC conversions and CPL selectivity.[18] However, there are still several problems need to be improved: (1) the $[HSO_3$-*b*-mim$]\cdot HSO_4$ is very costly, and this remains a barrier for its wider large-scale industrial application; (2) when the reaction was completed, the $[HSO_3$-*b*-mim$]\cdot HSO_4$ that combined in the hydroxylamine ionic liquid salt, could be recovered but not as well as the fresh one in the color and viscosity due to the influence of high reaction temperature (150 °C).[18]



Scheme 1 A direct and mild route to CPL from CYC and $(NH_2OH)_2\cdot$ILs.

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Herein, we report the stabilization of hydroxylamine with several relatively low-cost sulfobutyl hydrosulfate ionic liquids (ILs),[19] which results in the formation of a series of hydroxylamine ionic liquid salts (denoted $(NH_2OH)_2\cdot$ILs). Furthermore, the obtained hydroxylamine ionic liquid salts were successfully applied in direct synthesis of CPL from CYC under mild conditions (below 100 °C), as shown in Scheme 1.

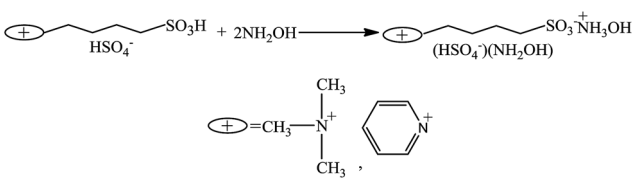
Experimental section

Preparation of the $(NH_2OH)_2\cdot$ILs

The $(NH_2OH)_2\cdot$ILs were prepared according to the method described in the literature.[18] The synthesis of hydroxylamine *N*,*N*,*N*-trimethyl-*N*-sulfobutyl hydrosulfate salt (as shown in Scheme 2) is given here as an example. *N*,*N*,*N*-trimethyl-*N*-sulfobutyl hydrosulfate ($[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$, 33.5 mmol) was added into a 250 mL three-necked flask equipped with a dropping funnel and a stirrer. The flask was then placed in a low-temperature reaction bath, and the temperature was continuously kept under 2 °C. The aqueous solution of hydroxylamine (83.8 mmol) was added dropwise to the three-necked flask that contained the $[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ while stirring. When the neutralization process was completed, a clear solution was obtained. The solution was then evaporated to dryness under reduced pressure to obtain the white hydroxylamine *N*,*N*,*N*-trimethyl-*N*-sulfobutyl hydrosulfate salt ($(NH_2OH)_2\cdot C_7H_{19}O_7NS_2$, denoted $(NH_2OH)_2\cdot[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$, 90.8%), mp 166.8–167.7 °C. Found: C, 23.64; H, 6.76; N, 11.6. Calc. for $(NH_2OH)_2\cdot C_7H_{19}O_7NS_2$: C, 23.40; H, 6.96; N, 11.7. Hydroxylamine 1-sulfobutyl pyridine hydrosulfate salt ($(NH_2OH)_2\cdot C_9H_{15}O_7NS_2$, denoted $(NH_2OH)_2\cdot[HSO_3$-*b*-Py$]\cdot HSO_4$, 88.9%) was prepared by the same method. The only difference was to replace the $[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ with $[HSO_3$-*b*-Py$]\cdot HSO_4$, mp 146.4–146.6 °C. Found: C, 28.84; H, 5.77; N, 10.99. Calc. for $(NH_2OH)_2\cdot C_9H_{15}O_7NS_2$: C, 28.50; H, 5.54; N, 11.08. The ionic liquid $[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ and $[HSO_3$-*b*-Py$]\cdot HSO_4$ were synthesized according to previous literature.[20]

Characterization of the $(NH_2OH)_2\cdot$ILs

The melting point was determined on a WRS-1B numeral melting point instrument. Element analysis was conducted with a Flash EA1112 elemental analyzer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX FT 400 MHz NMR spectrometer using DMSO-d_6 and D_2O as solvents, and the chemical shifts were expressed in ppm. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer in the 4000–400 cm^{-1} range using liquid film or KBr tablet. A DXR Raman Microscope (Thermo Scientific) with a 532 nm excitation laser was used to record the Raman spectra. TG was carried out on a SDT Q600 simultaneous DSC-TGA instrument at 10 K min^{-1} heating rate under a flow of air.



Scheme 2 Synthesis route of $(NH_2OH)_2\cdot$ILs.

Direct synthesis of caprolactam

The reaction was performed in a 100 mL three-necked flask equipped with a stirrer and a reflux condenser. Typically, 5 mmol CYC, 2.5 mmol $(NH_2OH)_2\cdot$ILs, 7.5 mmol $ZnCl_2$ and 10 mL acetonitrile were charged into the flask, and the reaction mixture was heated in an oil bath at 50–90 °C and kept for 1–5 h. At the end of the reaction, the resulting mixture was cooled and then the $ZnCl_2$ was removed by centrifugal separation. The concentrations of the obtained clear reaction liquid were analyzed with an Agilent 7890B gas chromatograph.

Results and discussion

Synthesis and characterization of the $(NH_2OH)_2\cdot$ILs

Several $(NH_2OH)_2\cdot$ILs, such as $(NH_2OH)_2\cdot[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ and $(NH_2OH)_2\cdot[HSO_3$-*b*-Py$]\cdot HSO_4$, were synthesized and characterized by NMR, FTIR and Raman spectra. ^{1}H NMR and ^{13}C NMR spectra (Fig. S1(a–d)†) demonstrated that each H and C atom could find the corresponding contribution in the $(NH_2OH)_2\cdot$ILs, and the resonance observed at the chemical shifts of 8–9 ppm in the ^{1}H NMR was attributed to the NH_3^+.[18,21] The FTIR spectra of $(NH_2OH)_2\cdot[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$, $(NH_2OH)_2\cdot[HSO_3$-*b*-Py$]\cdot HSO_4$ and $(NH_2OH)_2\cdot H_2SO_4$ was presented in Fig. 1(a). The NH_3^+ stretching mode (peaks at 3036 and 2729 cm^{-1}), the NH_3^+ deformation frequencies (peaks at 1620 and 1544 cm^{-1}) and the characteristic peaks of primary ammonium (the minor peak at approximately 2228 cm^{-1}) were all observed in the two $(NH_2OH)_2\cdot$ILs, indicating the existence of the NH_3^+ group from NH_2OH in the two $(NH_2OH)_2\cdot$ILs.[18,22,23] Furthermore, the Raman spectra of $(NH_2OH)_2\cdot[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ and $(NH_2OH)_2\cdot[HSO_3$-*b*-Py$]\cdot HSO_4$ was offered in Fig. 1(b). It showed clearly that the NH_3OH^+ species vibration bands existed in the two $(NH_2OH)_2\cdot$ILs, which provided another evidence for the presence of NH_3OH^+.[18,24,25]

The thermal stability of $(NH_2OH)_2\cdot[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ and $(NH_2OH)_2\cdot[HSO_3$-*b*-Py$]\cdot HSO_4$ was investigated in a temperature range between 25 and 1000 °C (Fig. 2). As shown in Fig. 2(a) and (b), the TG curves of the two $(NH_2OH)_2\cdot$ILs were much the same. Both of the mass loss process included four stages. The initial and final decomposition temperatures of $(NH_2OH)_2\cdot[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ were at about 160 °C and 592 °C. The values were 150 °C and 623 °C respectively for the $(NH_2OH)_2\cdot[HSO_3$-*b*-Py$]\cdot HSO_4$. The weight loss at about 260 °C (with theoretical value of 18.4% for $(NH_2OH)_2\cdot[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ and 17.4% for $(NH_2OH)_2\cdot[HSO_3$-*b*-Py$]\cdot HSO_4$) corresponded to the NH_2OHs stabilized by the $[HSO_3$-*b*-$N(CH_3)_3]\cdot HSO_4$ and $[HSO_3$-*b*-Py$]\cdot HSO_4$. Besides, the main mass loss occurred between 260–380 °C, which was resulted from the decomposition of the two sulfobutyl hydrosulfate ionic liquids that were used to stabilize the hydroxylamine. For comparison, the TG curves of $(NH_2OH)_2\cdot HCl$ and $(NH_2OH)_2\cdot H_2SO_4$ (Fig. 2(c)

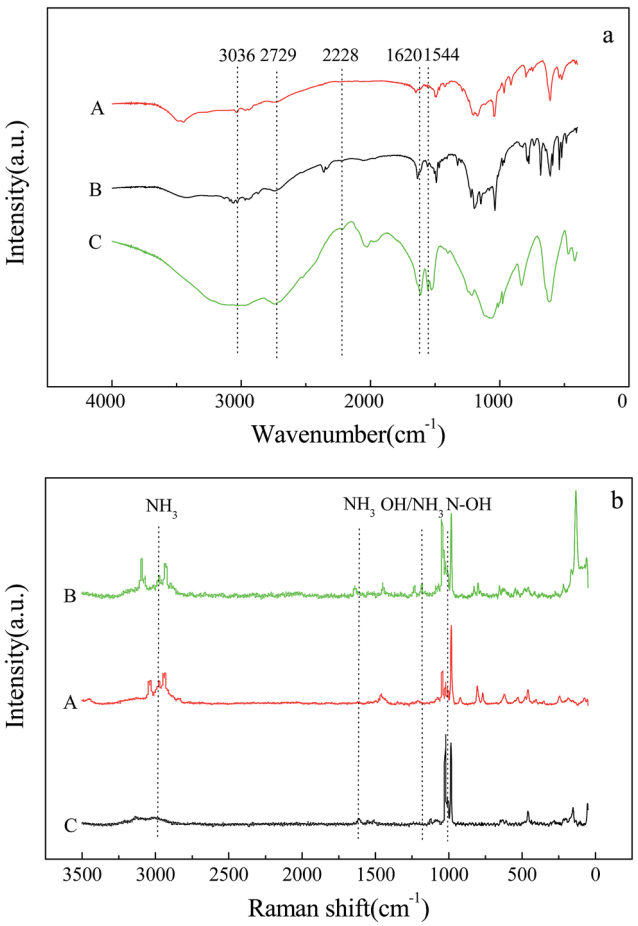


Fig. 1 FTIR spectra (a) and Raman spectra (b) of the novel $(NH_2OH)_2$·ILs and HAS. (A) $(NH_2OH)_2$·[HSO_3-*b*-$N(CH_3)_3$]·HSO_4; (B) $(NH_2OH)_2$·[HSO_3-*b*-Py]·HSO_4; (C) $(NH_2OH)_2$·H_2SO_4.

and (d)) were also presented.[18] Their initial decomposition temperatures were close to those of the two $(NH_2OH)_2$·ILs. Their final decomposition temperatures were 270 °C and 400 °C, respectively, which were much lower than those of the two $(NH_2OH)_2$·ILs. Moreover, their mass loss mainly occurred at about 200 °C, therefore their TG curves were much steeper than those of the two $(NH_2OH)_2$·ILs. In summary, $(NH_2OH)_2$·[HSO_3-*b*-$N(CH_3)_3$]·HSO_4 and $(NH_2OH)_2$·[HSO_3-*b*-Py]·HSO_4 had gentler weight loss curves and much higher final decomposition temperatures, indicating that their thermal stability were much better than those of $(NH_2OH)_2$·HCl and $(NH_2OH)_2$·H_2SO_4.

Direct synthesis of caprolactam from cyclohexanone and $(NH_2OH)_2$·ILs

Effect of solvent on direct synthesis of caprolactam. First of all, the reaction was performed with $(NH_2OH)_2$·[HSO_3-*b*-mim]·HSO_4 as the hydroxylamine salt. The effect of solvent on direct synthesis of CPL was summarized in Table 1. It could be seen that solvent strongly affected the results. When toluene or *N*,*N*-dimethylformamide was used as solvent, the product was mainly cyclohexanone oxime (COX), the CPL selectivity was no

Table 1 Effect of solvent on direct synthesis of CPL[a]

No	Solvent	X_{CYC} (%)	S_{CPL} (%)	S_{COX} (%)
1	Toluene	27.3	35.5	64.5
2	*N*,*N*-Dimethylformamide[b]	79.2	19.0	81.0
3	Acetonitrile	82.5	96.3	3.1

[a] Reaction conditions: CYC 5 mmol, n(CYC) : n($(NH_2OH)_2$·[HSO_3-*b*-mim]·HSO_4) : n($ZnCl_2$) = 2 : 1 : 3, solvent 10 mL, 80 °C, 4 h. [b] Homogeneous phase, others are all heterogeneous phase.

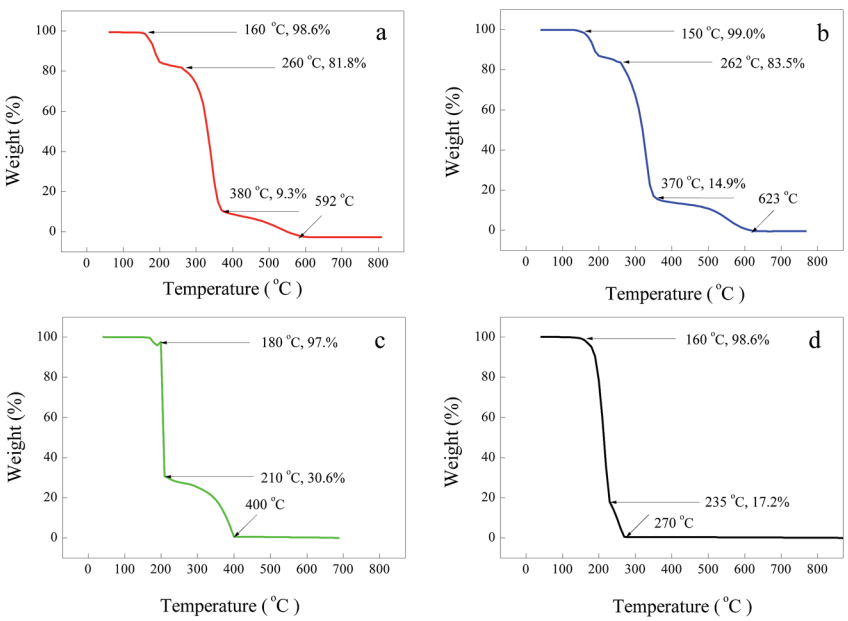


Fig. 2 TG curves of the $(NH_2OH)_2$·[HSO_3-*b*-$N(CH_3)_3$]·HSO_4 (a), $(NH_2OH)_2$·[HSO_3-*b*-Py]·HSO_4 (b), $(NH_2OH)_2$·H_2SO_4 (c) and $(NH_2OH)_2$·HCl (d).

more than 35.5%. While acetonitrile was used as solvent, the CPL selectivity was improved to 96.3%.

The present reaction includes oximation of CYC to COX, followed by the Beckmann rearrangement of COX to CPL. Being a multistep process, the outcome of the reaction depends on the reactivity of the substrate towards both oximation and Beckmann rearrangement.[15] As for the first step, it is believed that COX is produced through the nucleophilic attack of nitrogen electron pairs in the NH_2OH to the C═O carbon in the CYC.[26–28] Free NH_2OH,[16,27] resulted from the decomposition of hydroxylamine salt, is the nucleophile necessary for conversion of CYC to the corresponding COX. It was evident that, the aprotic polar solvents, such as acetonitrile and *N*,*N*-dimethylformamide, demonstrated an obvious promotion on the decomposition of hydroxylamine salt to form free NH_2OH[29–31] since high CYC conversions were obtained in these solvents. This solvent-promoted decomposition in aprotic polar solvents with high ability of electron pairs donor was probably due to the formation of hydrogen bond between the nitrogen electron pairs in the solvent and hydroxyl in the hydroxylamine salts.[29,32]

Furthermore, solvent also played an important role in the subsequent Beckmann rearrangement. Acetonitrile was found to be a suitable solvent for the rearrangement reaction.[33–35] Most probably the beneficial effect of acetonitrile was ascribed to its high reagent solubility,[16] especially that of $[HSO_3$-*b*-mim$]\cdot H_2SO_4$ (an *in situ* catalyst component for the Beckmann rearrangement) resulting from the decomposition of $(NH_2OH)_2\cdot[HSO_3$-*b*-mim$]\cdot H_2SO_4$. Hence, when acetonitrile was used as solvent, more COX was converted to CPL, which in turn promoted the oximation step (a reversible process) and improved the CYC conversion.[17] As for *N*,*N*-dimethylformamide, it could promote the oximation reaction. However, its weak basicity probably poisoned the acid catalyst and hindered the Beckmann rearrangement.[36–38] Hence, only trace amount of CPL was obtained when *N*,*N*-dimethylformamide was used as solvent. Considering the influence on oximation reaction as well as Beckmann rearrangement, acetonitrile seems to be a better choice for direct synthesis of CPL.

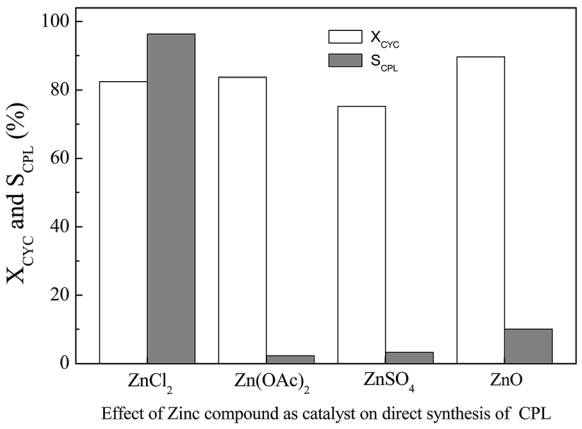


Fig. 3 Effect of Zinc compound as catalyst on direct synthesis of CPL. Reaction conditions: CYC 5 mmol, n(CYC) : $n((NH_2OH)_2\cdot[HSO_3$-*b*-mim$]\cdot HSO_4)$: n(zinc compound) = 2 : 1 : 3, acetonitrile 10 mL, 80 °C, 4 h.

Effect of zinc compound as catalyst on direct synthesis of caprolactam. The effect of zinc compound as catalyst on direct synthesis of CPL was shown in Fig. 3. When $Zn(OAc)_2$, $ZnSO_4\cdot 7H_2O$ or ZnO was used, the CPL selectivity was very low. An interesting finding was that when $ZnCl_2$ was used, most of the product was CPL, only trace COX was existed. Zhang *et al.*[33] reported that the form of a seven-ring intermediate compound was probably the reason for the catalytic function of $ZnCl_2$, which may also be helpful to understand the catalytic activity of $ZnCl_2$ herein. Hence, $ZnCl_2$ was a better catalyst for the present Beckmann rearrangement reaction.

Effect of molar ratio of $ZnCl_2$ to CYC, reaction temperature and time on direct synthesis of caprolactam. The effect of molar ratio of $ZnCl_2$ to CYC on CPL synthesis was studied and the result was displayed in Fig. 4(a). As we can see, the CYC conversion was close to 80% without adding $ZnCl_2$. Most of the product was COX and the CPL selectivity was only 17.8%.

With increasing of $ZnCl_2$ ratio, the CYC conversions changed a little. But the CPL selectivity increased greatly and reached a maximum value of 96.3% when the molar ratio of $ZnCl_2$ to CYC was 1.5, indicating that $ZnCl_2$ and the $[HSO_3$-*b*-mim$]\cdot HSO_4$ was an excellent composite catalyst for the Beckmann rearrangement. Most of the COX produced from the CYC and $(NH_2OH)_2\cdot[HSO_3$-*b*-mim$]\cdot HSO_4$ could be transformed to CPL. Nevertheless, when $ZnCl_2$ amount was further increased, the CPL selectivity decreased a little. As a result, 1.5 molar ratio of $ZnCl_2$ to CYC was sufficient to achieve a high CYC conversion and CPL selectivity.

The influence of reaction temperature and time were also investigated systematically. As depicted in Fig. 4(b) and (c), the CPL selectivity depended greatly on the reaction temperature and time. It increased rapidly with rising temperature from 50 to 80 °C, and then increased slightly when further rising the temperature. Concerning the reaction time, the CPL selectivity first increased, passing through a maximum at 4 h, and then decreased slightly by further prolonging reaction time. Hence, higher temperature (80–90 °C) and longer time (4 h) was suitable for CPL selectivity. The CYC conversion was less affected by the reaction temperature and time. It increased slightly from 50 to 70 °C, and then reduced a little with the temperature above 70 °C. This may be due to easier self-catalysis decomposition of hydroxylamine ionic liquid salt at higher temperature.[39,40] As for the influence of reaction time, the CYC conversion was nearly constant with prolonging reaction time, and a relatively higher CYC conversion can be obtained at a longer time. Hence, considering the CYC conversion and CPL selectivity, the optimum reaction condition was at 80 °C for 4 h.

Under the above mentioned optimal conditions, the CYC conversion and CPL selectivity were 82.5% and 96.3%, respectively. Our previous result was 100% CYC conversion and 91.3% CPL selectivity under solvent free conditions.[18] As we can see, when acetonitrile was used as solvent, the reaction temperature was remarkably decreased from 150 to 80 °C. Although the CYC conversion was decreased a little, the CPL selectivity was increased to 96.3%. Then the reactivity of the two novel prepared hydroxylamine ionic liquid salts on direct synthesis of

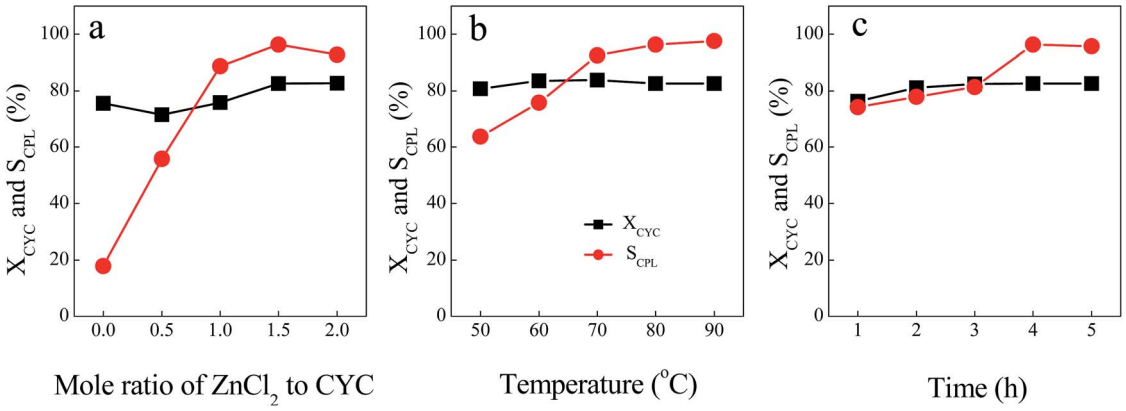


Fig. 4 Effect of molar ratio of $ZnCl_2$ to CYC, temperature and time on direct synthesis of CPL. Reaction conditions: CYC 5 mmol, n(CYC) : n($(NH_2OH)_2\cdot[HSO_3$-b-mim$]\cdot HSO_4$) = 2 : 1, acetonitrile 10 mL; (a) 80 °C, 4 h; (b) n(CYC) : n($ZnCl_2$) = 2 : 3, 4 h; (c) n(CYC) : n($ZnCl_2$) = 2 : 3, 80 °C.

CPL was also investigated as a contrast under the above optimal conditions.

Reactivity comparison of the three $(NH_2OH)_2\cdot$ILs. The effect of different $(NH_2OH)_2\cdot$ILs on direct synthesis of CPL was shown in Table 2. When $(NH_2OH)_2\cdot[HSO_3$-b-Py$]\cdot HSO_4$ or $(NH_2OH)_2\cdot[HSO_3$-b-mim$]\cdot HSO_4$ was used as the hydroxylamine salt, the CYC conversion was relatively lower. While $(NH_2OH)_2\cdot[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$ was used, the CYC conversion was significantly increased to 99.1%, the CPL selectivity was as high as 92.0%, and the only by-product was COX, indicating that $[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$ was superior in hydroxylamine stabilization and CPL synthesis than the other two ILs.

The present reaction was carried out in the presence of a strong Lewis acid $ZnCl_2$, together with the acid ionic liquid that released from the hydroxylamine ionic liquid salt. In order to demonstrate the role of $ZnCl_2$ and the acid ionic liquid in the rearrangement process, Beckmann rearrangement of COX was performed using catalytic amount of $[HSO_3$-b-$(CH_3)_3]\cdot H_2SO_4$ and/or $ZnCl_2$ as shown in Table S1.† It could be seen that $ZnCl_2$ was the main catalytic species for the Beckmann rearrangement. $[HSO_3$-b-$(CH_3)_3]\cdot H_2SO_4$ alone showed little catalytic activity. However, when combined with $ZnCl_2$, it could effectively enhance the catalytic activity of $ZnCl_2$. The results suggested that the cooperative effect between $ZnCl_2$ and ionic liquid played an important role in the rearrangement.[41] Furuya *et al.*[42] reported that HCl and $ZnCl_2$ could promote the rearrangement probably due to their chelation with nitrogen atoms of oxime. The intermediate formed through this process, respected to the COX, has a lower electronic density on the nitrogen atom and consequently a greater tendency to rearrange even without Brønsted acid.[37,43] Accordingly, it could be inferred that the cooperative effect between $[HSO_3$-b-$(CH_3)_3]\cdot H_2SO_4$ and $ZnCl_2$ was probably better than the other two ionic liquids and $ZnCl_2$, which was favor for the formation of the intermediate. Therefore, $(NH_2OH)_2\cdot[HSO_3$-b-$(CH_3)_3]\cdot H_2SO_4$ was found to be the best hydroxylamine salt in the present study.

Reactivity comparison of $(NH_2OH)_2\cdot[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$ and hydroxylamine inorganic acid salts. A comparison between the $(NH_2OH)_2\cdot[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$ and the traditional hydroxylamine inorganic acid salts, such as $(NH_2OH)_2\cdot H_2SO_4$ and $NH_2OH\cdot HCl$, was shown in Table 3. As we can see, no matter which kind of hydroxylamine salt was used, the CPL selectivity was almost the same. The CYC conversion was slightly increased in the order $NH_2OH\cdot HCl$ < $(NH_2OH)_2\cdot H_2SO_4$ < $(NH_2OH)_2\cdot[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$. Specifically, when $NH_2OH\cdot HCl$ was used, the CYC conversion and CPL selectivity were the lowest.

While $(NH_2OH)_2\cdot H_2SO_4$ was used, the CYC conversion and CPL selectivity were higher than those of HAL, meaning that CPL could be efficiently produced from CYC and $(NH_2OH)_2\cdot H_2SO_4$. As for $(NH_2OH)_2\cdot[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$, the CYC conversion and CPL selectivity were the highest, which were 99.1% and 92.0%, respectively. It shows that $[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$ not only can stabilize the hydroxylamine, but also can catalytic the Beckmann rearrangement of COX to CPL.

Table 2 Effect of different $(NH_2OH)_2\cdot$ILs on direct synthesis of CPL[a]

No	$(NH_2OH)_2\cdot$ILs	X_{CYC} (%)	S_{CPL} (%)	S_{COX} (%)
1	$(NH_2OH)_2\cdot[HSO_3$-b-mim$]\cdot HSO_4$	82.5	96.3	3.1
2	$(NH_2OH)_2\cdot[HSO_3$-b-Py$]\cdot HSO_4$	86.2	83.4	16.6
3	$(NH_2OH)_2\cdot[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$	99.1	92.0	8.0

[a] Reaction conditions: CYC 5 mmol, n(CYC) : n($(NH_2OH)_2\cdot$ILs) : n($ZnCl_2$) = 2 : 1 : 3, acetonitrile 10 mL, 80 °C, 4 h.

Table 3 Effect of different hydroxylamine salts on direct synthesis of CPL[a]

No	Hydroxylamine salt	X_{CYC} (%)	S_{CPL} (%)	S_{COX} (%)
1	$NH_2OH\cdot HCl$	93.2	91.2	8.8
2	$(NH_2OH)_2\cdot H_2SO_4$	96.6	91.8	8.2
3	$(NH_2OH)_2\cdot[HSO_3$-b-$N(CH_3)_3]\cdot HSO_4$	99.1	92.0	8.0

[a] Reaction conditions: CYC 5 mmol, n(CYC) : n(NH_2OH) : n($ZnCl_2$) = 2 : 2 : 3, acetonitrile 10 mL, 80 °C, 4 h.

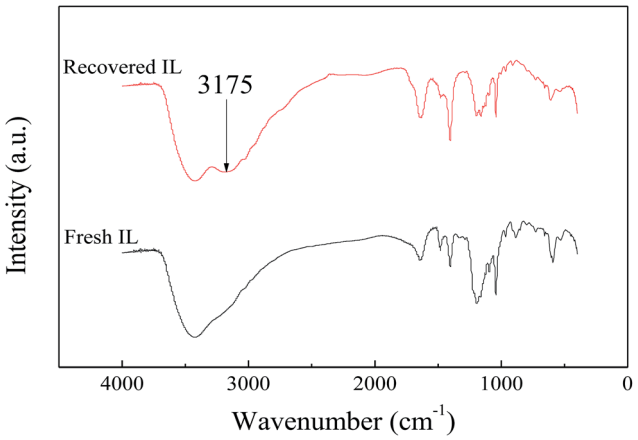


Fig. 5 FTIR spectra of the recovered and fresh $[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$.

Additionally, its reactivity is much the same, even better than H_2SO_4. Furthermore, as $(NH_2OH)_2\cdot[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$ was employed in CPL production, no strong acids was released. Therefore, less equipment corrosion and environmental pollution problems were encountered and no ammonium sulfate by-product was produced.

Recovery of the solvent, catalyst and ionic liquid. To determine whether the solvent, catalyst and the ionic liquid combined in the $(NH_2OH)_2\cdot$ILs could be recovered, a one-step synthesis of CPL from CYC and $(NH_2OH)_2\cdot[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$ with $ZnCl_2$ as catalyst and acetonitrile as solvent was carried out under the optimal reaction conditions.

At the end of the reaction, the resulting mixture was cooled to room temperature. $ZnCl_2$ and acetonitrile were recovered by centrifugal separation and vacuum distillation, respectively. Then the substrate was extraction four times with diethyl ether to sufficiently remove the possible organic compound, such as CYC, COX or CPL.[34] The leaving mixture was distilled with a rotary evaporator under vacuum to recover the $[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$. The FTIR spectra of the recovered and fresh $[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$ was presented in Fig. 5. It can be seen that they were highly similar except for a little peak at 3175 cm^{-1} from characteristic vibrations of CPL.[33,44] It was thus deduced that a little amount of CPL left in the recovered ionic liquid led to the subtle difference in the two FTIR spectra. The ionic liquid was structurally stable after the reaction. Further study was undertaken to understand the recyclability of the reaction media.

Conclusions

From the above results, some key conclusions could be outlined:

• Several novel relatively low-price hydroxylamine ionic liquid salts, $(NH_2OH)_2\cdot[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$ and $(NH_2OH)_2\cdot[HSO_3\text{-}b\text{-}Py]\cdot HSO_4$ were prepared, which proved to a certain degree that all of the sulfobutyl hydrosulfate ionic liquids with different cation could be used in hydroxylamine stabilization to form hydroxylamine ionic liquid salts.

• The three sulfobutyl hydrosulfate hydroxylamine ionic liquid salts were successfully applied in direct synthesis of CPL from CYC under mild conditions. $(NH_2OH)_2\cdot[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$ demonstrated improved reactivity than $NH_2OH\cdot HCl$ and $(NH_2OH)_2\cdot H_2SO_4$, the highest CYC conversion and CPL selectivity were 99.1% and 92.0%, respectively.

• When $(NH_2OH)_2\cdot[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$ was used in CPL production, the ionic liquid that combined in the $(NH_2OH)_2\cdot[HSO_3\text{-}b\text{-}N(CH_3)_3]\cdot HSO_4$ could be recovered. Therefore, less equipment corrosion and environmental pollution problems were encountered and no ammonium sulfate by-product was produced, achieving an eco-friendly route for direct synthesis of caprolactam.

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Notes and references

1 N. C. Marzianom, L. Ronchin, C. Tortato, A. Vavasori and C. Badetti, *J. Mol. Catal. A: Chem.*, 2007, **277**, 221–232.
2 D. Mao, Z. Long, Y. Zhou, J. Li, X. Wang and J. Wang, *RSC Adv.*, 2014, **4**, 15635–15641.
3 Y. Li, K. Wang, K. Qin and T. Wang, *RSC Adv.*, 2015, **5**, 25365–25371.
4 J. Zhang, K. Wang, Y. Lu and G. Luo, *AIChE J.*, 2012, **58**, 925–931.
5 J. N. Armor, *J. Catal.*, 1981, **70**, 72–83.
6 R. Raja, G. Sankar and J. M. Tomas, *J. Am. Chem. Soc.*, 2001, **123**, 8153–8154.
7 J. M. Tomas and R. Raja, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 13732–13736.
8 M. Anilkumar and W. F. Hoelderich, *Appl. Catal., B*, 2015, **165**, 87–93.
9 L. O. Cisneros, W. J. Rogers and M. Sam Mannan, *Thermochim. Acta*, 2004, **414**, 177–183.
10 W. Zhang, X. Su, Z. Hao, S. Qin, W. Qing and C. Xia, *Ind. Eng. Chem. Res.*, 2015, **54**, 100–107.
11 F. Zhao, K. You, C. Peng, S. Tan, R. Li, P. Liu, J. Wu and H. Luo, *Chem. Eng. J.*, 2015, **272**, 102–107.
12 Y. Xu, Z. Li, L. Gao, D. Zhang, X. Zhao, S. Wang and Y. Wang, *Ind. Eng. Chem. Res.*, 2015, **54**, 1068–1073.
13 H. Sharghi and M. Hosseini, *Synthesis*, 2002, **8**, 1057–1060.
14 S. Mahajan, B. Sharma and K. K. Kapoor, *Tetrahedron Lett.*, 2015, **56**, 1915–1918.
15 F. Aricò, G. Quartarone, E. Rancan, L. Ronchin, P. Tundo and A. Vavasori, *Catal. Commun.*, 2014, **49**, 47–51.
16 E. Rancan, F. Aricò, G. Quartarone, L. Ronchin, P. Tundo and A. Vavasori, *Catal. Commun.*, 2014, **54**, 11–16.
17 J. Zhang, Y. Lu, K. Wang and G. Luo, *Ind. Eng. Chem. Res.*, 2013, **52**, 6377–6381.

18 Z. Li, Q. Yang, X. Qi, Y. Xu, D. Zhang, Y. Wang and X. Zhao, *Chem. Commun.*, 2015, **51**, 1930–1932.
19 A. A. Hullio and G. M. Mastoi, *Orient. J. Chem.*, 2011, **27**, 1591–1612.
20 Y. Geng, L. Hu, X. Zhao, H. An and Y. Wang, *Chin. J. Chem. Eng.*, 2009, **17**, 756–760.
21 E. D. Bates, R. D. Mayton, I. Ntai and J. H. Davis Jr, *J. Am. Chem. Soc.*, 2002, **124**, 926–927.
22 J. Xie, *Application of Infrared Spectroscopy in Organic Chemistry and Medicinal Chemistry*, Science Press, Beijing, 1987, pp. 91–92.
23 S. Weng, *Fourier Transform Infrared Spectrometer*, Chemical Industry Press, Beijing. 2005, pp. 332–333.
24 C. A. Vandijk and R. G. Priest, *Combust. Flame*, 1984, **57**, 15–24.
25 L. Courthéoux, D. Amariei, S. Rossignol and C. Kappenstein, *Appl. Catal., B*, 2006, **62**, 217–225.
26 H. Zang, M. Wang, B. Cheng and J. Song, *Ultrason. Sonochem.*, 2009, **16**, 301–303.
27 D. Lorenzo, A. Romero and A. Santos, *Ind. Eng. Chem. Res.*, 2016, **55**, 6586–6594.
28 A. Elmakssoudi, K. Abdelouahdi, M. Zahouily, J. Clark and A. Solhy, *Catal. Commun.*, 2012, **29**, 53–57.
29 M. Matsumoto, M. Tanimura, T. Akimoto, N. Watanabe and H. K. Ijuin, *Tetrahedron Lett.*, 2008, **49**, 4170–4173.
30 O. Phillips, J. M. Schwartz and P. A. Kohl, *Polym. Degrad. Stab.*, 2016, **125**, 129–139.
31 R. Meng, S. Hu, X. Cao, F. Liu, F. Jin and P. Qu, *J. North Univ. China, Nat. Sci. Ed.*, 2016, **37**, 162–165.
32 J. Wang, X. Zhang, F. Wang and W. Cai, *Chem. Ind. Eng. Prog.*, 2016, **35**, 1309–1313.
33 X. Zhang, D. Mao, Y. Leng, Y. Zhou and J. Wang, *Catal. Lett.*, 2013, **143**, 193–199.
34 R. Core and R. Srivastava, *J. Mol. Catal. A: Chem.*, 2013, **376**, 90–97.
35 X. Liu, L. Xiao, H. Wu, Z. Li, J. Chen and C. Xia, *Catal. Commun.*, 2009, **10**, 424–427.
36 K. You, L. Mao, D. Yin, P. Liu and H. Luo, *Catal. Commun.*, 2008, **9**, 1521–1526.
37 L. Ronchin and A. Vavasori, *J. Mol. Catal. A: Chem.*, 2009, **313**, 22–30.
38 X. Wang, C. Chen, S. Chen, Y. Mou and S. Cheng, *Appl. Catal., A*, 2005, **281**, 47–54.
39 Q. Wang, C. Wei, L. M. Pérez, W. J. Rogers, M. B. Hall and M. Sam Mannan, *J. Phys. Chem. A*, 2010, **114**, 9262–9269.
40 L. Zhu, B. Guo, D. Tang, X. Hu, G. Li and C. Hu, *J. Catal.*, 2007, **245**, 446–455.
41 E. Rancan, F. Aricò, G. Quartarone, L. Ronchin and A. Vavasori, *Catal. Lett.*, 2015, **145**, 939–946.
42 Y. Furuya, K. Ishihara and H. Yamamoto, *J. Am. Chem. Soc.*, 2005, **127**, 11240–11241.
43 L. Ronchin, A. Vavasori and M. Bortoluzzi, *Catal. Commun.*, 2008, **10**, 251–256.
44 Z. Du, Z. Li, Y. Gu, J. Zhang and Y. Deng, *J. Mol. Catal. A: Chem.*, 2005, **237**, 80–85.