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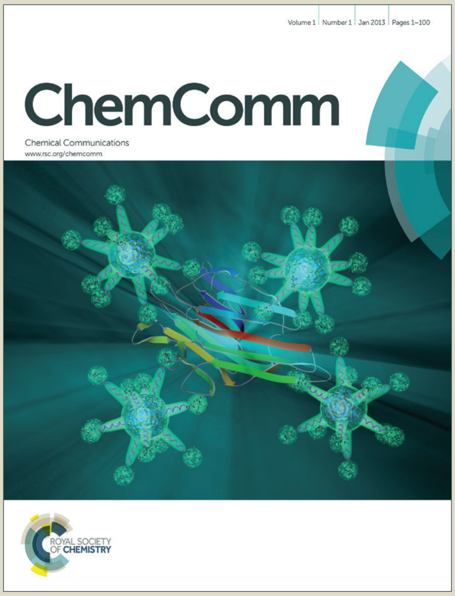
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A novel hydroxylamine ionic liquid salt resulting from the stabilization of NH_2OH by a SO_3H-functionalized ionic liquid

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Zhihui Li[a,b], Qiusheng Yang[a], Xudong Qi[b], Yuanyuan Xu[a], Dongsheng Zhang[a]*, Yanji Wang[a]* and Xinqiang Zhao[a]

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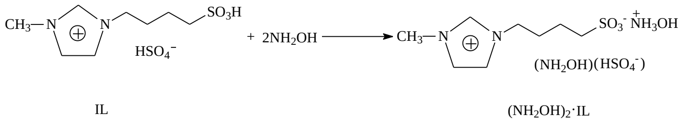
A SO_3H-functionalized ionic liquid was used as an alternative to conventional inorganic acids in hydroxylamine stabilization, leading to the formation of a novel hydroxylamine ionic liquid salt that exhibits improved thermal stability and reactivity in the one-step, solvent-free synthesis of caprolactam in comparison with hydroxylamine hydrochloride and hydroxylamine sulfate.

Hydroxylamine (NH_2OH) has important industrial uses, especially in the production of cyclohexanone oxime (COX) for caprolactam (CPL) synthesis.[1] However, handling hydroxylamine free base is a challenge because it is unstable and decomposes at room temperature.[2] Inorganic acids are normally used to stabilize hydroxylamine to form hydroxylamine salts, such as hydroxylamine sulfate (HAS) and hydroxylamine hydrochloride (HAL).[2a] However, severe problems, such as equipment corrosion and environmental pollution, are inevitably encountered when these salts are used in CPL production because they release strong acids. Hence, conventional inorganic acids are not the best choice to stabilize hydroxylamine, and it still remains challengeable to search for green and eco-friendly substances for hydroxylamine stabilization.

Ionic liquids (ILs) have been widely researched as green reaction media due to their favorable physico-chemical properties.[3] Among them, SO_3H-functionalized ILs are highly attractive[4] because they have the advantages of both liquid acids and solid acids, such as uniform acid sites, well fluidity, non-volatility and easy recovery, making them ideal medias or/and catalysts for Beckmann rearrangement.[5] As a result, an idea of whether the green SO_3H-functionalized ILs, instead of the traditional inorganic acids, could be used for stabilizing hydroxylamine was conceptualized. Herein, we report the stabilization of hydroxylamine with a SO_3H-functionalized IL, which results in the formation of a novel hydroxylamine IL salt that shows bettered reactivity in the one-step, solvent-free synthesis of CPL compared with HAL and HAS. To the best of our knowledge, this is the first report on stabilizing hydroxylamine with ILs.



Scheme 1 Proposed reaction between a SO_3H-functionalized IL and NH_2OH

1-Sulfobutyl-3-methyl imidazole hydrosulfate (IL) was used to stabilize the aqueous solution of hydroxylamine, and the hydroxylamine IL salt (denoted as $(NH_2OH)_2$·IL) was formed as depicted in Scheme 1. Based on the naming methods of inorganic acid hydroxylamine salts, the new synthesized complex was hydroxylamine 1-sulfobutyl-3-methyl imidazole hydrosulfate salt ($(NH_2OH)_2$·$C_8H_{16}O_7N_2S_2$, 16.6 g, 94.1%), mp 149.1-149.8 ℃. Found: C, 25.37; H, 5.97; N, 14.71; S, 16.55. Calc. for $(NH_2OH)_2$·$C_8H_{16}O_7N_2S_2$: C, 25.13; H, 5.76; N, 14.66; S, 16.75.

The structure of $(NH_2OH)_2$·IL was fully characterized by FTIR, Raman spectra, and NMR. The FTIR spectra of HAS and IL were also presented to aid in the analysis of the $(NH_2OH)_2$·IL spectra. The peaks at 3038 and 2725 cm^{-1} in the FTIR spectra of $(NH_2OH)_2$·IL (Fig. 1a) were assigned to the NH_3^+ stretching mode from the NH_3^+ group in the positive ion of $(NH_2OH)_2$·IL, which agree with those of HAS.[6] The minor peak at approximately 2040 cm^{-1} and those at 1614 and 1520 cm^{-1} in the FTIR spectra of $(NH_2OH)_2$·ILs were attributed to the characteristic peaks of primary ammonium salt and the NH_3^+ deformation frequencies, which also in agreement with those of HAS.[6] The above data indicate that the NH_3^+ group from NH_2OH indeed existed in $(NH_2OH)_2$·IL. Furthermore, the Raman spectra of $(NH_2OH)_2$·IL displays exactly the same vibration bands that correspond to the NH_3OH^+ species (Fig. 1b, Table S1, ESI†).[7] This finding provides another strong evidence for the presence of NH_3OH^+ in $(NH_2OH)_2$·IL. In addition, the absorption of SO_3, CH_3,

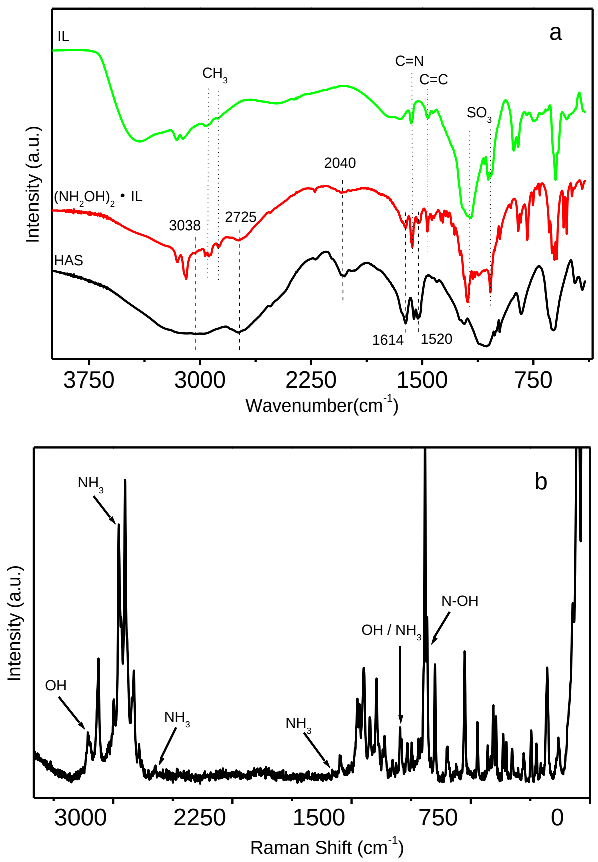


Fig. 1 (a) FTIR spectra of the $(NH_2OH)_2 \cdot$IL, IL and HAS; (b) Raman spectra of the $(NH_2OH)_2 \cdot$IL

C=C and C=N groups[6, 8] in the FTIR spectra of $(NH_2OH)_2 \cdot$IL (Fig. 1a) confirmed that IL also existed in $(NH_2OH)_2 \cdot$IL. The structure of $(NH_2OH)_2 \cdot$IL was also confirmed by the ^{1}H and ^{13}C NMR spectra (Fig. S1 a-d, ESI†). The ^{1}H NMR spectra of $(NH_2OH)_2 \cdot$IL were generally consistent with that of IL when D_2O was used as a solvent, but all of the chemical shifts were slightly larger. This can be attributed to the decreased electron cloud density at H in $(NH_2OH)_2 \cdot$IL due to hydrogen bond formation. Most notably, while the solvent D_2O was replaced by DMSO-d$_6$, a new resonance was observed at the chemical shifts of 8-9 ppm in the spectra of $(NH_2OH)_2 \cdot$IL, which was assigned to the NH_3^+.[9]

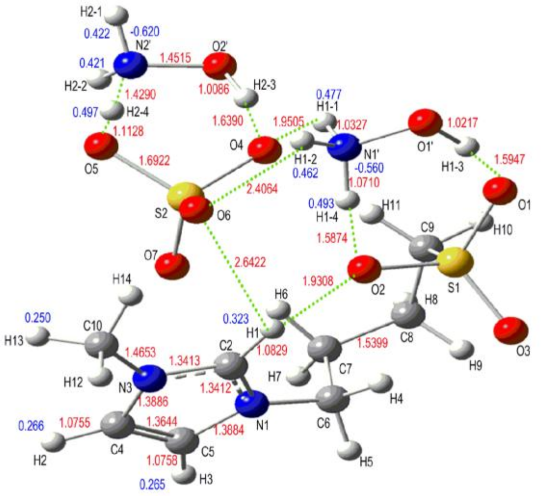


Fig. 2 Optimized geometry (distance unit: Å, red) and NBO charge (blue) of $(NH_2OH)_2 \cdot$IL

Density functional theory (DFT) calculations (Computational details, ESI†) were further performed to verify the structure.[10] The optimal structure and the distance between each atom and its NBO charge distribution are depicted in Fig. 2. The distances between the N atom from NH_2OH and the H atom from the corresponding acid in IL were 1.0710 Å (N1'-H1-4) and 1.4290 Å (N2'-H2-4), respectively. The former bond length was similar to that of a normal N-H bond (N1'-H1-1, 1.0327 Å). The bonded result was also confirmed by NBO analysis. Mayer bond orders of the former was 0.25 higher than that of the latter. The latter distance of N2'-H2-4 was shorter than the distance between H2-3 and O4 (1.6390 Å). This result shows that N2' and H2-4 has strong H-bond effect. A large network of H bonds or bonded forms was formed among the H, O and N atoms in $(NH_2OH)_2 \cdot$IL, which stabilized the two hydroxylamines. The results are consistent with the ^{1}H NMR.

The thermal stability of $(NH_2OH)_2 \cdot$IL, compared with those of IL, HAS and HAL, was investigated in a temperature range between 25 and 1000 ℃. The results are displayed in Fig. 3. The TG curve shows that the mass loss process of $(NH_2OH)_2 \cdot$IL was divided into four stages. The mass losses were 7.9% at 192 ℃, 13.7% at 281 ℃, 87.6% at 401 ℃ and 99.1% at 600 ℃. According to the results of the DFT computations, one NH_2OH was combined with the H^+ released by $-SO_3H$ in the anion of IL to form NH_3OH^+. Another NH_2OH was stabilized by strong H-bond effect with both HSO_4^- and $-SO_3H$. The former was more stable than the latter. Therefore, the first weight loss (with theoretical value of 8.6%) corresponded to the NH_2OH stabilized by the H-bond effect, and the second (with theoretical value of 17.3%) corresponded to the NH_2OH stabilized by the anion. After 281 ℃, the TG curve of $(NH_2OH)_2 \cdot$IL was much the same as that of the IL. Thus, the mass loss between 281 and 600 ℃ resulted from the decomposition of the SO_3H-functionalized IL that was used to stabilize the two hydroxylamines. Final decomposition products were all gases with 99.1% mass loss.

The TG curves of HAL and HAS (Fig. 3) showed two stages of mass loss that led to the complete transformation of hydroxylamine salt into gaseous products, which are in agreement with the literature.[2a,11] The TG curves of HAS and HAL were much steeper than that of $(NH_2OH)_2 \cdot$IL, indicating that HAS and HAL may explode easily on heating, and this may lead to explosive exothermic reaction in a confined space.[12] Moreover, the final decomposition temperature of $(NH_2OH)_2 \cdot$IL (600 ℃) was much higher than those of HAL (270 ℃) and HAS (400 ℃). In summary, $(NH_2OH)_2 \cdot$IL has a gentler weight loss curve and a much higher final decomposition temperature, indicating that it has bettered thermal stability than HAL and HAS.

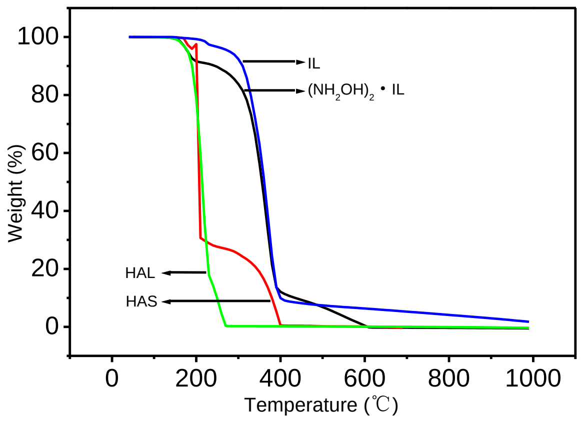
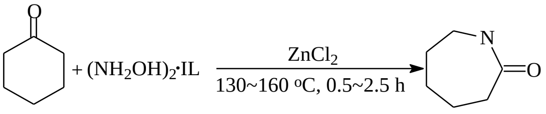


Fig. 3 TG curves of the $(NH_2OH)_2 \cdot$IL, IL, HAS and HAL



Scheme 2 One-step, solvent-free synthesis of CPL from CYC

The utilization of the novel $(NH_2OH)_2$·IL in the one-step, solvent-free synthesis of CPL from cyclohexanone (CYC) was tested, as shown in Scheme 2. The advantages of this one-step process[13] over the conventional double-step process[14] are its much shorter route, no generation of ammonium sulfate and environmental friendliness. Although $ZnCl_2$ based SO_3H-functionalized ILs have been used as green reaction media for Beckmann rearrangement,[5] insufficient information is available about the one-step synthesis of CPL from CYC with $ZnCl_2$ as catalyst. Table 1 summarizes the results. The optimum reaction condition was at 150 ℃ for 2 h, and the best molar ratio of $(NH_2OH)_2$·IL: CYC: $ZnCl_2$ was 1:2:2. Under the optimal reaction condition, most of the CYC was converted into CPL, corresponding to 91.0% yield and 91.0% selectivity toward CYC. Moreover, HAS and HAL were used in place of $(NH_2OH)_2$·IL under the optimized conditions. However, the CPL yields were slightly inferior to that of $(NH_2OH)_2$·IL. Therefore, $(NH_2OH)_2$·IL was an excellent substitute for HAL and HAS in CPL synthesis. A controlled reaction was performed to recover the IL, the FTIR spectra of the recovered and fresh IL were highly similar (Fig. S2, ESI†). This result demonstrate that the IL combined in $(NH_2OH)_2$·IL could be recovered. Additionally, an in situ IR study was carried out to monitor the reaction (In situ IR, ESI†). COX sharply increased at the beginning of the reaction and then decreased, while CPL appeared and increased gradually as the reaction proceeded. Further study was undertaken to understand the reaction mechanism and the recyclability of the reaction media, as well as other applications of this new hydroxylamine salts.

In summary, NH_2OH was successfully stabilized by a SO_3H-functionalized IL to form a novel hydroxylamine IL salt, the structure and composition of which were verified by experimental and theoretical (DFT computations) methods. The obtained hydroxylamine IL salt exhibits bettered reactivity in the one-step, solvent-free synthesis of CPL in comparison with HAL and HAS.

Table 1 One-step synthesis of CPL from CYC and $(NH_2OH)_2$·IL.[a]

No.	Catalyst (mmol)	T (℃)	t (h)	Y_{CPL} (%)	S_{CPL} (%)	S_{COX} (%)
1.	none	150	1.5	6.3	10.6	70.2
2.	ZnO (2)	150	1.5	2.5	2.5	97.5
3.	$Zn(OAc)_2$ (2)	150	1.5	30.0	31.2	23.9
4.	$ZnSO_4$ (2)	150	1.5	46.6	46.6	24.8
5.	$ZnCl_2$ (2)	150	1.5	75.1	76.1	11.9
6.	$ZnCl_2$ (1)	150	1.5	12.8	15.7	75.2
7.	$ZnCl_2$ (1.5)	150	1.5	55.8	55.8	22.2
8.	$ZnCl_2$ (2.5)	150	1.5	73.8	73.8	13.8
9.	$ZnCl_2$ (3)	150	1.5	64.4	64.4	19.8
10.	$ZnCl_2$ (2)	150	0.5	47.2	47.2	37.0
11.	$ZnCl_2$ (2)	150	1	52.1	52.1	33.4
12.	$ZnCl_2$ (2)	150	2	91.0	91.0	3.6
13.	$ZnCl_2$ (2)	150	2.5	45.2	45.2	38.2
14.	$ZnCl_2$ (2)	130	2	16.5	16.9	53.7
15.	$ZnCl_2$ (2)	140	2	49.8	49.8	50.2
16.	$ZnCl_2$ (2)	160	2	45.3	48.8	17.9
17[b].	$ZnCl_2$ (2)	150	2	88.3	89.8	1.4
18[c].	$ZnCl_2$ (2)	150	2	56.1	56.1	25.8

[a] Reaction conditions: CYC (1 mmol), $(NH_2OH)_2$·IL (2 mmol); [b] HAS (2 mmol); [c] HAL (4 mmol)

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[a] *Hebei Provincial Key Lab of Green Chemical Technology and High Efficient Energy Saving, Hebei University of Technology, Guang Rong Dao 8, Hongqiao Distric, Tianjin 300130 (China). Tel/Fax: 86-22-60200445; E-mail: yjwang@hebut.edu.cn; zds1301@hebut.edu.cn.*

[b] *School of Energy and Environmental Engineering, Hebei University of Technology, Tianjin 300401 (China).*

Electronic Supplementary Information (ESI) available: [Experimental and the characterization data; The density functional theory (DFT) calculations using the M062X hybrid functional with the Gaussian 09 program package.]. See DOI: 10.1039/c000000x/

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