Acidic ionic liquids, green and recyclable catalysts in the clean nitration of TAIW to CL-20 using HNO3 electrolyte

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Acidic ionic liquids, green and recyclable catalysts in the clean nitration of TAIW to CL-20 using HNO₃ electrolyte

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Abstract: A novel method for the synthesis of CL-20 by nitration of TAIW was investigated. HNO₃ electrolyte containing generated dinitrogen pentoxide and unreacted dinitrogen tetraoxide was directly used as nitrating agent and the result was encouraging. A series of SO₃H-functionalized ionic liquids were utilized to further improve the result. The satisfactory yield of CL-20 (94%) makes it a useful method for the green and clean synthesis of CL-20.

Keywords: CL-20, electrolyte, dinitrogen pentoxide, dinitrogen tetraoxide, TAIW
1 INTRODUCTION

Hexanitrohexaazaisowurtzitane (CL-20), one of the most powerful and futuristic high explosives, was first synthesized by Nielsen A T in 1987\(^\text{[1]}\). Over the past decades, effective methods of synthesizing CL-20 had attracted increasing interests. Nitrination is the final and crucial step. Efforts have been made for various nitrolyable precursors, such as TADBIW (tetraacetyl-dibenzyl-hexaazaisowurtzitan), TADFIW (tetraacetyl-diformyl-hexaazaisowurtzitan), TADEIW (tetraacetyl-diethyl- hexaazaisowurtzitan), etc, and TAIW (tetraacetyl-hexaazaisowurtzitan) has appeared to be favorable for its better stability and operability\(^\text{[2]}\). Nitrating agent is the other critical factor. The most commonly used nitrating agent is a relatively inexpensive mixture of concentrated nitric acid and sulphuric acid in different proportions, while it poses serious pollution threat to the environment\(^\text{[3]}\). In line with increasing global environmental safety regulations, other nitrating agents were studied. ZHAO\(^\text{[4]}\) reported nitrination of TAIW using fuming nitric acid with the yield of 93%-96%. However, it is not recommendable for its long reaction time of more than 20 h. Heteropolyacids and nitric acid were also tried, while the amount of nitric acid must be greatly excessive\(^\text{[5]}\).

In our previous work, \(\text{N}_2\text{O}_5/\text{HNO}_3\) is regarded as a promising nitrating agent\(^\text{[6-9]}\). However, two defects restrict its application. The first is the difficult purification and preservation of \(\text{N}_2\text{O}_5\). Although \(\text{N}_2\text{O}_5\) has been generated in the electrochemical process of \(\text{HNO}_3\), and isolated using organic solvent (\(\text{CH}_2\text{Cl}_2\)) for over 100 years\(^\text{[10]}\), none of the publications in open literature reported the direct use of \(\text{HNO}_3\) electrolyte as nitrating agent. The second is the lower activity of \(\text{N}_2\text{O}_5\), which is a long-standing problem in the nitration of N-heterocyclic compound, such as HMX(1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and CL-20.

Acidic ionic liquids (ILs) are deemed as one of the most promising alternatives of conventional acid catalysts for its benign solubility in organic and inorganic matters and high catalytic performance. Qian H\(^\text{[11]}\) proved ionic liquid is a superior catalyst in synthesis of HMX. In continuation of our previous studies on the
clean nitration\textsuperscript{[12-13]}, this work is focused on the utilization of easy-recovery and reusable acidic ionic liquids as an environmentally attractive catalyst to improve the nitrating ability. We demonstrate that, in an appropriate ionic liquid, it is possible to efficiently synthesize CL-20 using HNO\textsubscript{3} electrolyte without purification. The new synthetic method reported in this paper would make appreciable contribution to the subject of environmental friendly chemistry and it is available for industrial applications.

2 EXPERIMENTAL SECTION

2.1 Chemicals and equipments

All chemicals reported in this manuscript except HNO\textsubscript{3} electrolyte were obtained from commercial sources of reagent grade and used without further purification.

NMR spectra were recorded on a Bruker DRX300 spectrometer. Electrospray ionization mass spectroscopy (ESI-MS) was carried out with Finnigan TSQ Quantumm ultra AM LC/MS instrument. Elemental analysis was recorded on an Elementar Vario EL III. The product was analyzed by HPLC (high performance liquid chromatography) using a C18 column and a methyl alcohol /water mixture as eluent with a ratio of 50:50. The flow rate applied equalled 1 mL/min. The analysis was carried out at 40°C, using a UV detector at 230 nm wavelengths.

2.2 Synthesis of \textit{SO}_3\textsubscript{H}-functionalized ILs

In a typical experiment, a mixture of triethylamine (0.1mol) and 1,4-butanesultone (0.1mol) was charged into a 250 mL round-bottom flask. The reaction proceeded at 40°C for 24 h and vigorous stirred. After filtrating, the solid product was washed with ethyl ether (3×10 mL) and dried under vacuum (70°C, 0.1 MPa). Then, zwitterions (0.1mol) was dissolved in 50 mL de-ionized water, 0.1mol acid (benzene sulfonic acid, sulphuric acid, fluoboric acid, trifluoroacetic acid) was added dropwise with vigorously stirring and the reaction mixture stirred for an additional 6 h at 60°C. Extra water was removed by rotary evaporation (70°C, 0.1 MPa), and \textit{SO}_3\textsubscript{H}-functionalized ILs were obtained with the total yield of 68-83%.
Scheme 1. The synthesizing process of [Et₃N(CH₂)₅SO₃H][X] (X= BF₄, HSO₄, CF₃COO, Ph-SO₃)

2.3. Characterization of ILs

[Et₃N(CH₂)₅SO₃H][BF₄] ¹H NMR (300 MHz, d₆-DMSO): δ 1.15-1.18 (t, 9H), 1.88 (t, 2H), 2.91-2.94 (t, 2H), 3.22-3.32 (m, 8H), 3.32 (m, 2H), 4.23 (s, 1H). ¹³C NMR (75.5 MHz, DMSO): δ 54.88, 51.97, 47.35, 17.78, 7.00. Elemental analysis, Calcd: C, 36.93, H, 7.45, N, 4.31; Found: C, 36.91, H, 7.44, N, 4.31.

[Et₃N(CH₂)₅SO₃H][HSO₄] ¹H-NMR (300 MHz, D₂O): δ 1.08-1.11 (m, 9H), 1.64 (t, 2H), 2.77-2.81 (t, 2H), 3.00-3.14 (m, 8H). ¹³C NMR (75.5 MHz, D₂O): δ 56.38, 52.68, 50.17, 21.80, 19.84, 6.98. Elemental analysis, Calcd: C, 35.80, H, 7.53, N, 4.18; Found: C, 35.79, H, 7.53, N, 4.19.

[Et₃N(CH₂)₅SO₃H][CF₃COO] ¹H NMR (300 MHz, D₂O): δ 1.03-1.07 (t, 9H), 1.61 (m, 4H), 2.74-2.79 (t, 2H), 2.97-3.10 (m, 8H). ¹³C NMR (75.5 MHz, D₂O): δ 165.5, 117.4, 59.07, 54.83, 52.67, 24.15, 22.90, 7.86. Elemental analysis, Calcd: C, 41.01, H, 6.99, N, 3.99; Found: C, 41.00, H, 6.99, N, 3.99.

[Et₃N(CH₂)₅SO₃H][Ph-SO₃] ¹H NMR (300 MHz, D₂O): δ 1.05-1.08 (t, 9H), 1.64 (m, 4H), 2.23 (s, 3H), 2.80-2.82 (t, 2H), 3.01-3.11 (m, 8H), 7.19-7.22 (d, 2H), 7.51-7.54 (d, 2H). ¹³C NMR (75.5 MHz, D₂O): δ 143.6, 142.4, 129.5, 124.1, 58.69, 52.01, 51.83, 22.48, 20.51, 18.57, 7.55. Elemental analysis, Calcd: C, 49.85, H, 7.64, N, 3.42; Found: C, 49.84, H, 7.64, N, 3.43.

2.4 Preparation of HNO₃ electrolyte

HNO₃ electrolyte is prepared by controlling potential oxidation (approximately +1.85V) of dinitrogen tetraoxide in anhydrous nitric acid at platinum supported iron oxide anodes. The content of N₂O₅, N₂O₄
and HNO₃ was varied with the time and can be analyzed according to reference [17].

2.5 General procedure for the nitrolysis of TAIW to CL-20

Stoichiometric ratio of HNO₃ electrolyte and IL were placed in a 100 mL flask immersed in an ice-water bath. 3 g TAIW was added in batches and the mixture was stirred until the substrate was dissolved adequately. After a certain time at 90°C, 20 mL distilled water was added into the reaction solution in a dropwise manner and stirred for one hour, solid compound was obtained, filtered, washed with water, and dried in vacuum.

3 RESULTS AND DISCUSSION

3.1 Direct nitration using HNO₃ electrolyte

The electrochemical preparation of N₂O₅ from N₂O₄ and HNO₃ solution is the most economic and environmental process. N₂O₅ was purified and used in pure form in the nitration for all literatures reported before [18-22]. Considering the mechanism of the nitration of TAIW [23-25], we demonstrate that, N₂O₄ is useless or at least harmless during the whole reaction, and the electrolyte can be directly used without purification.

A series of experiments was carried out in the lab scale to verify our assumption and the optimized parameters are given in Table 1.

<table>
<thead>
<tr>
<th>Entry</th>
<th>HNO₃ electrolyte (wt%)</th>
<th>Yield/%</th>
<th>Purity/</th>
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<tr>
<td></td>
<td>N₂O₅</td>
<td>N₂O₄</td>
<td>HNO₃</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>0</td>
<td>85</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
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<td>10</td>
<td>5</td>
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<tr>
<td>5</td>
<td>12</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>5</td>
<td>85</td>
</tr>
</tbody>
</table>

* Reaction condition: m(TAIW)g : m(HNO₃ electrolyte)=3: 25, 90°C, 7h.

As comparison, entry 1 was conducted using pure N₂O₅/HNO₃ as nitrating agent with the yield of 84.2%. The nitrating agent in entries 2-5 was obtained by the electrolysis of N₂O₄ and HNO₃ solution, and
the concentration of each component varied with time. In entry 2, no N₂O₅ existed in the initial electrolyte.

As the electrolysis proceeded, N₂O₄ was gradually oxidized to N₂O₅, and the yield of CL-20 increased correspondingly. For the restriction of electrolytic technique, N₂O₄ can not be exhausted completely, and the maximum concentration of N₂O₅ was 12% unless the initial ratio of N₂O₄ and HNO₃ was changed (entry 5).

It was obvious to demonstrate that N₂O₅ was the key factor in the nitration. The yield of CL-20 was determined by the content of N₂O₅. Furthermore, as listed in entries 1 and 6, a pot of N₂O₄ has little effect on the results, which can be illustrated in Scheme 2.

![Scheme 2. Reaction mechanism of TAIW to CL-20](image)

Scheme 2. Reaction mechanism of TAIW to CL-20

As shown in Scheme 2, TAIW was nitrated to CL-20 in N₂O₅/HNO₃ solution. When HNO₃ electrolyte containing N₂O₄ and N₂O₅ was used, partly TAIW still reacted with N₂O₅ and converted to CL-20, while the others reacted with N₂O₄ and formed nitrosocompound at first, and then further nitrated to nitrocompound, for the latter owns better stability in the strongly acidic solution.

3.2 Reactivity of ionic liquids catalysts

The pronounced effects of ionic liquids on this reaction can be easily demonstrated from the results shown in Table 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>IL</th>
<th>Yield%</th>
<th>Purity%</th>
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<tr>
<td>1</td>
<td>none</td>
<td>84.2</td>
<td>92.8</td>
</tr>
<tr>
<td>2</td>
<td>[Et₃N(CH₃)₂SO₂H][CF₃CO₂]</td>
<td>85.9</td>
<td>91.5</td>
</tr>
<tr>
<td>3</td>
<td>[Et₃N(CH₃)₂SO₂H][BF₄]</td>
<td>88.3</td>
<td>96.2</td>
</tr>
<tr>
<td>4</td>
<td>[Et₃N(CH₃)₂SO₂H][HSO₄]</td>
<td>89.1</td>
<td>96.0</td>
</tr>
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As shown in Table 2, the SO₃H-functionalized ILs was essential for the nitration. The

[Et₃N(CH₂)₄SO₃H][CF₃CO₂] showed a slight promotion in the reaction process (entry 2), while the other
three ILs were proved to be very active, leading to an 88%-94% yield in the presence of 10% ILs (entries
3-5), and the [Et₃N(CH₂)₄SO₃H][Ph-SO₃] could give the best result of 94.3%.

Ultimately, the recyclability of ILs is central to their utilities. In order to investigate the reusable
properties of these Brønsted acidic ILs, recycle experiments of [Et₃N(CH₂)₄SO₃H][Ph-SO₃] were tested
according to the Fig.1. After reaction, IL was recovered from the nitric acid solution by removing HNO₃ and
water at 70°C under vacuum (0.07MPa) for 5 h. More than 95% IL was recovered and reused for the next
cycle. Results showed [Et₃N(CH₂)₄SO₃H][Ph-SO₃] can be reused at least five times without appreciable
decrease in yield (90%-92% yield of CL-20). It is worthy of noting, when the IL lost its activity after
repeated use, it could be easily recovered by being washed with dichloromethane in water, then removed
water at reduced pressure and applied in next reaction.

![](image)

**Fig.1 Recovery and recycle of ionic liquids**

3.3 Relationship of reactivity and acidity of ionic liquids
The measurement of the Brønsted acidic scale of ILs was conducted on an UV-240 spectrophotometer with 4-nitroaniline being used as a basic indicator according to the literature previously reported\(^\text{(26)}\). With the addition of acidic ILs, the absorbance of the unprotonated form of the basic indicator decreased, so the \([I]/[I^+]\) ratio could be calculated from the measured absorbance differences, and then the Hammett function, \(H_0\), is calculated by using eq. 1.

\[
H_0 = pK(I)_{aq} + \log([I]/[I^+])
\]

(1)

Where \(pK(I)_{aq}\) is the pKa value of 4-nitroaniline, \(pK(I)_{aq} = 0.99\), \([I]\) and \([I^+]\) are, respectively the molar concentrations of the unprotonated and protonated forms of 4-nitroaniline.

The results of acidities of four ILs are shown in Fig. 2.

![Fig.2 Absorption spectra of 4-nitroaniline in various ILs](image)

The maximal absorbance of the unprotonated form of 4-nitroaniline was observed at 350 nm in \(\text{CH}_2\text{Cl}_2\) (Fig. 2. spectra a). We could determine the \([I]/[I^+]\) ratio by measuring the absorbance when each IL was added (spectra b–e), and then the Hammett function \((H_0)\) is calculated (Table 3).

| Table 3. Hammett Function \((H_0)\) Values |
|-----------------------------------------|-------------------|
| IL                                      | Hammett function,\(H_0\) |
| [Et₃N(CH₂)₂SO₄H][HSO₄]                 | 0.38              |
| [Et₃N(CH₂)₂SO₄H][CF₃CO₂]               | 1.32              |
| [Et₃N(CH₂)₂SO₄H][Ph-SO₄]               | -0.27             |
| [Et₃N(CH₂)₂SO₄H][BF₄]                  | 0.43              |
Ultimately, we obtained the acidity order of four SO$_3$H-functionalized ILs:

$$[\text{Et}_3\text{N(CH}_2\text{)}_4\text{SO}_3\text{H}][\text{Ph-SO}_3\text{H}] > [\text{Et}_3\text{N(CH}_2\text{)}_4\text{SO}_3\text{H}][\text{HSO}_4\text{]} > [\text{Et}_3\text{N(CH}_2\text{)}_4\text{SO}_3\text{H}][\text{BF}_4\text{]} > [\text{Et}_3\text{N(CH}_2\text{)}_4\text{SO}_3\text{H}][\text{CF}_3\text{CO}_2\text{]}].$$

Compared with Table 3, ILs with stronger acidity shows better catalytic activities, for N$_2$O$_5$ was prone to dissociate to NO$_2^+$ and NO$_3^-$ in strongly acidic system, and the NO$_2^+$ was the truly attacking agent in the whole reaction.

4 CONCLUSION

In summary, a convenient and environmental friendly procedure for the synthesis of CL-20 by nitrolysis of TAIW using HNO$_3$ electrolyte and ionic liquids has been developed with the advantages of simple manipulation, short reaction time and good yields. Compared with other catalysts, SO$_3$H-functionalized ILs are readily available, in favor of environment, green and can be reused at least five times without significant loss of activity. Furthermore, the direct use of HNO$_3$ electrolyte without purification seems to be a major step forward in the area of clean nitration. The satisfactory yield of CL-20 (94 %) makes it a useful method for the green synthesis of CL-20. Therefore, the new synthetic method reported here would greatly contribute to the environmentally greener procedure and be suitable for industrial applications.

ACKNOWLEDGMENTS

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REFERENCES


Graphical abstract

Taiw and HNO₃ electrolyte

Recycling IL recovery ratio: 95%

Less pollution Easy to recycle

Distillation

CL-20

HNO₃ and H₂O

Inspissation for further electrolysis