Synthesis of some Potential High Energy Materials using Metal Nitrates; An approach towards Environmental Benign Process

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A novel and efficient method for the synthesis of various promising high energy materials (HEMs) like nitrotriazolone (NTO), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), bis (2,2-dinitropropyl) nitramine (BDNPN), 1,1-diamino-2,2-dinitro ethylene (FOX-7) etc. using metal nitrates/sulphuric acid as nitrating agent has been described successfully. The synthesized materials have been characterized using various spectroscopic techniques as well as thermal studies and the data obtained confirmed their structure. From the study it was revealed that this method certainly an alternative method of preparation of high energy materials (HEMs) in place of the conventional nitration mixture.

Keywords: Nitration, Metal nitrates, Insensitive, High Energy Materials

Introduction

The mission for novel high energy materials (HEMs) with highest possible performance and low vulnerability led to the development of advanced insensitive power packed materials1 such as triaminotrinitrobenzene (TATB), nitrotriazolone (NTO), dinitrotetraoxa diazatetracyclo dodecance (TEX), 1,1-diamino-2,2-dinitro ethylene (FOX-7), 2,4, 6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and 2, 6-diamino-3, 5-dinitropyrazine-N-oxide (LLM-105). Many of these insensitive HEMs are at various stages of pilot plant production in different countries. However, the synthesis of HEMs by the conventional methods led to formation of large quantity of toxic liquid and gaseous wastes. Due to this all over the globe research and development programs are to produce HEMs without leaving any toxic wastes.

In present work, we are reporting an alternative nitration method for the synthesis of various important high energy materials such as NTO, FOX-7, BDNPN [bis (2,2-dinitropropyl) nitramine], 4-NI (4-nitroimidazole), CL-20 etc. which are the energetic molecules from important class of futuristic ingredients for insensitive munitions (IMs) with superior performance. Nitration is one of the most important reaction steps during the synthesis of HEMs. Conventional nitration processes generates lots of acid wastes creating environmental pollution. Apart from pollution, the other problems associated with the use of conventional nitrating agent is that, if the substrate molecule is deactivated due to presence of strong electron withdrawing groups such as NO₂, C=O and SO₂ (attached to nitrogen or carbon or oxygen) the conventional nitration fails. Even if the nitration of deactivated substrates is carried out under harsher conditions using conventional nitrating agents, the yields and purity of the product (s) are poor. Another fate for the failure of nitration is stability of substrates and their intermediates involved in strong acidic conditions. To overcome these drawbacks, the use of certain novel catalytic materials, based on metal oxides, zeolites, inorganic metal triflorates8 in association with conventional nitrating agents has introduced a novel approach. However, the information available on the use of conventional nitrating agents in presence of novel catalytic materials is scanty.

The selection of a nitrating agent for a particular nitration reaction is mainly dependent on the type of substrate molecule being nitrated. Most commonly used nitrating agent is the mixture of concentrated nitric acid and sulphuric acid. Conventionally used nitrating agents pose serious threat of pollution, thereby necessitating efficient and costly effluent treatment. An alternative approach is sought for the synthesis of HEMs using new nitrating agents.
Recently, some new nitration methods and new nitrating agents have been developed, which can be used under mild conditions. The salts of nitronium ions, NO$_2$BF$_4$ and NO$_2$PF$_6$, N$_2$O$_5$, solids as catalysts or as supports for other reagents, Clay-DNPO, small-pore zeolite, H-ZSM-5 are being used for the nitration of various organic compounds$^{6-17}$. Application of inorganic nitrates Bi(Ni$\text{NO}_3$)$_3$, CAN, Na$\text{NO}_3$, K$\text{NO}_3$, Ca$(\text{NO}_3)_{2}$, Li$\text{NO}_3$ etc. for the nitration of aromatic compounds have already been reported$^{12-19}$.

Considering the importance of above mentioned HEMs, we have attempted the synthesis of these molecules using a novel and alternate method keeping in mind the concept of environmental benign approach. We are reporting here the use of inorganic nitrates like potassium nitrate (K$\text{NO}_3$), sodium nitrate (Na$\text{NO}_3$) and silver nitrate (Ag$\text{NO}_3$) with sulphuric acid (H$_2$SO$_4$) as mild nitrating agents for the selective nitration.

**Experimental**

**Materials and Methods**

All the reagents and chemicals used in the present study were of AR grade and used as such. The synthesized compounds were characterized by their melting points and were uncorrected. IR spectra were recorded (KBr pellets) on Shimadzu FTIR-8400 Spectrophotometer. $^1$H-NMR spectra were recorded on Varian Mercury Spectrometer at 300 MHz using TMS as internal standard. DSC studies were undertaken on a Perkin Elmer DSC-7 instrument operating at heating rate 10°C/min in nitrogen atmosphere with 1 mg of sample. Elemental analysis was carried out with a CE Instrument (Model CHN-1110). [Caution: All the synthesized compounds described here are energetic materials. Appropriate safety precautions were taken while carrying out the reactions].

**General procedure for the synthesis of insensitive high explosives**

Required quantity of concentrated sulfuric acid (98%) was taken in two necked round bottom flask and cooled to 5°C. Metal nitrate was added portion wise to the sulphuric acid under stirring by keeping the temperature below 10°C. The substrate was added to the nitrating mixture at 10°C under continuous stirring for about 30 minutes. The temperature of the reaction mixture was allowed to rise to desired temperature and further stirred for 2 to 4 hours (the quantity of reactants and substrates along with their reaction conditions are listed in Table 1). After completion of the reaction (monitored by TLC technique), reaction mixture was allowed to attain room temperature. Then, the reaction mixture was poured in to crushed ice (50 g) and stirred to enhance the precipitation. The solid precipitate was filtered and washed with minimum quantity of cool water. The products were dried in a water-jacketed oven at 50°C.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Duration (hrs)</th>
<th>Temp. (°C)</th>
<th>Reagents used and yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4-Triazolone (TO) (0.5g, 0.0059mol)</td>
<td>NTO</td>
<td>2</td>
<td>45-50</td>
<td>H$_2$SO$_4$ (98%) (20 ml) Na$\text{NO}_3$ (0.63g, 0.0074 mol) 68</td>
</tr>
<tr>
<td>Bis-2,2-dinitopropylamine (BDNPA) (1g, 0.0036 mol)</td>
<td>BDNPN</td>
<td>2</td>
<td>40-45</td>
<td>H$_2$SO$_4$ (98%) (20 ml) Na$\text{NO}_3$ (0.383g, 0.0045 mol) 63</td>
</tr>
<tr>
<td>2,6,8,12-Tetraacetyl -2,4,6,8,10,12-hexaaazaisowurtizane (TAIW) (1g, 0.003 mol)</td>
<td>CL-20</td>
<td>2.5</td>
<td>45-50</td>
<td>H$_2$SO$_4$ (98%) (25 ml) Na$\text{NO}_3$ (1.913g, 0.0225 mol) 60</td>
</tr>
<tr>
<td>4,6-dihydroxy-2-methylpyrimidine (1g, 0.0082 mol)</td>
<td>FOX-7</td>
<td>3</td>
<td>10-25</td>
<td>H$_2$SO$_4$ (98%) (25 ml) Na$\text{NO}_3$ (1.743g, 0.0205 mol) 74</td>
</tr>
<tr>
<td>Imidazole (0.5g, 0.0074 mol)</td>
<td>4-NI</td>
<td>4</td>
<td>45-50</td>
<td>H$_2$SO$_4$ (98%) (20 ml) Na$\text{NO}_3$ (0.79g, 0.0093 mol) 49</td>
</tr>
</tbody>
</table>
Results and discussions

The synthesized compounds (Table 2) were characterized by spectroscopic and thermal techniques. The characterization data of the products are summarized in Table 3. The results revealed from the experiments suggest that metal nitrate/H₂SO₄ nitration agent requires milder reaction conditions as well as lesser reaction time. The yield obtained by this method (Table 1 & Fig. 1) is comparable with the conventional method of preparation of the respective HEMs. Among the three metal nitrates AgNO₃ was found to be more efficient nitration agent for the synthesis of HEMs. From the experimental results the reactivity of the three metal nitrates towards the nitration is found to be in the order AgNO₃＞KNO₃＞NaNO₃. This nitration method does not release any hazardous nitric oxides during the nitration against to the case of concentrated nitric/sulphuric acids mixture. Therefore, this nitration method can be considered as ecofriendly process. Further, this method does not require stringent cooling condition in the preparation of FOX-7.

<table>
<thead>
<tr>
<th>Product</th>
<th>IR (cm⁻¹)</th>
<th>¹H NMR (δ ppm)</th>
<th>DSC (°C)</th>
<th>Elemental (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chemical shift (δ ppm)</td>
<td>Solvent used</td>
<td></td>
</tr>
<tr>
<td>NTO</td>
<td>3196 (-NH), 1689 (-C=O), 1540 and 1336 (-NO₂) etc.</td>
<td>8.28, (bs, 2H, -NH&lt;)</td>
<td>DMSO-D₆</td>
<td>257 (Exo.)</td>
</tr>
<tr>
<td>CL-20</td>
<td>3040 and 2844 (-CH), 1614, 1556 and 1332 (-NO₂) etc.</td>
<td>8.19 (s, 2 H, -CH&lt;) &amp; 8.35 (s, 4 H, -CH&lt;)</td>
<td>(CD₃)₂CO</td>
<td>253 (Exo.)</td>
</tr>
<tr>
<td>4-NI</td>
<td>3448 and 3141 (-NH), 3010 (-CH), 1557 and 1496 (-NO₂), 1332 (C=N) etc.</td>
<td>13.1 (bs, 1H, -NH&lt;) &amp; 8.3 (s, 1H, -CH&lt;) &amp; 7.7 (s, 1H, -CH&lt;)</td>
<td>DMSO-D₆</td>
<td>305 (Endo.)</td>
</tr>
<tr>
<td>BDNPN</td>
<td>2987 (-CH), 1580, 1554, and 1372 (-NO₂) etc.</td>
<td>5.1 (s, 4H, -CH₂) &amp; 3.32 (s, 6H, -CH₃)</td>
<td>DMSO-D₆</td>
<td>187 (Exo.)</td>
</tr>
<tr>
<td>FOX-7</td>
<td>3420 and 3149 (-NH₂), 1554, 1517 and 1354 (-NO₂) etc.</td>
<td>8.9 (bs, 4H, -NH₂)</td>
<td>DMSO-D₆</td>
<td>234 (Exo.) and 278 (Exo.)</td>
</tr>
</tbody>
</table>

* Theoretical value

Conclusion

The present study described the synthesis of various HEMs e.g. CL-20, FOX-7, NTO, BDNPN and nitromidazole using metal nitrate/H₂SO₄ as a nitration agent under milder reaction conditions as well as lesser reaction time. The synthesized compounds have been characterized by NMR, IR as well as thermal techniques. Since, this method of
nitration is not associated with the evaluation of hazardous nitric oxides, hence this approach can be considered as an attempt towards the environmental benign process. From the results it can be concluded that this method certainly an alternative method of preparation of high energy materials (HEMs) in place of the conventional nitric/sulphuric nitration mixture. The efficacy of the three metal nitrates towards nitration is found to be in the order AgNO$_3$ > KNO$_3$ > NaNO$_3$.

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References