Studies on Energetic Compounds — Part Nineteen: Preparation and Thermolysis of N-Methylanilinium and N,N-Dimethylanilinium Nitrates and Perchlorates

Gurdip Singh*, Inder Pal Singh Kapoor and Smiju Jacob

Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273 009, India

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Nitrates and perchlorates salts of N-methylaniline and N,N-dimethylaniline have been prepared and characterised. Thermal and explosive characteristics of these salts are studied by TG, DSC, DTA, DTG and ignition delay measurements. Although the kinetics of thermolysis of these salts were evaluated by fitting TG data in nine mechanism-based kinetic models but the parabolic law gives the best fits. Slow thermolysis involves proton transfer and rapid thermolysis leads to ignition to yield gaseous products.

Introduction

As a part of research programme on high energetic compounds1-11 (HEC) and keeping in view their technological use in pyrotechnics, explosives and solid propellants, the preparation and thermolysis of N-methylanilinium and N,N-dimethylanilinium nitrates and perchlorates are reported. Although several perchlorates and nitrates of ring substituted arylamines are known1-7 but studies on salts of N-methyl substituted arylamines are not yet available in literature.

Experimental Procedure

Materials

N-Methylaniline (E-Merck), N,N-dimethylaniline (BDH), Conc. nitric acid (AR, Qualigens), perchloric acid (E-Merck), silica gel G (TLC grade, Qualigens), nitron (CDH) were used as received.

Preparation and Characterisation of Nitrates and Perchlorates

N-Methylanilinium and N,N-dimethylanilinium nitrates and perchlorates were prepared by the reaction

\[
\text{H}_2\text{N(CH}_3\text{)NO}_3 + \text{HClO}_4 \rightarrow \text{H}_2\text{N(CH}_3\text{)}\text{N}^+ + \text{ClO}_4^- + \text{H}_2\text{O}
\]

of 20 per cent HNO\textsubscript{3} with N-methyl and N,N-dimethylaniline (1:1), respectively, at 0-5°C (Scheme 1). N-methylanilinium and N,N-dimethylanilinium perchlorates were prepared by reacting 20 per cent HClO\textsubscript{4} with N-methyl and N,N-dimethylaniline (1:1), respectively, at room temperature (Scheme 1). The mixture was concentrated at 60°C under rotatory vacuum evaporator (JSGW). It was cooled to obtain crystalline solids. All the four salts were recrystallised from absolute alcohol, crystals were vacuum dried and purity was checked by TLC. Moreover, these salts were characterised by gravimetric (using nitron reagent)\textsuperscript{12} and IR\textsuperscript{13} spectra. Their structures and physical properties are presented in Table 1.
Table 1 – Physical parameters, TLC and analytical data (using nitron reagent) and spectral data on N-methylanilinium and N,N-dimethylanilinium nitrates and perchlorates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mol. formula</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>TLC Eluent#</th>
<th>Spot</th>
<th>FTIR</th>
<th>RF</th>
<th>Analytical data (g.)</th>
<th>FTIR (in KBR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-methylanilinium nitrate (N-MAN)</td>
<td>C₁₂H₁₀N₂O₃</td>
<td>Brownish needles</td>
<td>60</td>
<td>a:b</td>
<td>Grey</td>
<td>0.81</td>
<td>0.2210</td>
<td>0.2206</td>
<td>3431s, 2380s (N-H), 2900s (CH₃), 1765s (C=O), 1610s (C-N), 1575s (C=C), 1235s (N=O), 760s (C-H)</td>
</tr>
<tr>
<td>N,N-dimethylanilinium nitrate (N,N-DMAP)</td>
<td>C₁₄H₁₄N₂O₃</td>
<td>Yellowish needles</td>
<td>78</td>
<td>a:b</td>
<td>Brown</td>
<td>0.82</td>
<td>0.1004</td>
<td>0.1019</td>
<td>3430s, 2443s (N-H), 2861s (CH₃), 899s (C-N), 796s (C=O), 1384s (NO₂)</td>
</tr>
<tr>
<td>N-methylanilinium perchlorate (N-MAP)</td>
<td>C₁₆H₁₄N₂ClO₄</td>
<td>Greenish needles</td>
<td>62</td>
<td>a:b:c</td>
<td>Greenish-black</td>
<td>0.82</td>
<td>0.3718</td>
<td>0.3956</td>
<td>2860s (CH₃), 629s (ClO₄), 1610s (C-N), 1575s (C=C), 1350s (C=O), 827s (C-N), 796s (C=O)</td>
</tr>
<tr>
<td>N,N-dimethylanilinium perchlorate (N,N-DMAP)</td>
<td>C₁₈H₁₈N₂ClO₄</td>
<td>Greenish-black</td>
<td>71</td>
<td>a:b:c</td>
<td>Brownish</td>
<td>0.83</td>
<td>0.0902</td>
<td>0.0931</td>
<td>2860s (CH₃), 629s (ClO₄), 1610s (C-N), 1575s (C=C), 1350s (C=O), 899s (C-N), 630s (ClO₄)</td>
</tr>
</tbody>
</table>

# a= chloroform, b= carbon tetrachloride, c= methanol; locating reagent-iodine

Figure 1 – Non-isothermal TG of N-MAN, N,N-DMAN, N-MAP and N,N-DMAP

Thermal Decomposition Studies on Nitrates and Perchlorates

Thermal decomposition of N-methylanilinium and N,N-dimethyl-anilinium nitrates and perchlorates was carried out using following techniques.

Non-isothermal TG

TG studies on nitrates and perchlorates (wt 30 mg, 100-200 mesh) were undertaken in static air at a heating rate of 5°C/min using indigenously fabricated TG apparatus fitted with temperature indicator cum controller (Model CT 808T Century) and bucket type...
platinum crucible (h = 1 cm and diam = 1 cm). Per cent decomposed (α) vs temperature (°C) plot is given in Figure 1. The overall decomposition temperature are given in Table 2.

**Isothermal TG**

Isothermal TG analysis of N-methylanilinium and N,N-dimethylanilinium nitrates and perchlorates were carried out in static air using the same apparatus as mentioned above and 30 mg of the sample (100-200 mesh) at appropriate temperatures 135°C, 150°C, 165°C, 175°C for nitrates and 175°C, 190°C, 200°C, 220°C for perchlorates. Per cent decomposition (α) verses time (min) plot are shown in Figure 2.

**Differential Scanning Calorimetry (DSC)**

DSC thermograms on these nitrates and perchlorates were obtained on a Mettler TA 4000 in nitrogen atmosphere (flow rate 40 cm²/min). Weighed samples (Sartorius–Werke Type 2405 electro balance, Germany) were sealed with sample sealer. A pin hole was made at the top of the lid so that the product gases could escape during decomposition. The sample and the reference pans were positioned at the centre of the holder cells and were covered with aluminium domes. The thermograms (Figure 3) were recorded at a heating rate of 10°C/min using Hewlett Packard 7475A plotter. DSC endothermic and exothermic peaks are given in Table 2.

![Graph showing isothermal TG of N-MAN, N,N-DMAN, N-MAP and N,N-DMAP](image)

### Table 2 - Thermal analytical data on N-methylanilinium and N,N-dimethylanilinium nitrates and perchlorates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Overall decomposition (°C)</th>
<th>Endothermic (°C)</th>
<th>ΔH (J/g)</th>
<th>Exothermic (°C)</th>
<th>ΔH (J/g)</th>
<th>Peak temperature (°C)</th>
<th>Peak temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-MAN</td>
<td>44-253</td>
<td>59</td>
<td>63.7</td>
<td>202.2</td>
<td>1102.3</td>
<td>66, 212</td>
<td>208</td>
</tr>
<tr>
<td>N,N-DMAN</td>
<td>78-464</td>
<td>79.5</td>
<td>85.5</td>
<td>187.7</td>
<td>1067.1</td>
<td>148</td>
<td>142</td>
</tr>
<tr>
<td>N-MAP</td>
<td>48-345</td>
<td>63.3</td>
<td>145.8</td>
<td>255.3</td>
<td>3973.2</td>
<td>85, 230.8</td>
<td>224</td>
</tr>
<tr>
<td>N,N-DMAP</td>
<td>84-212*</td>
<td>72.6</td>
<td>16.7</td>
<td>244.2</td>
<td>3308.3</td>
<td>86.3, 239</td>
<td>232</td>
</tr>
</tbody>
</table>

*Explosion temperature*
Figure 3 – DSC thermograms of N-MAN, N,N-DMAN, N-MAP and N,N-DMAP

Figure 4 – Simultaneous TG, DTA-DTG thermograms of N-MAN, N,N-DMAN, N-MAP and N,N-DMAP

Simultaneous TGA-DTA-DTG

Simultaneous TGA-DTA-DTG thermograms on nitrates and perchlorates were obtained on a Mettler Toledo TGA/SDTA 851 (Switzerland) in nitrogen atmosphere (flow rate 50 cm³/min). Weiged empty sample pan (Alumina crucible, size 70μl) tared (zeroed), then weight of the sample along with the
Table 3 — Ignition delay (tid), ignition temperature (IT), activation energy for ignition (E*), oxygen balance (OB) and velocity of detonation (VOD) for N-methylanilinium and N,N-dimethylanilinium nitrates and perchlorates

<table>
<thead>
<tr>
<th>Compound</th>
<th>tid (sec) at</th>
<th>IT (°C)</th>
<th>E* (KJ mol⁻¹)</th>
<th>OB</th>
<th>VOD (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>225°C</td>
<td>250°C</td>
<td>275°C</td>
<td>300°C</td>
<td>325°C</td>
</tr>
<tr>
<td>N-MAN</td>
<td>DNI</td>
<td>128±2</td>
<td>87±2</td>
<td>70±1.3</td>
<td>56.3±1.1</td>
</tr>
<tr>
<td>N,N-DMAN</td>
<td>DNI</td>
<td>125±2</td>
<td>61.3±2.9</td>
<td>55±3.3</td>
<td>44.6±0.6</td>
</tr>
<tr>
<td>N-MAP</td>
<td>DNI</td>
<td>114±6.6</td>
<td>82.3±1.5</td>
<td>63.6±1.1</td>
<td>54.3±2.2</td>
</tr>
<tr>
<td>N,N-DMAP</td>
<td>DNI</td>
<td>96.3±3</td>
<td>73.6±2.4</td>
<td>59.3±1.5</td>
<td>49±1.3</td>
</tr>
</tbody>
</table>

Figure 5 — Kinetic analysis of N-MAN, N,N-DMAN, N-MAP and N,N-DMAP by parabolic law

Ignition Delay and Ignition Temperature Measurements

Twenty milligram of the sample was taken in an ignition tube (h = 5 cm and diam = 0.4 cm) and the time between the insertion of the sample tube in the crucible is observed by the inbuilt microbalance. The weight of the sample is displayed in the monitor of the computer continuously along with the temperature. The thermograms (Figure 4) were recorded at a heating rate of 15°C/min and peak temperatures from DTA and DTG plots are given in Table 2.
Results and Discussions

It is evident from TG curves (in static air) presented in Figure 1 that N-MAN, N,N-DMAN and N-MAP show weight loss (\(\epsilon\)) up to 60-70 per cent except N,N-DMAP, which explode at 266 °C. Scheme 2 represents that all these salts, except N,N-DMAP undergo thermolysis which involves N-H bond heterolysis (proton transfer)\(^{17}\) via an activated complex to form parent amine and acid molecule in condensed phase. The latter then undergo oxidation-reduction reactions to yield gaseous products and carbonaceous residue. The former explode at 266 °C.

The kinetics of thermal decomposition of these salts were evaluated using nine mechanism based kinetic models\(^{14-16}\). Out of the nine-kinetic models tested, only the parabolic law (Eq. 1) was found to fit the TG data (Figure 6). The rate constants (\(k\)), activation energy (\(E_a\)) and correlation coefficients (\(r\)) are reported in Table 4. The value of activation energies for N-methyl substituted salts were higher than the N,N-DMAP.

Scheme 2 - Schematic representation of N-Methylanilinium and N,N-Dimethylanilinium Nitrates and Perchlorates.

\[ t_{ig} = B \exp \left(\frac{E^*}{RT}\right) \]  
\[ \text{OB} = \frac{[(x - 2y - 2)100]}{n} \]  
\[ \text{VOD} = 8578 + 33.74 \times \text{OB} \]
Table 4 – Rate constant (k), correlation coefficient (r) and activation energy (Ea) for thermal decomposition of N-methylanilinium and N,N-dimethylanilinium nitrates and perchlorates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parabolic law (a²) equation rate constant (k x 10⁻³ min⁻¹) (°K)</th>
<th>r</th>
<th>Ea (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-MAN</td>
<td>37.06 (408), 16.97 (423), 10.92 (438)</td>
<td>0.9912</td>
<td>68.4</td>
</tr>
<tr>
<td>N, N-DMAN</td>
<td>1.16 (408), 1.98 (423), 4.21 (438)</td>
<td>0.9735</td>
<td>48.6</td>
</tr>
<tr>
<td>N-MAP</td>
<td>0.85 (448), 1.35 (463), 2.09 (473)</td>
<td>0.9978</td>
<td>62.2</td>
</tr>
<tr>
<td>N, N-DMAP</td>
<td>0.84 (448), 1.26 (463), 2.00 (473)</td>
<td>0.9962</td>
<td>57.4</td>
</tr>
</tbody>
</table>

Figure 6 – Plots of log tₐ vs 1/T(°K) for N-MAN, N,N-DMAN, N-MAP and N,N-DMAP

than the N,N-dimethyl derivatives. This may be due to the strong steric hindrance of methyl groups though they have strong inductive effect.

Although these salts are stable at room temperature and ignite when subjected to a sudden high temperature (>225 °C for nitrates and >250 °C for perchlorates). Therefore, it was of interest to undertake rapid thermolysis (ignition delay studies) of these salts. However not much difference was observed in ignition temperatures.

Oxygen balance and VOD (Table 3) of perchlorates are high which indicates that they are more prone to ignition than nitrates. A linear relationships were obtained when E* and VOD plotted against Td (Figure 7).

It can be concluded that thermolysis involves competitive decomposition reaction paths. The proton transfer seems to control the decomposition of these salts and free radicals are predominantly involved in thermal reactions induced by heat energy.

Figure 7 – Plots of E* and VOD vs Td (°C)

Acknowledgements

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References