Decomposition Pathways for Aqueous Hydroxylammonium Nitrate Solutions: a DFT Study

Yu-ichiro Izato,* Mitsuo Koshi, Atsumi Miyake

Yokohama National University,
79-7 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama
(KANAGAWA), Japan
*E-mail: izato-yuichiro-hk@ynu.jp

Abstract: Hydroxylammonium nitrate (hydroxylamine nitrate, HAN) is one of the most promising candidates as a replacement for commonly used liquid mono-propellants such as hydrazine. The reaction pathways involved in the initial and the catalytic decomposition of HAN in aqueous solution were determined using quantum chemistry calculations incorporating solvent effects. Optimized structures were obtained for the reactants, products and transition states at the ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory and the total electron energies of these structures were calculated at the CBS-QB3 level of theory. In the initial decomposition, the ion-neutral NH$_3$OH$^-$-HNO$_3$ reaction, the neutral-neutral NH$_3$O-HNO$_3$ reaction and the HNO$_3$ self-decomposition pathways were all found to have reasonable energy barriers, with values of 91.7 kJ/mol, 88.7 kJ/mol and 89.8 kJ/mol, respectively. The overall reaction resulting from any of these pathways can be written as: HAN → HONO + HNO + H$_2$O. The ionic reaction is dominant during the initial decomposition of HAN in aqueous solution because NH$_2$OH$^-$ and NO$_3^-$ are the major species in such solutions. We also developed six catalytic mechanisms and each of these schemes provided the same global reaction: NH$_2$OH + HONO → N$_2$O + 2H$_2$O. The ρ-ONONO$_2$ oxidizing scheme is the most plausible based on the energy barrier results.

Keywords: hydroxylamine nitrate, reaction pathway, liquid-phase reaction, density functional theory
1 Introduction

Hydroxylammonium nitrate (hydroxylamine nitrate, HAN), having the chemical formula $[\text{NH}_3\text{OH}]^+[\text{NO}_3]^-$, is one of the most promising candidates as a replacement for commonly used liquid mono-propellants such as hydrazine [1-3]. As such, there have been many experimental and theoretical studies concerning the combustion behaviour of the so-called next generation HAN-based propellants [4-11]. Previous research has demonstrated that some HAN-based solutions exhibit extremely high burning rates, and this property has limited the usefulness of such solutions in certain applications [3-6] because overly high burning rates can sometimes lead to serious accidents [12-14]. Therefore, the development of advanced techniques to control the combustion of HAN-based propellants is essential.

A detailed chemical reaction model is a helpful step in any investigation of rapid transient phenomena such as propellant ignition and flame extinction. Khare et al. [15] studied the ignition behaviour of HAN/water solutions and developed a theoretical model incorporating gas [16, 17] and condensed phase reactions that include electrolysis of ionic liquids and the Lee and Litzinger model [18]. This prior work calculated the ignition delay of aqueous HAN solutions using the model and discussed the appropriateness of electrolytically-induced ignition systems for HAN-based propellants. The Lee and Litzinger model [18] consists of the following eight reactions:

\begin{align*}
\text{HAN} + \text{H}_2\text{O} & \rightleftharpoons \text{NH}_2\text{OH} + \text{HNO}_3 + \text{H}_2\text{O} \\ 
\text{NH}_2\text{OH} + \text{HNO}_3 & \rightleftharpoons \text{HONO} + \text{HNO} + \text{H}_2\text{O} \\ 
\text{NH}_2\text{OH} + \text{HONO} & \rightleftharpoons \text{N}_2\text{O} + 2\text{H}_2\text{O} \\ 
2\text{HNO} & \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O} \\ 
\text{NH}_2\text{OH} + \text{HNO} & \rightleftharpoons \text{N}_2 + 2\text{H}_2\text{O} \\ 
3\text{HONO} & \rightleftharpoons 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O} \\ 
\text{HNO} + \text{HNO}_3 & \rightleftharpoons 2\text{HONO} \\ 
\text{HONO} + \text{HNO}_3 & \rightleftharpoons 2\text{NO}_2 + \text{H}_2\text{O}
\end{align*}

Lee and Litzinger [18] developed a reduced reaction model based on previously proposed reaction mechanisms [19, 20], and were able to predict the reaction rates by simulating the experimental decomposition process and applying an inverse analysis technique.

The aim of the present study was to gain a better understanding of the chemical reactions of HAN during its initial and catalytic decomposition, and to develop a detailed reaction model on the basis of an \textit{ab initio} study. To this
end, we conducted thermal assessments using *ab initio* quantum chemistry calculations, which are helpful with regard to determining which reactions can be excluded from the mechanism based on thermodynamic arguments. As an example, if a reaction is found to be highly endothermic, or considerably more endothermic than a competing pathway, then that reaction may be safely omitted from the mechanism. This paper presents a detailed reaction scheme for HAN decomposition.

2 Computational

The geometries of the reactants, products, and transition states were optimized at the ωB97XD/6-311++G(d,p) level [21] of theory using the Gaussian 09 program package [22]. Gordon *et al.* [21] developed the ωB97XD method, which includes empirical dispersion forces and is believed to be reliable when applied to systems with weak van der Waals forces. This group also reported that the ωB97XD method yields satisfactory accuracy for kinetics and non-covalent interactions. During the computations, transition states (TSs) were extensively searched for, and, if found, an intrinsic reaction coordinate (IRC) calculation was conducted in order to assign reactants and products to the TS. The energies of the corresponding molecules were evaluated at the CBS-QB3 [23] level of theory, since this is a reasonable time-expense complete basis method. In this study, the geometries and frequencies were calculated at the ωB97XD/6-311++G(d,p) level, the optimized geometries were fixed with no changes allowed and the energies were calculated using the CBS-QB3 method. Solvent effects were included by applying the self-consistent reaction field (SCRF) and polarizable continuum model (PCM) options [24] within the program when investigating the liquid reactions in water.

3 Results and Discussion

Important reactions occurring in the HAN decomposition and the associated energy barriers and energy changes calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory are summarized in Tables 1 and 2. Figure 1 depicts the important chemical species during the decomposition.
Table 1. Important reactions in the decomposition of HAN with thermodynamic parameters calculated at the \( \omega \text{B97XD/6-311++G(d,p)/SCRF} = (\text{solvent} = \text{water}) \) and CBS-QB3//\( \omega \text{B97XD/6-311++G(d,p)/SCRF} = (\text{solvent} = \text{water}) \) levels of theory

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>( \omega \text{B97XD/6-311++G(d,p)} )</th>
<th>CBS-QB3//( \omega \text{B97XD/6-311++G(d,p)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \Delta E_0^{(1)} )</td>
<td>( \Delta E_0^{(2)} )</td>
</tr>
<tr>
<td>R1</td>
<td>( \text{HNO}_3 \rightleftharpoons \text{OH} + \text{NO}_2 )</td>
<td>no TS</td>
<td>192.3</td>
</tr>
<tr>
<td>R2</td>
<td>( \text{NH}_2\text{OH} + \text{HNO}_3 \rightleftharpoons \text{NH}_2(\text{O})\text{OH} + \text{HNO}_2 ) (TS1)</td>
<td>183.1</td>
<td>73.0</td>
</tr>
<tr>
<td>R3</td>
<td>( \text{NH}_2\text{OH} + \text{HNO}_3 \rightleftharpoons \text{NH}_2(\text{O})\text{NO}_2 + \text{H}_2\text{O} ) (TS2)</td>
<td>125.1</td>
<td>-13.9</td>
</tr>
<tr>
<td>R4</td>
<td>( \text{NH}_2(\text{O})\text{NO}_2 \rightleftharpoons \text{HONO} + \text{HNO} ) (TS3)</td>
<td>51.3</td>
<td>-15.4</td>
</tr>
<tr>
<td>R5</td>
<td>( \text{NH}_2(\text{O})\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONO} + \text{HNO} ) (TS4)</td>
<td>7.0</td>
<td>-15.4</td>
</tr>
<tr>
<td>R6</td>
<td>( \text{NH}_3 + \text{HNO}_3 \rightleftharpoons \text{NH}_2(\text{O})\text{NO}_2 + \text{H}_2\text{O} ) (TS5)</td>
<td>91.9</td>
<td>-55.3</td>
</tr>
<tr>
<td>R7</td>
<td>( \text{NH}_2\text{ONO}_2 \rightleftharpoons \text{HONO} + \text{HNO} ) (TS6)</td>
<td>57.2</td>
<td>-24.9</td>
</tr>
<tr>
<td>R8</td>
<td>( \text{NH}_2\text{ONO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONO} + \text{HNO} ) (TS7)</td>
<td>31.2</td>
<td>-24.9</td>
</tr>
<tr>
<td>R9</td>
<td>( \text{NH}_2(\text{O})^+ + \text{HNO}_3 \rightleftharpoons [\text{NH}_2\text{OH-NO}_2-\text{H}_2\text{O}]^+ ) (TS8A)</td>
<td>95.1</td>
<td>91.9</td>
</tr>
<tr>
<td>R10</td>
<td>( [\text{NH}_2\text{OH-NO}_2-\text{H}_2\text{O}]^+ \rightleftharpoons \text{NH}_2(\text{OH})\text{NO}_2^+ + \text{H}_2\text{O} ) (TS8B)</td>
<td>15.1</td>
<td>-59.6</td>
</tr>
<tr>
<td>R11</td>
<td>( \text{NH}_2(\text{O})^+ + \text{HNO}_3 \rightleftharpoons [\text{NH}_2\text{OH-NO}_2-\text{H}_2\text{O}]^+ ) (TS9A)</td>
<td>94.1</td>
<td>91.1</td>
</tr>
<tr>
<td>R12</td>
<td>( [\text{NH}_2\text{OH-NO}_2-\text{H}_2\text{O}]^+ \rightleftharpoons \text{NH}_2(\text{OH})\text{NO}_2^+ + \text{H}_2\text{O} ) (TS9B)</td>
<td>9.9</td>
<td>-58.8</td>
</tr>
<tr>
<td>R13</td>
<td>( \text{NH}_2(\text{OH})\text{NO}_2^+ + \text{NO}_3^- \rightleftharpoons \text{NH}(\text{OH})\text{NO}_2 + \text{HNO}_3 )</td>
<td>no TS</td>
<td>-124.0</td>
</tr>
<tr>
<td>R14</td>
<td>( \text{NH}(\text{OH})\text{NO}_3 \rightleftharpoons \text{NH}(\text{O})\text{N}(\text{O})\text{OH} ) (TS10)</td>
<td>77.4</td>
<td>76.6</td>
</tr>
<tr>
<td>R15</td>
<td>( \text{NH}(\text{O})\text{N}(\text{O})\text{OH} \rightleftharpoons \text{HONO} + \text{HNO} ) (TS11)</td>
<td>63.5</td>
<td>-18.8</td>
</tr>
<tr>
<td>R16</td>
<td>( \text{NH}(\text{OH})\text{NO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}(\text{O})\text{N}(\text{O})\text{OH} + \text{H}_2\text{O} ) (TS12)</td>
<td>60.2</td>
<td>76.6</td>
</tr>
<tr>
<td>R17</td>
<td>( \text{NH}(\text{OH})\text{NO}_3 \rightleftharpoons \text{NH}_2(\text{O})\text{NO}_2 ) (TS13)</td>
<td>237.1</td>
<td>73.1</td>
</tr>
<tr>
<td>R18</td>
<td>( \text{NH}(\text{OH})\text{NO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_2(\text{O})\text{NO}_2 + \text{H}_2\text{O} ) (TS14)</td>
<td>114.4</td>
<td>73.1</td>
</tr>
<tr>
<td>R19</td>
<td>( \text{HNO}_3 + \text{HNO}_3 \rightleftharpoons \text{N}_2\text{O}_5 + \text{H}_2\text{O} ) (TS15)</td>
<td>91.6</td>
<td>52.9</td>
</tr>
<tr>
<td>R20</td>
<td>( \text{NH}_2(\text{OH}) + \text{N}_2\text{O}_5 \rightleftharpoons \text{NH}_2\text{O-NO}_3 + \text{HNO}_3 + \text{H}_2\text{O} ) (TS16)</td>
<td>11.2</td>
<td>-140.0</td>
</tr>
<tr>
<td>R21</td>
<td>( \text{NH}_2(\text{OH})^+ + \text{N}_2\text{O}_5 \rightleftharpoons \text{NH}_2\text{OH-NO}_3^+ + \text{HNO}_3 + \text{H}_2\text{O} ) (TS17)</td>
<td>64.6</td>
<td>-20.6</td>
</tr>
</tbody>
</table>

1 Energy barrier in the forward direction [kJ/mol]; 2 Total energy change of reaction [kJ/mol]

Copyright © 2017 Institute of Industrial Organic Chemistry, Poland
Table 2. Important reactions in the HAN/HONO catalytic decomposition with thermodynamic parameters calculated at the ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) and CBS-QB3/ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) levels of theory

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>ωB97XD/6-311++G(d,p)</th>
<th>CBS-QB3/ωB97XD/6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\Delta E_0) (^1)</td>
<td>(\Delta E_0) (^2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta rE_0) (^1)</td>
<td>(\Delta rE_0) (^2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta E_0) (^1)</td>
<td>(\Delta E_0) (^2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta rE_0) (^1)</td>
<td>(\Delta rE_0) (^2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta E_0) (^1)</td>
<td>(\Delta E_0) (^2)</td>
</tr>
<tr>
<td>R22</td>
<td>(\text{NH}_2\text{OH} + \text{HONO} \rightleftharpoons \text{NH}_2(\text{O})\text{NO} + \text{H}_2\text{O}) (TS18)</td>
<td>64.9</td>
<td>45.2</td>
</tr>
<tr>
<td>R23</td>
<td>(\text{NH}_2(\text{O})\text{NO} \rightleftharpoons 2\text{HNO}) (TS19)</td>
<td>103.4</td>
<td>49.4</td>
</tr>
<tr>
<td>R24</td>
<td>(\text{NH}_2\text{OH} + \text{HONO} \rightleftharpoons [\text{NH}(\text{OH})-\text{ON}] + \text{H}_2\text{O}) (TS20)</td>
<td>157.9</td>
<td>144.3</td>
</tr>
<tr>
<td>R25</td>
<td>([\text{NH}(\text{OH})-\text{ON}] \rightleftharpoons 2\text{HNO}) (TS21)</td>
<td>-5.5</td>
<td>-49.7</td>
</tr>
<tr>
<td>R26</td>
<td>(\text{NH}_2\text{OH}^+ + \text{HONO} \rightleftharpoons [\text{NH}_2\text{OH}-\text{NO-H}_2\text{O}]^+) (TS22A)</td>
<td>21.2</td>
<td>26.0</td>
</tr>
<tr>
<td>R27</td>
<td>([\text{NH}_2\text{OH}-\text{NO-H}_2\text{O}]^+ \rightleftharpoons \text{NH}_2(\text{OH})\text{NO} + \text{H}_2\text{O}) (TS22B)</td>
<td>17.7</td>
<td>-8.3</td>
</tr>
<tr>
<td>R28</td>
<td>(\text{NH}_2\text{OH}^+ + \text{HONO} \rightleftharpoons [\text{NH}_2\text{OH}-\text{NO-H}_2\text{O}]^+) (TS23A)</td>
<td>22.6</td>
<td>24.9</td>
</tr>
<tr>
<td>R29</td>
<td>([\text{NH}_2\text{OH}-\text{NO-H}_2\text{O}]^+ \rightleftharpoons \text{NH}_2(\text{OH})\text{NO}^+ + \text{H}_2\text{O}) (TS23B)</td>
<td>15.5</td>
<td>-7.2</td>
</tr>
<tr>
<td>R30</td>
<td>(\text{NH}_2(\text{OH})\text{NO}^+ + \text{NH}_2\text{OH} \rightleftharpoons \text{NH}(\text{OH})\text{NO} + \text{NH}_2\text{OH}^+)</td>
<td>no TS</td>
<td>-85.9</td>
</tr>
<tr>
<td>R31</td>
<td>(\text{NH}_2(\text{OH})\text{NO}^+ + \text{NO}_3^- \rightleftharpoons \text{NH}(\text{OH})\text{NO} + \text{HNO}_3)</td>
<td>no TS</td>
<td>-90.5</td>
</tr>
<tr>
<td>R32</td>
<td>(\text{NH}(\text{OH})\text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{H}_2\text{O}) (TS24)</td>
<td>234.1</td>
<td>-209.6</td>
</tr>
<tr>
<td>R33</td>
<td>(\text{NH}(\text{OH})\text{NO} + \text{H}_2\text{O} \rightleftharpoons \text{N}_2\text{O} + 2\text{H}_2\text{O}) (TS25)</td>
<td>94.8</td>
<td>-209.6</td>
</tr>
<tr>
<td>R34</td>
<td>(\text{HNO}_3 + \text{HONO} \rightleftharpoons t-\text{ONONO}_2 + \text{H}_2\text{O}) (TS26)</td>
<td>11.2</td>
<td>10.3</td>
</tr>
<tr>
<td>R35</td>
<td>(\text{HNO}_3 + \text{HONO} \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O}) (TS27)</td>
<td>124.1</td>
<td>-20.1</td>
</tr>
<tr>
<td>R36</td>
<td>(\text{NH}_2\text{OH} + t-\text{ONONO}_2 \rightleftharpoons \text{NH}_2(\text{O})\text{NO} + \text{HNO}_3) (TS28)</td>
<td>-48.4</td>
<td>-78.5</td>
</tr>
<tr>
<td>R37</td>
<td>(\text{NH}_2\text{OH} + t-\text{ONONO}_2 \rightleftharpoons \text{NH}_2(\text{OH})\text{NO}^+ + \text{H}_2\text{O}) (TS29)</td>
<td>42.1</td>
<td>7.4</td>
</tr>
<tr>
<td>R38</td>
<td>(\text{HONO} + \text{HONO} \rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O}) (TS30)</td>
<td>45.3</td>
<td>-6.3</td>
</tr>
<tr>
<td>R39</td>
<td>(\text{NH}_2\text{OH} + \text{N}_2\text{O}_3 \rightleftharpoons [\text{NH}_2(\text{O})\text{NO-HONO}]) (TS31A)</td>
<td>-1.0</td>
<td>26.1</td>
</tr>
<tr>
<td>R40</td>
<td>([\text{NH}_2(\text{O})\text{NO-HONO}] \rightleftharpoons \text{NH}(\text{OH})\text{NO} + \text{HNO}_2) (TS31B)</td>
<td>-31.3</td>
<td>-67.6</td>
</tr>
<tr>
<td>R41</td>
<td>(\text{NH}_2\text{OH}^+ + \text{N}_2\text{O}_3 \rightleftharpoons [\text{NH}_2(\text{OH})\text{NO-HONO}]^+) (TS32A)</td>
<td>25.9</td>
<td>31.3</td>
</tr>
<tr>
<td>R42</td>
<td>([\text{NH}_2(\text{OH})\text{NO-HONO}]^+ \rightleftharpoons \text{NH}_2(\text{OH})\text{NO}^+ + \text{HONO}) (TS32B)</td>
<td>24.1</td>
<td>-7.3</td>
</tr>
</tbody>
</table>

1 Energy barrier in the forward direction [kJ/mol]; 2 Total energy change of reaction [kJ/mol].

Reaction R1 in Table 1 is the HO–N bond cleavage of HNO₃ and, following this cleavage, a high speed radical chain reaction develops. Since the activation energy for the homolysis of HNO₃ is very high (205.0 kJ/mol) this represents the rate-controlling step for the radical chain reaction. Therefore, reactions that have a higher energy barrier value than that for cleavage of HNO₃ are omitted as candidates for the thermal decomposition reaction of HAN in the condensed phase.
3.1 The initial decomposition

3.1.1 The neutral-neutral reaction of NH$_2$OH and HNO$_3$

This work identified and investigated three neutral-neutral reaction pathways, two of which begin with neutral NH$_2$OH and HNO$_3$ molecules. These two pathways are associated with the following chemical reactions:

\[ \text{NH}_2\text{OH} + \text{HNO}_3 \rightarrow \text{NH}_2(\text{O})\text{OH} + \text{HNO}_2 \]  \hspace{1cm} (R2)

\[ \text{NH}_2\text{OH} + \text{HNO}_3 \rightarrow \text{NH}_2(\text{O})\text{NO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (R3)

Figure 2 shows the potential energy profiles for these two initial reactions, including the optimized structures of the transition states (TSs) and intermediate complexes. In the mechanism that proceeds via TS1, cleavage of the N–OH bond in HNO$_3$ triggers its decomposition and the resulting OH combines with NH$_2$OH to form NH$_2$(OH)$_2$ as the TS. The remaining NO$_2$ species then removes an H from the NH$_2$(OH)$_2$ to generate NH$_2$(O)OH and HNO$_2$. The energy barrier for this process was calculated to be 186.5 kJ/mol at the CBS-QB3/$\omega$B97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.
Figure 2. Potential energy profiles* for the bimolecular reaction of NH₂OH and HNO₃

*The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

In the mechanism that proceeds via TS2, decomposition also begins with cleavage of the N–OH bond in HNO₃, such that the HNO₃ decomposes to OH and NO₂. The OH subsequently subtracts H from NH₂OH to form TS2, while the dissociated NO₂ combines with the −NH₂ group in the dehydrogenated NH₂O to form NH₂(O)NO₂. The associated energy barrier was determined to be 124.8 kJ/mol. Hence, the R3 process is preferable to R2 on a thermodynamic basis because its energy barrier is lower.

We also investigated the decomposition of NH₂(O)NO₂, the product of R3, which proceeds via the following reaction:

\[
\text{NH₂(O)NO₂} \rightarrow \text{HONO} + \text{HNO} \quad (\text{R4})
\]

The schematic potential energy profiles of the two possible reaction pathways and optimized structures for the reactants, TSs and products are shown in Figure 3. In one path, NH₂(O)NO₂ decomposes to HONO and HNO by intramolecular H transfer to generate TS3, with an energy barrier of 53.1 kJ/mol. In another pathway (R5), water molecules assist in the intramolecular proton transfer (a common effect in many reactions) such that TS4 has a ring structure. In this second scenario, the water catalytic effect decreases the energy barrier to 17.0 kJ/mol. Often in such calculations, the TS in the absence of an explicit solvent effect involves a highly strained ring since the strained ring structure is
necessary to transfer the H from one position in the molecule to another. The result is typically a highly energetic barrier to the reaction. The inclusion of solvent molecules allows the ring structure to be larger in size, thus reducing the ring strain and lowering the transition state energy compared to that required for a smaller cyclic transition state structure. Because both energy barrier heights of the R4 and R5 pathways are much lower than that for R3, the rate determining step is believed to be R3. Although the energy barrier values determined for this neutral-neutral bimolecular reaction are lower than that for HNO₃ cleavage, these values are still much higher than those associated with other mechanisms, as discussed later.

Figure 3. Potential energy profiles* for the decomposition of the intermediate species NH₂(O)NO₂
*The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

3.1.2 The neutral-neutral reaction of NH₃O and HNO₂
Some theoretical calculations have predicted that the NH₃O isomer is sufficiently stable to be kinetically relevant and may play a key role in many reactions of HAN in aqueous solution [25-28]. Felnadez et al. [26] calculated the value for the tautomeric equilibrium between NH₂OH and NH₃O⁻ in aqueous solution to be Kₖ = ([NH₃O⁻][/NH₂OH]) = 2.6 × 10⁻², and this isomerization mechanism has been fully investigated on the basis of ab initio calculations [27, 28]. We therefore identified and investigated a reaction involving NH₃O and a subsequent reaction as follows:
\[ \text{NH}_3\text{O} + \text{HNO}_3 \rightarrow \text{NH}_2\text{ONO}_2 + \text{H}_2\text{O} \] \hspace{2cm} (R6)

\[ \text{NH}_2\text{ONO}_2 (+ \text{H}_2\text{O}) \rightarrow \text{HONO} + \text{HNO} (+ \text{H}_2\text{O}) \] \hspace{2cm} (R7, R8)

Figure 4 depicts the potential energy profile and the optimized structure for the TS and intermediates for this pathway. The decomposition begins with cleavage of the N–OH bond of HNO\(_3\), following which the dissociated OH abstracts H from NH\(_3\)O while the NO\(_2\) simultaneously combines with the O– of NH\(_2\)O to form TS5. This series of reactions is exothermic and generates H\(_2\)O and NH\(_2\)ONO\(_2\) with an energy barrier of 88.7 kJ/mol.

**Figure 4.** Potential energy profile\(^*\) for the bimolecular reaction of NH\(_3\)O and HNO\(_3\)

\(^*\)The energy profile was calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

Figure 5 presents the potential energy profiles and the optimized structures for the decomposition of the intermediate species NH\(_2\)ONO\(_2\). Here, NH\(_2\)ONO\(_2\) decomposes to HONO and HNO by intramolecular H transfer and the presence of water assists this process (R8), just as in R4. The energy barrier was found to be 88.6 kJ/mol, so R6 is considered to be the rate determining step. The maximum energy barrier of the pathway involving NH\(_3\)O is the lowest of all of the neutral-neutral bimolecular pathways shown above, indicating that NH\(_3\)O plays an important role in HAN decomposition.
3.1.3 The ion-neutral reaction of NH$_3$OH$^+$ and HNO$_3$

In aqueous solution, HAN typically dissociates to form the ion pair NH$_3$OH$^+$ and NO$_3^−$. This work therefore examined reactions involving NH$_3$OH$^+$ as described below. It should be noted that we were unable to identify any plausible reactions starting with NO$_3^−$ in this study. Figure 6 shows the potential energy profiles and optimized structures for this pathway. This reaction starts with a proton transfer from NH$_3$OH$^+$ to HNO$_3$, after which the protonated H$_2$NO$_3^+$ decomposes to H$_2$O and NO$_2^+$. The NO$_2^+$ then combines with NH$_2$OH to form NH$_2$(OH)NO$_2^+$. The energy barrier was calculated to be 94.2 kJ/mol. The resulting NH$_2$(OH)NO$_2^+$ is evidently deprotonated by NO$_3^−$, which is plentiful in aqueous HAN solutions, to give NH(OH)NO$_2$. Thus, the reaction process eventually yields NH(OH)NO$_2$ and H$_2$O, along with a heat output of 106 kJ/mol.
Figure 6. Potential energy profiles* for the bimolecular reaction of NH$_3$OH$^+$ and HNO$_3$

*The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

We also assessed the decomposition of the intermediate NH(OH)NO$_2$ as described below.

\[
\text{NH}_3\text{OH}^+ + \text{HNO}_3 \rightarrow \text{NH}_2(\text{OH})\text{NO}_2^+ + \text{H}_2\text{O} \quad \text{(R9, R11)}
\]

Figure 7 depicts the potential energy profiles and optimized structures for the decomposition of NH(OH)NO$_2$. The decomposition pathways can be roughly separated into two groups. The first consists of pathways that proceed via NH(OH)N(O)OH. Here, NH(OH)NO$_2$ transitions to NH(OH)N(O)OH via an intermolecular H transfer from −OH to NO$_2$ to give TS10, after which the N–N bond in NH(OH)N(O)OH undergoes cleavage to generate HONO and HNO, giving TS14. The other group involves pathways that progress via NH$_2$(O)NO$_2$. NH(OH)NO$_2$ transitions to NH$_2$(O)NO$_2$ by intramolecular H transfer from an −OH to an −NH$_2$ group to give TS13. The decomposition of NH$_2$(O)NO$_2$ has already been discussed above. The presence of water assists both reactions leading to TS12 and TS14. The intramolecular H transfer reaction R17 has a very large energy barrier of 233.1 kJ/mol, and this reaction requires the presence of water to proceed.
Figure 7. Potential energy profiles* for the decomposition of the intermediate NH(OH)NO$_2$.*The energy profiles were calculated at the CBS-QB3/ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

3.1.4 The self-decomposition of HNO$_3$

Two molecules of HNO$_3$ may decompose to yield N$_2$O$_5$ and H$_2$O as follows:

\[
\text{HNO}_3 + \text{HNO}_3 \rightarrow \text{N}_2\text{O}_5 + \text{H}_2\text{O} \quad (R19)
\]

The same type of reaction in the gas phase was theoretically investigated previously [29]. We examined this self-decomposition reaction and the subsequent processes and Figure 8 depicts the potential energy profile and optimized structures. The energy barrier and heat of reaction were determined to be 89.8 kJ/mol. This reaction starts with a proton transfer from one HNO$_3$ to the other. The protonated H$_2$NO$_3^+$ subsequently decomposes to H$_2$O and NO$_2^+$ and the NO$_2^+$ binds to the deprotonated NO$_3^-$ to form N$_2$O$_5$.

Figure 8. Potential energy profile* for the self-decomposition of HNO$_3$.*The energy profile was calculated at the CBS-QB3/ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory
NH$_2$OH + N$_2$O$_5$ → NH$_2$ONO$_2$ + HNO$_3$ \hspace{1cm} (R20)
NH$_3$OH$^+$ + N$_2$O$_5$ → NH$_2$(OH)NO$_2^+$ + HNO$_3$ \hspace{1cm} (R21)

Figure 9 shows the potential energy profile for R20 and the optimized structures. The energy barrier was calculated as 27.5 kJ/mol. The neutral-neutral reaction of N$_2$O$_5$ and NH$_2$OH begins with the decomposition of N$_2$O$_5$ to NO$_2$ and NO$_3$^- and the resulting NO$_2$ immediately combines with NH$_2$OH to form NH$_2$(OH)NO$_2$ as TS16. The NO$_3$ removes an H from NH$_2$(OH)NO$_2$ to yield NH$_2$(O)NO$_2$ and HNO$_3$. The NH$_2$(O)NO$_2$ decomposition process has already been discussed above.

Figure 9. Potential energy profile* for the bimolecular reaction of NH$_2$OH and N$_2$O$_5$

The energy profile was calculated at the CBS-QB3/ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

Figure 10 depicts the potential energy profile for R21 along with the optimized structures. The energy barrier was determined to be 50.9 kJ/mol. The ion-neutral reaction of NH$_3$OH$^+$ and N$_2$O$_5$ starts with the decomposition of N$_2$O$_5$ to NO$_2^+$ and NO$_3^-$, which removes a proton from NH$_3$OH$^+$ to give HNO$_3$ and NH$_2$OH as TS17. The dissociated NO$_2^+$ combines with NH$_2$OH to yield NH$_2$(OH)NO$_2^+$. The decomposition of NH$_2$(OH)NO$_2^+$ has been discussed above.
Because the energy barrier associated with R19 is higher than those for R20 and R21, the rate determining step is believed to be R19.

### 3.1.5 The reaction scheme of initial decomposition of HAN

The schemes below summarize the sets of reactions investigated in this study.

**Scheme 1.** Neutral-neutral reaction mechanism I

\[
\begin{align*}
\text{HAN} + \text{H}_2\text{O} &\rightarrow \text{NH}_2\text{OH} + \text{HNO}_3 + \text{H}_2\text{O} \quad (1) \\
\text{NH}_2\text{OH} + \text{HNO}_3 &\rightarrow \text{NH}_2(\text{O})\text{NO}_2 + \text{H}_2\text{O} \quad (R3) \\
\text{NH}_2(\text{O})\text{NO}_2 (+ \text{H}_2\text{O}) &\rightarrow \text{HNO} + \text{HONO} (+ \text{H}_2\text{O}) \quad (R4, R5) \\
\text{HAN} &\rightarrow \text{HNO} + \text{HONO} + \text{H}_2\text{O} \quad (9)
\end{align*}
\]

**Scheme 2.** Neutral-neutral reaction mechanism II

\[
\begin{align*}
\text{HAN} + \text{H}_2\text{O} &\rightarrow \text{NH}_2\text{OH} + \text{HNO}_3 + \text{H}_2\text{O} \quad (1) \\
\text{NH}_2\text{OH} &\rightarrow \text{NH}_3\text{O} \quad (10) \\
\text{NH}_3\text{O} + \text{HNO}_3 &\rightarrow \text{NH}_2\text{ONO}_2 + \text{H}_2\text{O} \quad (R6) \\
\text{NH}_2\text{ONO}_2 (+ \text{H}_2\text{O}) &\rightarrow \text{HNO} + \text{HONO} (+ \text{H}_2\text{O}) \quad (R7, R8) \\
\text{HAN} &\rightarrow \text{HNO} + \text{HONO} + \text{H}_2\text{O} \quad (9)
\end{align*}
\]

**Scheme 3.** Ion-neutral reaction mechanism

\[
\begin{align*}
\text{HAN} &\rightarrow \text{NH}_3\text{OH}^+ + \text{NO}_3^- \quad (11) \\
\text{NH}_3\text{OH}^+ + \text{HNO}_3 &\rightarrow \text{NH}_2(\text{OH})\text{NO}_2^+ + \text{H}_2\text{O} \quad (R10)
\end{align*}
\]
NH₂(OH)NO₂⁺ + NO₃⁻ → NH(OH)NO₂ + HNO₃  \hspace{1cm} (R13)
NH(OH)NO₂ (+ H₂O) → NH(O)N(O)OH (+ H₂O) \hspace{1cm} (R14, R16)
NH(O)N(O)OH → HNO + HONO \hspace{1cm} (R15)
HAN → HNO + HONO + H₂O \hspace{1cm} (9)

**Scheme 4.** HNO₃ self-decomposition mechanism I

HAN + H₂O → NH₂OH + HNO₃ + H₂O \hspace{1cm} (1)
HNO₃ + HNO₃ → N₂O₅ + H₂O \hspace{1cm} (R19)
N₂O₅ + NH₂OH → NH₂(O)NO₂ + HNO₃ \hspace{1cm} (R20)
NH₂(O)NO₂ (+ H₂O) → HNO + HONO (+ H₂O) \hspace{1cm} (R4, R5)
HAN → HNO + HONO + H₂O \hspace{1cm} (9)

**Scheme 5.** HNO₃ self-decomposition mechanism II

HAN → NH₃OH⁺ + NO₃⁻ \hspace{1cm} (11)
HNO₃ + HNO₃ → N₂O₅ + H₂O \hspace{1cm} (R19)
N₂O₅ + NH₃OH⁺ → NH₂(O)NO₂⁺ + HNO₃ \hspace{1cm} (R20)
NH₂(OH)NO₂⁺ + NO₃⁻ → NH(OH)NO₂ + HNO₃ \hspace{1cm} (R13)
NH(OH)NO₂ (+ H₂O) → NH(O)N(O)OH (+ H₂O) \hspace{1cm} (R14, R16)
NH(O)N(O)OH → HNO + HONO \hspace{1cm} (R15)
HAN → HNO + HONO + H₂O \hspace{1cm} (9)

Regardless of the mechanism, the overall initial decomposition reaction can be written using one formula: HAN → HONO + HNO + H₂O. The maximum energy barrier values were 124.8 kJ/mol (Scheme 1), 88.7 kJ/mol (Scheme 2), 91.7 kJ/mol (Scheme 3) and 89.8 kJ/mol (Schemes 4 and 5). With regard to the energy barriers, Schemes 2, 3, 4 and 5 are all plausible. In water, HAN is known to primarily dissociate into the ion pair NH₃OH⁺ and NO₃⁻, so the concentrations of NH₂OH and HNO₃ will be low. In addition, the concentration of NH₃O will be less than that of NH₂OH based on the constant for the equilibrium between NH₂OH and NH₃O⁻ in aqueous solution: K₆ = ([⁺NH₃O⁻])/[NH₂OH]) = 2.6 × 10⁻² [26]. Therefore, we concluded that the ionic reaction represented by Scheme 3 is dominant during the initial HAN decomposition in a standard aqueous solution. However, the primary pathway will vary with the chemical states and concentrations of the species in HAN solutions. Under acidic conditions, for example, Scheme 5 might be more plausible than Scheme 3 due to the high concentration of HNO₃. Thus, these schemes should all be considered depending on the reaction conditions in order to develop an advanced reaction model capable of accurately predicting the combustion behaviour of this propellant system.

According to Lee and Litzinger [18], the activation energy, Eₐ, of the reaction
NH₂OH + HNO₃ → HONO + HNO + H₂O is 27.6 ±2.9 kJ/mol. This is much lower than the energy barrier values, ∆E₀, obtained from the present study. Lee and Litzinger obtained both Eₐ and frequency parameter values by an inverse analysis technique. Therefore, it is important to compare the magnitude of the rate coefficients. We calculated the rate coefficients using the transition state theory for the TSs and reactants investigated in this study. The rate coefficient from this study was much slower than the one from Ref. [18]. Detail kinetic modelling must be conducted in future work. Gowland and Stedman [30] experimentally obtained an Eₐ of 104.6 kJ/mol for the reaction between HNO₃ and NH₃OH⁺ in aqueous solution. This value is in good agreement with our calculated ∆E₀ of 91.7 kJ/mol. According to Brill et al. [31], “While the Eₐ values reported for the decomposition of aqueous HAN under different conditions vary significantly, modest confidence can still be placed in the fact that higher concentrations of HAN yield Eₐ in the 60-70 kJ/mol range, but Eₐ values above 100 kJ/mol are possible for lower concentrations.” In the future, the reaction pathways presented in this paper should therefore be validated by constructing a quantitative model and simulating the reaction behaviour of HAN/water solutions. The simulation will provide an explanation for variations in the activation energy under various conditions.

3.2 The catalytic decomposition of HAN/HONO

3.2.1 HONO + NH₂OH/NH₃OH⁺ reactions
We identified and investigated both the neutral-neutral reaction of HONO and NH₂OH and the ion-neutral reaction of HONO and NH₃OH⁺. Going from neutral NH₂OH and HONO molecules to products, two pathways were obtained, involving the following chemical reactions:

\[ \text{NH}_2\text{OH} + \text{HONO} \rightarrow \text{NH}_2(\text{O})\text{NO} + \text{H}_2\text{O} \text{ (TS18)} \] \hspace{2cm} (R22)
\[ \text{NH}_2(\text{O})\text{NO} \rightarrow 2\text{HNO} \text{ (TS19)} \] \hspace{2cm} (R23)
\[ \text{NH}_2\text{OH} + \text{HONO} \rightleftharpoons [\text{NH(OH)-ON}] + \text{H}_2\text{O} \text{ (TS20)} \] \hspace{2cm} (R24)
\[ [\text{NH(OH)-ON}] \rightleftharpoons 2\text{HNO} \text{ (TS21)} \] \hspace{2cm} (R25)

Figure 11 shows the potential energy diagram, including the optimized structures of the TSs and intermediate complexes of reactants and products for the neutral-neutral reaction of NH₂OH and HONO. In the mechanism that proceeds via TS18, hydrogen transfer from the OH group of NH₂OH to HONO triggers the bimolecular reaction and the H₂ONO with the added hydrogen subsequently dissociates to H₂O and NO via TS18, as shown in Figure 11. The dissociated
NO then combines with NH$_2$O to give NH$_2$(O)NO. The energy barrier to this process was calculated to be 74.9 kJ/mol.

**Figure 11.** Potential energy* diagram for the HONO-NH$_2$OH reaction
*The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

In the TS20 mechanism, the bimolecular reaction also starts with hydrogen transfer from NH$_2$OH to HONO, but the hydrogen dissociates from the NH$_2$ group in NH$_2$OH to give TS20 as shown in Figure 12. The HONO with the hydrogen subsequently dissociates to H$_2$O and NO, again *via* TS18. The energy barrier for this pathway was determined to be 171.2 kJ/mol. This value is much higher than that for R22 because the N–H bond is significantly stronger than the O–H bond. R24 and R25 are of less interest because the energy barrier for R24 is much higher than that for R22.

**Figure 12.** Potential energy* diagram for the decomposition of the intermediate NH$_2$(O)NO
*The energy profile was calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.
We also identified and investigated NH$_2$(O)NO decomposition through reaction R23. Figure 13 presents the potential energy diagram for the reaction and the optimized structures for the TS, reactant and products. Here NH$_2$(O) NO decomposes to two HNO molecules by intramolecular hydrogen transfer that proceeds through TS2. The energy barrier was calculated to be 80.4 kJ/mol. The resulting HNO is known to decompose to N$_2$O and H$_2$O in an exothermic reaction [8]. This series can be summarized as a single global reaction:

$$\text{NH}_2\text{OH} + \text{HONO} \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$$ (3)

In aqueous solution, HAN typically dissociates to form the ion pair NH$_3$OH$^+$ and NO$_3^-$ . We therefore also identified and investigated reactions related to NH$_3$OH$^+$ as follows:

$$\text{NH}_3\text{OH}^+ + \text{HONO} \rightarrow \text{NH}_2(\text{OH})\text{NO}^+ + \text{H}_2\text{O} \quad (\text{TS22 and 23})$$ (R26-R29)

$$\text{NH}_2(\text{OH})\text{NO}^+ + \text{NH}_3\text{OH} \rightarrow \text{NH}(\text{OH})\text{NO} + \text{NH}_3\text{OH}^+$$ (R30)

$$\text{NH}_2(\text{OH})\text{NO}^+ + \text{NO}_3^- \rightarrow \text{NH}(\text{OH})\text{NO} + \text{HNO}_3$$ (R31)

Figure 14 shows the potential energy diagram and the optimized TSs and intermediates for this pathway. Both reactions begin with proton transfer from NH$_3$OH$^+$ to HONO, and the protonated HONO subsequently decomposes to H$_2$O and NO$^+$ via TS22A or TS23A. The reactions yield similar intermediate
complexes, $[\text{NH}_2\text{OH}-\text{NO}-\text{H}_2\text{O}]^+$, to IM5A and IM6A. These intermediate complexes rearrange such that NO$^+$ combines with NH$_2$OH to yield NH$_2$(OH)NO$^+$ as TS22B and TS23B. The rate determining steps appear to be R26 and R28 because these represent the highest energy barriers in this series of reactions: 23.6 kJ/mol and 22.6 kJ/mol, respectively. NH$_2$(OH)NO$^+$ can be deprotonated to NH(OH)NO by NO$_3^-$ or NH$_2$OH, both of which are abundantly present in aqueous HAN solutions. This reaction eventually yields NH(OH)NO and H$_2$O with an exothermic heat of reaction of 106 kJ/mol. Because the associated reaction barriers are much lower than that for the decomposition, the exothermic reaction of NH$_3$OH$^+$ with HONO proceeds following the decomposition.

Figure 14. Potential energy$^*$ diagram for the decomposition of the intermediate NH(OH)NO$_2$

*The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

This work also investigated the decomposition of the intermediate NH(OH)NO as follows:

$$\text{NH(OH)NO} (+ \text{H}_2\text{O}) \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} (+ \text{H}_2\text{O}) \text{ (TS24, TS25)} \quad (R32, R33)$$

Figure 15 presents the associated potential energy diagram and the optimized structures for the TSs and intermediates. Here, water molecules assist the reaction, acting as hydrogen-transfer agents. Although the unimolecular
decomposition of NH(OH)NO has a high energy barrier of 222.3 kJ/mol, the presence of water decreases the barrier to 95.8 kJ/mol. This series of reactions can be written as one global reaction:

\[ \text{NH}_3\text{OH}^+ + \text{HONO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + \text{H}_3\text{O}^+ \]

**Figure 15.** Potential energy diagram for the HNO\(_3\)-HONO reaction
*The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

**3.2.2 \(\text{HNO}_3 + \text{HONO} \) reaction and \(\text{t-ONONO}_2 + \text{NH}_2\text{OH}/\text{NH}_3\text{OH}^+\) reactions**

HONO can react with not only NH\(_2\)OH but also HNO\(_3\). This work therefore identified reactions in the HNO\(_3\) + HONO system, the beginning of which can be represented by the following:

\[ \text{HNO}_3 + \text{HONO} \rightarrow \text{trans-ONONO}_2 + \text{H}_2\text{O} \quad \text{(TS26)} \quad \text{(R34)} \]
\[ \text{HNO}_3 + \text{HONO} \rightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O} \quad \text{(TS27)} \quad \text{(R35)} \]

Figure 16 shows the potential energy diagram and the optimized TS and intermediate structures. The energy barrier for R34 was calculated to be 11.4 kJ/mol. The reaction starts with the dissociation of OH from HONO and a subsequent proton transfer from HNO\(_3\) to HONO to give TS26. The dissociated NO\(^+\) combines with NO\(_3^-\) to form trans-ONONO\(_2\) (t-ONONO\(_2\)). R35 also involves a proton transfer, but from HONO to HNO\(_3\) to produce TS27. The energy barrier for R35 was 128.5 kJ/mol, a value that is much higher than that for R34. This higher barrier occurs because HONO is a weaker acid than HNO\(_3\). Consequently, R34 is much more likely than R35 on a thermodynamic basis.
Following the formation of t-ONONO\textsubscript{2}, there are two paths: a neutral reaction and an ionic reaction. We identified and investigated the following reactions:

\begin{align*}
\text{R36} & : \quad \text{NH}_2\text{OH} + \text{t-ONONO}_2 & \rightarrow & \text{NH(OH)}\text{NO} + \text{HNO}_3 \quad (\text{TS28}) \\
\text{R37} & : \quad \text{NH}_3\text{OH}^+ + \text{t-ONONO}_2 & \rightarrow & \text{NH}_2(\text{OH})\text{NO}^+ + \text{HNO}_3 \quad (\text{TS29})
\end{align*}

Figure 17. Potential energy\textsuperscript{*} diagram for the reaction of t-ONONO\textsubscript{2} with NH\textsubscript{3}OH\textsuperscript{+}
\textsuperscript{*}The energy profiles were calculated at the CBS-QB3//\omega B97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

Figure 17 presents the potential energy diagram for R36 and the optimized structures of the TS and intermediates. The neutral-neutral reaction of t-ONONO\textsubscript{2} and NH\textsubscript{2}OH begins with the decomposition of t-ONONO\textsubscript{2} to NO\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-}, after which the dissociated NO\textsuperscript{+} combines with NH\textsubscript{2}OH to form NH\textsubscript{2}(OH)NO\textsuperscript{+}, while the NO\textsubscript{3}\textsuperscript{-} immediately abstracts a proton from NH\textsubscript{2}(OH)NO\textsuperscript{+} to yield NH(OH) NO and HNO\textsubscript{3} (as TS28), as shown in Figure 17. The potential energy diagram demonstrates that this reaction has no barrier, meaning that the reaction proceeds.
exothermically to give NH(OH)NO and HNO₃ immediately after t-ONONO₂ has reacted with NH₂OH. The NH(OH)NO subsequently decomposes to N₂O and H₂O with a significant heat release, as in R32.

Figure 18 provides the potential energy diagram for R37 and the optimized TS and intermediate structures. The energy barrier height was determined to be 26.6 kJ/mol. The ionic reaction of NH₃OH⁺ and t-ONONO₂ starts with a proton transfer from NH₃OH⁺ to t-ONONO₂, after which the protonated t-ONONO₂ decomposes to HNO₃ and NO⁺, and the NO⁺ then combines with NH₂OH as TS29. The NH₂(OH)NO⁺ is deprotonated to yield NH(OH)NO in an exothermic reaction series corresponding to R36 and R37.

![Figure 18. Potential energy diagram for the self-decomposition reaction of HONO](image)

*The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311++G(d,p)/SCRF = (solvent = water) level of theory.

R36 and R37 have either no energy barrier or a lower barrier than R34 and therefore R34 is the rate determining step in this series of reactions.

3.2.3 HONO + HONO self-decomposition and N₂O₃ + NH₂OH/NH₃OH⁺ reactions

Two molecules of HONO may decompose to yield N₂O₃ and H₂O as follows:

\[
\text{HONO} + \text{HONO} \rightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O} \quad (\text{TS30})
\]

(R38)

We identified and investigated this self-decomposition reaction and Figure 19 shows the potential energy diagram and the associated optimized structures. The energy barrier and heat of reaction were calculated to be 50.4 kJ/mol. This reaction is initiated by a proton transfer from one HONO to the other. The
protonated H$_2$ONO$^+$ decomposes to H$_2$O and NO$^+$ and the NO$^+$ then combines with ONO$^-$ to form N$_2$O$_3$.

**Figure 19.** Potential energy$^*$ diagram for the reaction of N$_2$O$_3$ with NH$_2$OH

$^*$The energy profiles were calculated at the CBS-QB3//ωB97XD/6-311+G(d,p)/SCRF = (solvent = water) level of theory.

After the formation of N$_2$O$_3$, there are two possible paths: a neutral reaction and an ionic reaction that is the same as the one that follows the formation of t-ONONO$_2$. We identified and investigated reactions related to N$_2$O$_3$ as shown below.

\[
\begin{align*}
NH_2OH + N_2O_3 &\rightarrow NH_2ONO + HONO (TS31) \quad (R39, R40) \\
NH_3OH^+ + N_2O_3 &\rightarrow NH_2(OH)NO^+ + HONO (TS32) \quad (R41, R42)
\end{align*}
\]

Figure 20 presents the potential energy diagram for R39 and R40, and the optimized structures of the TSs and intermediates for these pathways. The neutral reaction of N$_2$O$_3$ and NH$_2$OH starts with the decomposition of N$_2$O$_3$ to NO$_2$ and NO, after which the NO$_2$ immediately abstracts a hydrogen from NH$_2$OH to form NH$_2$(O)NO and HONO as TS31A. The dissociated NO combines with NH$_2$O to form NH(OH)NO and HNO$_2$ as TS31B. The NH$_2$(O)NO decomposes to two HNO molecules according to R23. The potential energy diagram shows that this reaction has no barrier. Therefore this exothermic reaction proceeds immediately to yield NH(OH)NO and HNO$_2$ once N$_2$O$_3$ has attacked NH$_2$OH.
Figure 20. Potential energy profiles\(^*\) for the reaction of \( \text{N}_2\text{O}_3 \) with \( \text{NH}_3\text{OH}^+ \)
\(^*\)The energy profiles were calculated at the CBS-QB3//\(6-311++G(d,p)\) level of theory.

Figure 11 shows the potential energy diagram for R41 and R42, and the optimized structures. The maximum energy barrier was calculated to be 33.9 kJ/mol. The ionic reaction of \( \text{NH}_3\text{OH}^+ \) and \( \text{N}_2\text{O}_3 \) starts with the decomposition of \( \text{N}_2\text{O}_3 \) to \( \text{NO}^+ \) and \( \text{NO}_2^- \), after which the dissociated \( \text{NO}_2^- \) abstracts a proton from \( \text{NH}_3\text{OH}^+ \) to yield HONO and \( \text{NH}_2\text{OH} \) as TS32A. The dissociated \( \text{NO}^+ \) combines with \( \text{NH}_2\text{OH} \) to form \( \text{NH}_2(\text{OH})\text{NO}^+ \). R39-40 and R41-42 have either no energy barrier or a lower barrier than R38. We therefore concluded that R38 is the rate determining step in this series of reactions.

3.2.4 Reaction scheme of HAN/HONO catalytic decomposition
Various sets of HONO-catalyzed reactions were investigated in this study based on the above results. We divided the HAN-HONO reactions into three groups according to the oxidizer that attacks \( \text{NH}_2\text{OH} \) or \( \text{NH}_3\text{OH}^+ \). These oxidizers were: HONO (Schemes 1 and 2), \( t\)-ONONO\(_2\) (Schemes 3 and 4) and \( \text{N}_2\text{O}_3 \) (Schemes 5 and 6). We additionally divided each scheme into two sub-schemes based on the target reductant, either neutral \( \text{NH}_2\text{OH} \) or ionic \( \text{NH}_3\text{OH}^+ \), to obtain six types of schemes.

**Scheme 1.** HONO-\( \text{NH}_2\text{OH} \) system reactions
\[\text{NH}_2\text{OH} + \text{HONO} \rightarrow \text{NH}_2(\text{O})\text{NO} + \text{H}_2\text{O} \quad \text{(R22)}\]
\[\text{NH}_2(\text{O})\text{NO} \rightarrow \text{HNO} + \text{HNO} \quad \text{(R23)}\]
\[\text{HNO} + \text{HNO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad \text{(4)}\]
\[\text{NH}_2\text{OH} + \text{HONO} \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \quad \text{(3)}\]
Scheme 2. HONO-NH$_3$OH$^+$ system reactions

\[
\begin{align*}
\text{NH}_2\text{OH}^+ + \text{HONO} & \rightarrow \text{NH}_2(\text{OH})\text{NO}^+ + \text{H}_2\text{O} \\
\text{NH}_2(\text{OH})\text{NO}^+ + \text{NO}_3^- & \rightarrow \text{NH}(\text{OH})\text{NO} + \text{HNO}_3
\end{align*}
\]  
(R26-29)

\[
\begin{align*}
\text{NH}_2\text{OH} + \text{HNO}_3 & \rightarrow \text{NH}_3\text{OH}^+ + \text{NO}_3^- \\
\text{NH}(\text{OH})\text{NO} (+ \text{H}_2\text{O}) & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} (+ \text{H}_2\text{O})
\end{align*}
\]  
(R32, 32)

\[
\begin{align*}
\text{NH}_2\text{OH} + \text{HONO} & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}
\end{align*}
\]  
(3)

Scheme 3. $t$-ONONO$_2$-NH$_2$OH system reactions

\[
\begin{align*}
\text{HNO}_3 + \text{HONO} & \rightarrow \text{$t$-ONONO}_2 + \text{H}_2\text{O} \\
\text{$t$-ONONO}_2 + \text{NH}_2\text{OH} & \rightarrow \text{NH}(\text{OH})\text{NO} + \text{HNO}_3
\end{align*}
\]  
(R34)

\[
\begin{align*}
\text{NH}(\text{OH})\text{NO} (+ \text{H}_2\text{O}) & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} (+ \text{H}_2\text{O})
\end{align*}
\]  
(R32, 33)

\[
\begin{align*}
\text{NH}_2\text{OH} + \text{HONO} & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}
\end{align*}
\]  
(3)

Scheme 4. $t$-ONONO$_2$-NH$_3$OH$^+$ system reactions

\[
\begin{align*}
\text{HNO}_3 + \text{HONO} & \rightarrow \text{$t$-ONONO}_2 + \text{H}_2\text{O} \\
\text{$t$-ONONO}_2 + \text{NH}_3\text{OH}^+ & \rightarrow \text{NH}_2(\text{OH})\text{NO}^+ + \text{HNO}_3
\end{align*}
\]  
(R34)

\[
\begin{align*}
\text{NH}_2(\text{OH})\text{NO}^+ + \text{NH}_2\text{OH} & \rightarrow \text{NH}(\text{OH})\text{NO} + \text{NH}_3\text{OH}^+ \\
\text{NH}(\text{OH})\text{NO} (+ \text{H}_2\text{O}) & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} (+ \text{H}_2\text{O})
\end{align*}
\]  
(R32, 33)

\[
\begin{align*}
\text{NH}_2\text{OH} + \text{HONO} & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}
\end{align*}
\]  
(3)

Scheme 5. N$_2$O$_3$-NH$_2$OH system reactions

\[
\begin{align*}
\text{HONO} + \text{HONO} & \rightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O} \\
\text{N}_2\text{O}_3 + \text{NH}_2\text{OH} & \rightarrow \text{NH}(\text{OH})\text{NO} + \text{HNO}_2
\end{align*}
\]  
(R38)

\[
\begin{align*}
\text{HNO}_2 & \rightarrow \text{HONO} \\
\text{NH}(\text{OH})\text{NO} (+ \text{H}_2\text{O}) & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} (+ \text{H}_2\text{O})
\end{align*}
\]  
(11)

\[
\begin{align*}
\text{NH}_2\text{OH} + \text{HONO} & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}
\end{align*}
\]  
(3)

Scheme 6. N$_2$O$_3$-NH$_3$OH$^+$ system reactions

\[
\begin{align*}
\text{HONO} + \text{HONO} & \rightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O} \\
\text{N}_2\text{O}_3 + \text{NH}_3\text{OH}^+ & \rightarrow \text{NH}_2(\text{OH})\text{NO}^+ + \text{HONO}
\end{align*}
\]  
(R39, R40)

\[
\begin{align*}
\text{NH}_2(\text{OH})\text{NO}^+ + \text{NO}_3^- & \rightarrow \text{NH}(\text{OH})\text{NO}_2 + \text{HNO}_3 \\
\text{NH}(\text{OH})\text{NO} (+ \text{H}_2\text{O}) & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} (+ \text{H}_2\text{O})
\end{align*}
\]  
(R32, 33)

\[
\begin{align*}
\text{NH}_2\text{OH} + \text{HONO} & \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}
\end{align*}
\]  
(3)

Adding both sides of Schemes 1 to 6 and cancelling the intermediates, the global reaction for each of these can be written as a single reaction: 
\[\text{NH}_2\text{OH} + \text{HONO} \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}.\] In Schemes 1 and 2, HONO directly attacks \(\text{NH}_2\text{OH}\) or \(\text{NH}_3\text{OH}^+\) to yield \(\text{N}_2\text{O}\) and \(\text{H}_2\text{O}\) (or \(\text{H}_3\text{O}^+\)) and the energy barriers for the rate determining steps were 74.9 kJ/mol (R22) and 22.6 kJ/mol (R26),
respectively. In Schemes 3 and 4, HONO attacks HNO\textsubscript{3} to give \(t\)-ONONO\textsubscript{2} and this compound subsequently attacks NH\textsubscript{2}OH or NH\textsubscript{3}OH\textsuperscript{+} to form N\textsubscript{2}O and H\textsubscript{2}O (or H\textsubscript{3}O\textsuperscript{+}). The energy barrier for the rate determining step in Schemes 3 or 4 was 11.4 kJ/mol (R34). Schemes 5 and 6 involve the decomposition of two HONO molecules to yield N\textsubscript{2}O\textsubscript{3}, with the N\textsubscript{2}O\textsubscript{3} attacking NH\textsubscript{2}OH or NH\textsubscript{3}OH\textsuperscript{+} to generate N\textsubscript{2}O and H\textsubscript{2}O (or H\textsubscript{3}O\textsuperscript{+}). The energy barrier for the rate determining step in Schemes 5 or 6 was 50.4 kJ/mol (R17). Schemes 3 and 4 are therefore the most likely based on a consideration of the energy barrier heights for all of the schemes. According to Lee and Litzinger [18], the activation energy of the reaction NH\textsubscript{2}OH + HONO \rightarrow N\textsubscript{2}O + H\textsubscript{2}O is 13.8 \pm 0.8 kJ/mol. This \(E\textsubscript{a}\) value is in good agreement with the determined for R34 (11.4 kJ/mol). Thus, we concluded that either Scheme 3 or Scheme 4 is dominant in the reactions of the HAN/HONO system.

4 Conclusions

The decomposition pathway of HAN in aqueous solution was investigated on the basis of \textit{ab initio} calculations performed at the \(\omega\)B97XD/6-311++G(d,p)/SCRF = (solvent = water) and CBS-QB3//\(\omega\)B97XD/6-311++G(d,p)/SCRF = (solvent = water) levels of theories.

Mechanisms for the charge neutral-neutral bimolecular reactions (NH\textsubscript{2}OH + HNO\textsubscript{3} \rightarrow HNO + HONO + H\textsubscript{2}O and NH\textsubscript{3}O + HNO\textsubscript{3} \rightarrow HNO + HONO + H\textsubscript{2}O), ion-neutral bimolecular reaction (NH\textsubscript{3}OH\textsuperscript{+} + HNO\textsubscript{3} \rightarrow HNO + HONO + H\textsubscript{2}O + H\textsuperscript{+}) and HNO\textsubscript{3} self-decomposition (HNO\textsubscript{3} + HNO\textsubscript{3} \rightarrow N\textsubscript{2}O\textsubscript{5}) were developed. The maximum energy barrier for each of these reactions were calculated as 124.8 kJ/mol, 88.7 kJ/mol, 91.7 kJ/mol and 89.8 kJ/mol, respectively. Each of these reaction schemes appears to be thermodynamically viable and all yield the same products. The overall initial decomposition reaction can be summarized using a single equation: HAN \rightarrow HONO + HNO + H\textsubscript{2}O. The primary scheme will depend on the concentrations of the various species in the reaction solution. HAN dissociates to form ion pairs in water, with NH\textsubscript{3}OH\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{-} being the major species. Therefore, we concluded that the NH\textsubscript{3}OH\textsuperscript{+} + HNO\textsubscript{3} reaction mechanism is dominant during the initial HAN decomposition in aqueous solution. The associated energy barrier of 91.7 kJ/mol is in good agreement with the activation energy reported in a previous study [31].

The HAN/HONO catalytic decomposition pathways following the initial decomposition of HAN were investigated based on density functional theory calculations. These calculations were performed at the same levels of theory.
We developed six mechanisms and each of these schemes provided the same global reaction: \( \text{NH}_2\text{OH} + \text{HONO} \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \). These schemes can be classed according to the combinations of oxidizers (HONO, \( t\)-ONONO\(_2\) or \( \text{N}_2\text{O}_3\)) and reductants (\( \text{NH}_2\text{OH} \) or \( \text{NH}_3\text{OH}^+ \)). In the HONO oxidizing scheme, HONO directly attacks \( \text{NH}_2\text{OH} \) or \( \text{NH}_3\text{OH}^+ \) to yield \( \text{N}_2\text{O} \) and \( \text{H}_2\text{O} \) (or \( \text{H}_3\text{O}^+ \)) (\( = 171.2 \text{ kJ/mol or 74.9 kJ/mol} \) respectively). In the \( t\)-ONONO\(_2\) scheme, HONO reacts with HNO\(_3\) to give \( t\)-ONONO\(_2\) (\( = 11.4 \text{ kJ/mol} \)) and the \( t\)-ONONO\(_2\) oxidizes \( \text{NH}_2\text{OH} \) or \( \text{NH}_3\text{OH}^+ \) (\( = -44.8 \text{ kJ/mol or 22.6 kJ/mol} \) respectively). In the \( \text{N}_2\text{O}_3\) mechanism, two HONO molecules decompose to yield \( \text{N}_2\text{O}_3 \) (\( = 50.4 \text{ kJ/mol} \)) and the \( \text{N}_2\text{O}_3\) oxidizes \( \text{NH}_2\text{OH} \) or \( \text{NH}_3\text{OH}^+ \) (\( = -1.7 \text{ kJ/mol or 33.9 kJ/mol} \) respectively). Based on the energy barrier results, the \( t\)-ONONO\(_2\) oxidizing scheme is the most plausible.

References

Decomposition Pathways for Aqueous Hydroxylammonium Nitrate...


