Decay Mechanism of NO$_3^\cdot$ Radical in Highly Concentrated Nitrate and Nitric Acidic Solutions in the Absence and Presence of Hydrazine

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ABSTRACT

The decay mechanism of NO$_3^\cdot$ has been determined through a combination of experiment and calculation for 7 mol dm$^{-3}$ solutions of deaerated aqueous LiNO$_3$ and HNO$_3$, in the absence and presence of hydrazine (N$_2$H$_4$, N$_2$H$_5^+$ and N$_2$H$_6^{2+}$). In the absence of hydrazine, the predominant NO$_3^\cdot$ decay pathways are strongly dependent upon the pH of the solution. For neat neutral pH LiNO$_3$ solutions (7 mol dm$^{-3}$), NO$_3^\cdot$ produced by the pulse is fully consumed within 160 μs by OH$^-$ (37%), H$_2$O (29%), NO$_2^-$ (17%), and NO$_2$ (17%). For acidic HNO$_3$ solutions (7 mol dm$^{-3}$), radiolytically produced NO$_3^\cdot$ is predominantly consumed within 1 ms by HNO$_2$ (15%) and NO$_2$ (80%). Intervening formulations exhibit the mechanistic transition from neat LiNO$_3$ to neat HNO$_3$. In highly acidic nitric acid solution, hydrazine exists mainly as N$_2$H$_5^+$ and N$_2$H$_6^{2+}$ both of which rapidly consume NO$_3^\cdot$ in addition to other decay mechanisms, with rate constants of 2.9 (± 0.9) × 10$^7$ and 1.3 (± 0.3) × 10$^6$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively.
INTRODUCTION

Concentrated aqueous solutions of nitrate ion (NO$_3^-$) and undissociated nitric acid (HNO$_3$) are commonly used in the nuclear industry for the dissolution of radionuclides, e.g. in spent nuclear fuel reprocessing solvent systems and in the storage of highly radioactive liquid waste.$^{1,2}$ In these environments, NO$_3^-$ and HNO$_3$ are subjected to intense multi-component radiation fields which induce radiolytic degradation.$^{1,3}$ The direct and indirect effects of radiation lead to the formation of a number of radiolytic products, particularly nitrogen oxides (e.g. NO$_3^-$, NO$_2^-$, N$_2$O$_4$, NO$_2^-$, and HNO$_2$) which play a significant role in altering the physical and chemical properties of aqueous NO$_3^-$/HNO$_3$ solutions and solvent systems.$^{1,3}$ The proportions of these nitrogen oxides are dependent upon the respective concentrations of NO$_3^-$ and HNO$_3$, and the nature of the irradiation conditions (type of radiation and its associated energy).$^4$ The radiolytic formation of these species can be described by the simplified reaction scheme given in Table 1.

Table 1. Reaction scheme and rate constants for the radiolytic formation of key nitrogen oxides (NO$_3^-$, NO$_2^-$, N$_2$O$_4$, NO$_2^-$, and HNO$_2$) from the radiolysis of aqueous NO$_3^-$ and HNO$_3$.

<table>
<thead>
<tr>
<th>Number</th>
<th>Chemical Reaction</th>
<th>Rate Constant (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO$_3^-$ ⇔ NO$_3^-$* → NO$_2^-$ + O</td>
<td>N/A</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>NO$_3^-$ ⇔ NO$_3^-$* → NO$_3^*$ + e$^-$</td>
<td>N/A</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>HNO$_3$ ⇔ HNO$_3^*$ → HNO$_2$ + O</td>
<td>N/A</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>NO$<em>3^-$ + e$</em>{pre}$ → NO$_3^2^-$</td>
<td>$1 \times 10^{13}$</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>NO$<em>3^-$ + e$</em>{aq}$ → NO$_3^2^-$</td>
<td>$9.7 \times 10^9$</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>NO$_3^-$ + H$^+$ → HNO$_3$$^-$</td>
<td>$1.0 \times 10^7$</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>NO$_3^2^-$ + H$_2$O → NO$_2^+$ + 2OH$^-$</td>
<td>$1.0 \times 10^3$</td>
<td>8, 9</td>
</tr>
<tr>
<td>8</td>
<td>HNO$_3$$^-$ → NO$_2^+$ + OH$^-$</td>
<td>$2.0 \times 10^5$ (s$^{-1}$)</td>
<td>8, 9</td>
</tr>
<tr>
<td>9</td>
<td>NO$_2^+$ + NO$_2^+$ → N$_2$O$_4$</td>
<td>$4.5 \times 10^8$</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>N$_2$O$_4$ + H$_2$O → HNO$_2$ + HNO$_3$</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>11</td>
<td>HNO$_2$ → NO$<em>2^-$ + H$</em>{aq}^+$</td>
<td>$3 \times 10^7$ (s$^{-1}$)</td>
<td>11</td>
</tr>
</tbody>
</table>

The radiolytic formation and decay of the nitrate radical (NO$_3^-$) is of practical importance to these nuclear applications, as it is a significant driver of chemical change, be it through the formation of secondary radiolytic products (e.g. electron transfer from inorganic species, hydrogen abstraction from saturated organic species, and radical addition to unsaturated
organic species), or through the oxidation \((E^\circ = 2.45 - 2.67 \text{ V}_{\text{NHE}})\) of important metal ions (e.g. uranium, plutonium and fission products). Consequently, numerous pulse radiolysis and photolysis experiments have been performed to determine the radiolytic formation and decay pathways of \(\text{NO}_3^-\), a reaction scheme for which is given in Table 2.

**Table 2.** Reaction scheme and rate constants for \(\text{NO}_3^-\) formation and decay pathways for the radiolysis of deaerated aqueous solutions of \(\text{NO}_3^-\) and HNO₃.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>Rate Constant (\text{dm}^3\text{ mol}^{-1}\text{s}^{-1})</th>
<th>Model (This work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) (Table 1)</td>
<td>(\text{NO}_3^- \rightarrow \text{NO}_3^- \rightarrow \text{NO}_3^- \rightarrow \text{NO}_3^- \rightarrow \text{e}^-)</td>
<td>N/A</td>
<td>N/A (^5)</td>
</tr>
<tr>
<td>12</td>
<td>(\text{HNO}_3 + \text{OH}^- \rightarrow \text{NO}_3^- + \text{OH}^-)</td>
<td>(1.9 \times 10^7)</td>
<td>(5.3 \times 10^7) (^{12})</td>
</tr>
<tr>
<td>13</td>
<td>(\text{NO}_3^- + \text{NO}_3^- \rightarrow \text{N}_2\text{O}_6)</td>
<td>(4.0 \times 10^6)</td>
<td>(4.0 \times 10^6) (^{13})</td>
</tr>
<tr>
<td>14</td>
<td>(\text{NO}_3^- + \text{NO}_2^- \rightarrow \text{NO}_3^- + \text{NO}_2^-)</td>
<td>(4.4 \times 10^9)</td>
<td>(4.4 \times 10^9) (^{14})</td>
</tr>
<tr>
<td>15</td>
<td>(\text{NO}_3^- + \text{HNO}_2 \rightarrow \text{HNO}_3 + \text{NO}_2^-)</td>
<td>(2.0 \times 10^8)</td>
<td>(8.0 \times 10^6) (^{14})</td>
</tr>
<tr>
<td>16</td>
<td>(\text{NO}_3^- + \text{NO}_2^- \rightarrow \text{N}_2\text{O}_5)</td>
<td>(1.1 \times 10^9)</td>
<td>(1.0 \times 10^9) (^{13})</td>
</tr>
<tr>
<td>17</td>
<td>(\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{OH}^-)</td>
<td>(3.0 \times 10^2)</td>
<td>(3.0 \times 10^2) (^{13})</td>
</tr>
<tr>
<td>18</td>
<td>(\text{NO}_3^- + \text{OH}^+ \rightarrow \text{NO}_2^- + \text{HO}_2^+)</td>
<td>(1.0 \times 10^{10})</td>
<td>(1.2 \times 10^{10}) (^{15})</td>
</tr>
<tr>
<td>19</td>
<td>(\text{NO}_3^- + \text{HO}_2^- \rightarrow \text{HNO}_3 + \text{O}_2)</td>
<td>(3.0 \times 10^9)</td>
<td>(3.0 \times 10^9) (^{14})</td>
</tr>
<tr>
<td>20</td>
<td>(\text{NO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{HNO}_3 + \text{HO}_2^+)</td>
<td>(7.1 \times 10^6)</td>
<td>(7.1 \times 10^6) (^{16})</td>
</tr>
</tbody>
</table>

Systematic picosecond pulse radiolysis experiments have demonstrated that \(\text{NO}_3^-\) exhibits two key formation pathways. \(^{17,18}\)

i. A fast formation pathway attributed to direct radiation effects on \(\text{NO}_3^-\) (2); although this fast component has been shown to conceal additional ultra-fast chemical processes such as ‘dry hole’ trapping (\(\text{H}_2\text{O}^+ + \text{NO}_3^- \rightarrow \text{H}_2\text{O} + \text{NO}_3^-\)), though further experimental evidence is required. \(^{19}\) Direct effect formation of \(\text{NO}_3^-\) is dependent upon the electron fraction of \(\text{NO}_3^-\) relative to water. \(^{20}\) Consequently, this pathway becomes significant at high \(\text{NO}_3^-\) concentrations (> 0.5 mol dm\(^{-3}\)). \(^{17,19}\)

ii. A slow formation process involving the hydroxyl radical (\(\text{OH}^-\)) abstracting a proton from \(\text{HNO}_3\) (12). This process necessitates the presence of undissociated \(\text{HNO}_3\) \((\text{HNO}_3 \rightleftharpoons \text{NO}_3^- + \text{H}^+)\) \(^{21}\) and thus is only viable in highly acidic solutions.
Once formed, NO₃⁻ rapidly decays by reacting with water and other radiolytic species (e.g. reactions 13 to 20 in aqueous NO₃⁻ and HNO₃ solutions), ultimately leading to the formation of secondary radiolysis products and complete consumption of NO₃⁻ within microsecond timescales. However, there is still some uncertainty in the relative contributions of these NO₃⁻ reactions. It was initially suggested that the main decay pathways of NO₃⁻ were via recombination (13) and/or reaction with NO₂⁻ (16). Recombination of NO₃⁻ is unlikely as a significant decay pathway due to the reaction being very slow compared to other available routes, and the low probability of two NO₃⁻ radicals interacting within the radiation track relative to interacting with water or other radiolysis products. Although the reaction rate of NO₃⁻ with NO₂⁻ is sufficiently high, formation of NO₂⁻ is purely by indirect effects (e.g. reactions 7 to 9, 14 to 16, and 18), and consequently can be expected to only become a significant decay pathway at later times, e.g. late nanosecond to early microsecond timescales. Hence, decay processes involving water and primary radiolysis products would be expected to dominate at shorter timescales (e.g. OH⁻, H₂O₂, NO₂⁻, and HNO₂). Pulse experiments performed by Katsumura et al. investigated the reaction of NO₃⁻ with a number of scavenger species in 6 mol dm⁻³ aqueous HNO₃ solution, including H₂O₂ and HNO₂. The rate constants for these scavenging reactions were adjusted to give the best fitting of experimental results. However, no quantitative mechanistic description has been provided thus far.

Hydrazinium (N₂H₅⁺) is commonly used as an anti-nitrous agent in spent nuclear fuel reprocessing solvent systems to rapidly react with nitrous acid (HNO₂) which is formed due to the instability of HNO₃. The purpose of which is to inhibit HNO₂ redox reactions with plutonium and other redox active metal ions, thereby promoting efficient extraction and product stream purity. In basic solution, hydrazine exist mainly as the N₂H₄ molecule. However, in acidic solutions, hydrazine exists as up to two protonated hydrazinium ion forms, N₂H₅⁺ and/or N₂H₆²⁺.

\[
\begin{align*}
N₂H₄ + H^+ & \rightleftharpoons N₂H₅⁺ & \text{pK}_{a1} & \approx 7.9 & (21) \\
N₂H₅⁺ + H^+ & \rightleftharpoons N₂H₆²⁺ & \text{pK}_{a2} & \approx -1 & (22)
\end{align*}
\]

Both protonated species present very different reactivity’s towards NO₃⁻, which leads to a number of mechanistic complexities. For example, in concentrated HNO₃ solutions (> 6 mol dm⁻³), two very different rate constants are given for the reaction of N₂H₅⁺ with NO₃⁻.


\[
N_2H_5^+ + \text{NO}_3^- \rightarrow N_2H_4^+ + \text{NO}_3^- + H^+ \quad k_{23} = 1.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

\[
k'_{23} = 6.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\] (23)

Furthermore, neither of these studies considered that both protonated forms of hydrazine could be present in solution at the same time in varying proportions, each of which possessing a different rate of reaction with \(\text{NO}_3^-\). This is further exacerbated as the acid dissociation constant for the second protonation reaction (pK\(_{\text{a2}}\)) is unclear, although some authors have proposed pK\(_{\text{a2}}\) values of approximately -1.31

The presented research evaluates the decay mechanism of \(\text{NO}_3^-\) in the absence and presence of hydrazine, from the radiolysis of deaerated 7 mol dm\(^{-3}\) aqueous solutions of lithium nitrate (LiNO\(_3\)) and HNO\(_3\), by using a combination of pulse radiolysis and multi-scale modelling techniques to provide: (i) quantitative mechanistic insight into the decay pathways of \(\text{NO}_3^-\); (ii) rate constants for the reactions of \(N_2H_5^+\) and \(N_2H_6^{2+}\) with \(\text{NO}_3^-\); (iii) the acid dissociation constant for the protonation of \(N_2H_5^+\) (pK\(_{\text{a2}}\)).

**METHODOLOGY**

**EXPERIMENT**

LiNO\(_3\) (Suprapur), HNO\(_3\) (Ultrapur and fresh), and \(N_2H_4\) (Ultrapur) were supplied by Sigma Aldrich. All chemicals were used without further purification. Ultra-pure water (18.2 M\(\Omega\)cm) was used to make up all solutions. The solutions were bubbled with Ar to remove O\(_2\) and other gases. The experiments were performed at room temperature.

A transient absorption setup with a streak camera installed in experimental area EA-3 of the electron pulse facility ELYSE at Paris-Sud University was used. The electron beam irradiation was performed using the picosecond pulse radiolysis facility delivering a repetition rate of 5 Hz, electron-pulses with an energy of 8 MeV. The dose deposited per pulse in the samples was deduced from the measurements of the transient absorbance of e\(_{\text{aq}}^-\) in water and verified just before each series of experiments. Typically, the electron pulse had a half width (FHWM) of 15 ps and a charge of ~6 nC. More details of the system configuration are described elsewhere.\(^{32,33}\) An optical quartz cell with an optical path length of 1 cm containing the sample was placed as close as possible to the output window of the electron beam to minimize divergence. Generally results are obtained from the average of 200 pulses (40 s for the measurements time). The solution from a stock of 200 mL is refreshed by using a peristaltic pump with a high flow rate of 200 mL min\(^{-1}\). The accumulated
The amount of HNO₂ radiolytically produced in solution is very low because the volume of irradiation is only 120 μL, and HNO₂ is diluted in 200 mL, and the solution is deaerated by Ar, which removes also N₂O₄.

**MULTI-SCALE MODELLING**

Multi-scale modelling was used to provide quantitative mechanistic analysis for the aforementioned experiments. The multi-scale modelling methodology is outlined in Figure 1. The multi-scale modelling approach relies on a combination of stochastic radiation track chemistry and deterministic kinetics models to provide a satisfactory description of the events occurring during the radiolysis of aqueous solutions. The model comprises four components which address the following four time regimes: track structure formation (< 1 femtosecond); physicochemical processes (< 1 picosecond); nonhomogeneous reaction kinetics (< 1 microsecond), and; homogeneous bulk chemistry (> 1 microsecond).

**Figure 1.** Schematic outline of the multi-scale modelling approach.

The stochastic component of the multi-scale model, stages 1 to 3 in Figure 1, uses well established radiation track structure formation and diffusion-kinetic independent reaction times models to simulate the physical and chemical processes occurring within a radiation track to a given time between the point of energy transfer up to the complete spatial relaxation of the radiation chemical track at about 1 μs when the products of radiolysis can be considered to be homogeneously distributed in bulk solution.³⁴⁻³⁶ The stochastic component of the model provides radiolytic yields representative of the experimental system concerned at a given time regime, as initial parameters to allow the calculation of the formation rates of the products of radiolysis in the deterministic model.
The deterministic model for bulk homogeneous radiation chemistry, stages 3 and 4 in Figure 1, is based upon a more extensive reaction scheme than that listed in tables 1 and 2, comprising water radiolysis reactions and reactions of NO$_3^-$/HNO$_3$ and its radiation-induced product species. The chemistry is expressed as a set of coupled kinetic differential equations which were solved using the FACSIMILE software package. Both the stochastic and deterministic components of the multi-scale model are based on experimentally determined physical and chemical parameters. The multi-scale modelling formalism and these parameters have been described in detail elsewhere. The calculations presented in this research used stochastically calculated radiolytic yields corresponding to 10 ns after energy transfer by fast electron irradiation. The 10 ns transition point was selected on the basis of (i) being longer than the time taken for the majority significant scavenging processes to occur (i.e. more than 4 times longer than the half-lives for scavenging of e$_{\text{pre}}$/e$_{\text{aq}}$ and OH$^\cdot$ by NO$_3^-$ and HNO$_3$, respectively), and (ii) because it coincides with the experimental time period after the electron pulse width at which measurements were taken. These radiolytic yields provide the indirect effect contribution to NO$_3^\cdot$ formation and the concentrations of the other primary radiolysis species, which in conjunction with direct effects yields were corrected for the respective electron fractions of water and NO$_3^-$/HNO$_3$ before being used as initial parameters in the deterministic model to simulate the radiolysis of deaerated aqueous NO$_3^-$/HNO$_3$ solutions to 1 ms, with time intervals of 100 ns.

RESULTS AND DISCUSSION

Absorption Spectra of NO$_3^\cdot$. The transient absorption spectra for NO$_3^\cdot$ measured in this work at 100 ns for deaerated aqueous 7 mol dm$^{-3}$ LiNO$_3$ and HNO$_3$ solutions is given in Figure 2. Both spectra show the characteristic three peaks absorption band for NO$_3^\cdot$: 600, 640, and 680 nm, in agreements with previous results but with higher spectral resolution obtained by the streak camera.
Figure 2. Transient absorption spectra of NO$_3^-$ recorded at 100 ns after the electron pulse for deaerated (with Ar) aqueous 7 mol dm$^{-3}$ LiNO$_3$ (▬) and 7 mol dm$^{-3}$ HNO$_3$ (▬) solutions, at 38 Gy pulse$^{-1}$.

Comparison of the two spectra clearly shows that the absorption intensity of NO$_3^-$ from HNO$_3$ is significantly greater than that from LiNO$_3$, thus radiolysis of concentrated HNO$_3$ solutions results in the formation of more NO$_3^-$, which is in agreement with previous findings concerning direct (2) and indirect (12) formation of NO$_3^-$.$^4,5,14,17,19$

Decay Kinetics of NO$_3^-$. The concentration and absorption of NO$_3^-$ is given as a function of time and solution composition in Figure 3. Multi-scale modelling calculations provide predictions in good agreement with experiment. This agreement has been predominantly attained by changing the literature rate constants for two reactions:

i. The reaction rate of OH$^-$ with HNO$_3$ (12) has been reported in the literature by Katsumura et al. as being $5.3 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$, although initially reported as $1.4 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$. The rate constant used in this work by fitting the experimental data was $1.9 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$. This value is not in agreement with the two previously reported values. The rate of this process establishes the importance of indirect effect on NO$_3^-$ formation ($G$(NO$_3^-$)$_{\text{indirect}} = 2.6$ for 7 mol dm$^{-3}$ HNO$_3$ determined by stochastic calculations at 10 ns) and thus the initial yield of NO$_3^-$ at 10 ns. The calculations performed for this research found that rate constants higher than
1.9 × 10^7 dm^3 mol^{-1} s^{-1} lead to significantly higher NO_3^- yields than those observed experimentally, with the extent of deviation increasing with decreasing HNO_3 concentration; a consequence of relatively low OH^- yield, progressively increasing undissociated HNO_3 concentration, and the resultant effects on scavenging capacity of HNO_3 for OH^-.

The rate constants reported by Katsumura et al. were determined using HNO_3 dissociation data from Redlich et al. although their presented fractions of HNO_3 dissociation are significantly lower than the literature data sets for HNO_3 concentrations ≥ 4 mol dm^{-3} (~0.34 mol dm^{-3} lower). Calculations presented here are based on HNO_3 dissociation data from Davis and De Bruin, of which there is little deviation between the two published HNO_3 data sets for the HNO_3 concentrations used in this work.^{39,40}

ii. The reaction rate of NO_3^- with HNO_2 (15) was reported by Katsumura et al. as 8.0 × 10^6 dm^3 mol^{-1} s^{-1}, determined by simulation and fitting to experimental results for 6 mol dm^{-3} HNO_3 solutions by the addition of HNO_2 (2.3 × 10^{-4} and 1.25 × 10^{-3} mol dm^{-3}).^{14} The rate constant used in this work was 2.0 × 10^8 dm^3 mol^{-1} s^{-1}. The reaction scheme presented by Katsumura et al. is conservative at best, as it does not appear to incorporate any secondary chemistry for HNO_2 (e.g. reaction with OH^-, H_2O_2 and HNO_3), which ultimately deplete its concentration. Whereas the multi-scale modelling approach used here incorporates an extensive reaction scheme inclusive of secondary radiation induced reactions, which has been rigorously evaluated with regards to the radiolytic yields of NO_2^- and HNO_2 for a wide range of NO_3^- and HNO_3 concentrations (1 × 10^{-3} to 6 mol dm^{-3});^{37} consequently their secondary chemistry has been more satisfactorily incorporated. Hence, the higher rate constant used in our calculations accommodates for depletion of HNO_2 by secondary chemistry, and is necessary to attain good agreement at longer timescales, i.e. ≥ 400 μs.

The initial yield of NO_3^- observed at ~10 ns increases dramatically with increasing HNO_3 concentration, although its decay kinetics slows leading to progressively longer lifetimes (up to milliseconds). These observations are most evident for the two extreme cases (neat 7 mol dm^{-3} LiNO_3(aq) and HNO_3(aq)), a quantitative mechanistic analysis for which is given in Figure 4.
Figure 3. Concentration and absorption (at 640 nm) of NO$_3^*$ as a function of time from the radiolysis (38 Gy pulse$^{-1}$) of deaerated: 7 mol dm$^{-3}$ LiNO$_3$ (▲), 7 mol dm$^{-3}$ LiNO$_3$ + 1 × 10$^{-3}$ mol dm$^{-3}$ HNO$_3$ (●), 6.9 mol dm$^{-3}$ LiNO$_3$ + 0.1 mol dm$^{-3}$ HNO$_3$ (▼), and 7 mol dm$^{-3}$ HNO$_3$ (■); fitted lines are from multi-scale modelling calculations.

The formation of NO$_3^*$ from the radiolysis of neutral aqueous NO$_3^-$ solutions is purely by direct effects (1) and thus dependent upon the electron fraction of NO$_3^-$ relative to water. In 7 mol dm$^{-3}$ LiNO$_3$(aq) solution (Figure 4 – top) the electron fraction of NO$_3^-$ is approximately 0.28, providing an initial NO$_3^*$ concentration of 5.36 × 10$^{-6}$ mol dm$^{-3}$, the decay of which is completed within 160 μs. Note that the calculated concentrations are a function of dose (Gy = J kg$^{-1}$) and thus averaged over the cylindrical electron beam profile volume. According to our fits using the multi-scale modelling simulation code, the key processes responsible for this rapid decay involve the reaction of NO$_3^*$ with OH$^*$ (37%), H$_2$O (29%), NO$_2^-$ (17%), and NO$_2$ (17%).

However, the formation of NO$_3^*$ from the radiolysis of aqueous HNO$_3$ is from direct (1) and indirect (2) effect pathways due to the presence of undissociated HNO$_3$. Consequently, the initial concentration of NO$_3^*$ in 7 mol dm$^{-3}$ HNO$_3$(aq) solution (Figure 4 – bottom) is 1.39 × 10$^{-5}$ mol dm$^{-3}$ at approximately 10 ns, the decay of which is complete within approximately 1 ms. The key processes responsible for this slower decay involve the reaction of NO$_3^*$ with HNO$_2$ (15%) and NO$_2$ (80%).
The drastic shift in the importance of $\text{NO}_3^-$ decay processes, in going from pure $\text{LiNO}_3(aq)$ to pure $\text{HNO}_3(aq)$, is due to the effect of lowering pH with increasing undissociated $\text{HNO}_3$ concentration. As the fraction of $\text{HNO}_3$ increases, the pH of the system decreases leading to a greater extent of undissociated $\text{HNO}_3$ and $\text{HNO}_2$. The implications of which are as follows:

i. There is progressively more undissociated $\text{HNO}_3$ available for reaction with $\text{OH}^-$ ($\sim 1.96 \text{ mol dm}^{-3}$ in 7 mol dm$^{-3} \text{ HNO}_3$)$^{39,40}$

ii. Consumption of $\text{OH}^-$ by $\text{HNO}_3$ rapidly removes one of the key oxidising processes responsible for the rapid decay of $\text{NO}_3^-$ in pure $\text{LiNO}_3(aq)$ solutions. However, this process has further implications, as it establishes an equilibrium with the reaction of $\text{NO}_3^-$ with $\text{H}_2\text{O}$ (17) at timescales $>10$ ns; $\text{HNO}_3 + \text{OH}^- \rightleftharpoons \text{NO}_3^- + \text{H}_2\text{O}$. Although this equilibrium lies in favour of $\text{NO}_3^-$ and $\text{H}_2\text{O}$ formation ($2.54 \times 10^{-7} \text{ mol dm}^{-3}$), the process ultimately removes the importance of two key $\text{NO}_3^-$ decay processes in $\text{HNO}_3(aq)$ solution.

iii. Formation of $\text{HNO}_2$ ($\text{HNO}_2 \rightleftharpoons \text{NO}_2^- + \text{H}^+$, $\text{pK}_a = 3.2$) also reduces the rate at which $\text{NO}_3^-$ decays, relative to $\text{NO}_3^-$ solutions. This is because $\text{HNO}_2$ is less reactive towards $\text{NO}_3^-$ ($k_{15} = 2.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Furthermore, $\text{HNO}_2$ is more reactive towards other water and $\text{NO}_3^-/\text{HNO}_3$ radiolysis products (e.g. $\text{OH}^-$, $\text{H}_2\text{O}_2$, and $\text{HNO}_2$), relative to $\text{NO}_2^-$. Consequently, there is effectively less $\text{HNO}_2$ available to undergo reaction with $\text{NO}_3^-$. 

Figure 4. (top) Concentration and absorption of NO$_3^-$ as a function of time from the radiolysis (38 Gy pulse$^{-1}$) of deaerated 7 mol dm$^{-3}$ LiNO$_3$ solution: Experiment (■); Multi-scale model calculation (▬); Predicted concentration of NO$_3^-$ consumed by NO$_2$ (16), NO$_2^-$ (14), OH$^-$ (18), and H$_2$O (17). (bottom) Concentration and absorption of NO$_3^-$ as a function of time from the radiolysis (38 Gy pulse$^{-1}$) of deaerated 7 mol dm$^{-3}$ HNO$_3$ solution: Experiment (■); Multi-scale model calculation (▬); Predicted concentration of NO$_3^-$ produced by reaction of OH$^-$ with HNO$_3$; Predicted concentration of NO$_3^-$ consumed by NO$_2$ (16), and HNO$_2$ (15).
iv. The drastic increase in the importance of the NO$_2^\cdot$ decay pathway (16) arises from the increased availability of NO$_3^-$ due to the ‘inhibition’ of OH$^.$ and H$_2$O decay pathways, and the reduced concentration HNO$_2$ and its lower reactivity towards NO$_3^-$.

**Reactivity of NO$_3^-$ with hydrazine.** The reactivity of NO$_3^-$ with the hydrazine molecule and hydrazinium ions, was studied for four aqueous solutions containing a constant 7 mol dm$^{-3}$ concentration of NO$_3^-$ and an increasing concentration of H$_{aq}^+$ (0.1, 1.0, 3.0; and 7.0 mol dm$^{-3}$ HNO$_3$). Figure 5 shows the change in NO$_3^-$ absorption at 640 nm for 7 mol dm$^{-3}$ HNO$_3$ in the presence of several total hydrazine concentrations ($[\text{NH}]_{\text{Total}}$), defined as follows:

$$[\text{NH}]_{\text{Total}} = [N_2H_4] + [N_2H_5^+] + [N_2H_6^{2+}]$$  \hspace{1cm} (24)

![Figure 5](image_url)

**Figure 5.** Absorption of NO$_3^-$ at 640 nm as a function of time from the radiolysis (40 Gy pulse$^{-1}$) of deaerated: 7 mol dm$^{-3}$ HNO$_3$ without hydrazine (■), 7 mol dm$^{-3}$ HNO$_3$ + 2 × 10$^{-3}$ mol dm$^{-3}$ NH$_{Tot}^+$ (○), 7 mol dm$^{-3}$ HNO$_3$ + 1 × 10$^{-3}$ mol dm$^{-3}$ NH$_{Tot}^+$ (△), 7 mol dm$^{-3}$ HNO$_3$ + 1 × 10$^{-2}$ mol dm$^{-3}$ N$_2$H$_4$ (▼), and 7 mol dm$^{-3}$ HNO$_3$ + 0.1 mol dm$^{-3}$ NH$_{Tot}$ (★). **Inset:** Example decay in the logarithm scale for the absorbance of NO$_3^-$ as function of time for deaerated aqueous 7 mol dm$^{-3}$ HNO$_3$ solution in the presence of a total hydrazine concentration ($[\text{NH}]_{\text{Total}}$).

Given that the acid dissociation constant for N$_2$H$_4$/N$_2$H$_5^+$ is 7.9, the amount of N$_2$H$_4$ present under the investigated conditions is negligible. Consequently, the decay kinetics of NO$_3^-$ in the presence of a given hydrazine concentration takes the following form:
\[
\frac{-d[NO_3^*]}{dt} = k_{\text{overall}}[NO_3^*]+(k_{N_2H_5^+}[N_2H_5^+][NO_3^*])+(k_{N_2H_6^{2+}}[N_2H_6^{2+}][NO_3^*])
\]  \hspace{1cm} (25)

The first term of the decay stands for the decay in the absence of hydrazine with an overall rate constant of \( k_{\text{overall}} \). Equation (25) can be expressed as:

\[
\frac{-d[NO_3^*]}{dt} = k_{\text{overall}}[NO_3^*]+(k_{\text{obs}}[NH][\text{Total}[NO_3^*]]) = (k_{\text{overall}} + k_{\text{obs}}[NH][\text{Total}])[NO_3^*]
\]  \hspace{1cm} (26)

with

\[
k_{\text{obs}} = \frac{k_{N_2H_5^+}+k_{N_2H_6^{2+}}[H^+]}{1+K_{a2}[H^+]},
\]  \hspace{1cm} (27)

\[
K_{a1} = \left( \frac{[N_2H_5^+]}{[N_2H_4^+][H^+]} \right),
\]  \hspace{1cm} (28)

and

\[
K_{a2} = \left( \frac{[N_2H_6^{2+}]}{[N_2H_5^+][H^+]} \right),
\]  \hspace{1cm} (29)

Considering that the amount of hydrazine is larger than the NO\(_3^*\), it is possible to consider the reaction as a pseudo-first order reaction by plotting the logarithm of the absorbance of NO\(_3^*\) as a function of time. The slope of linear variation of logarithm of absorbance decay of NO\(_3^*\) with time corresponds to the value \( k_{\text{obs}}[NH]_{\text{Total}} \) (Figure 5 - inset). From these kinetic spectra the value of \( k_{\text{obs}} \) can be deduced for each acidic solution containing different concentration of total hydrazine (Figure 6 and 7). In order to avoid direct radiolysis of hydrazine, the maximum concentration considered was \( 7 \times 10^{-2} \) mol dm\(^{-3}\). For example, when the concentration of HNO\(_3\) is 7 mol dm\(^{-3}\), \( k_{\text{obs}} = 1.6 (\pm 0.2) \times 10^6 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) (Figure 6).
Figure 6. Variation of $k_{\text{obs}}$ with $[\text{NH}]_{\text{Total}}$ for argon purged aqueous 7 mol dm$^{-3}$ HNO$_3$ solutions; (40 Gy pulse$^{-1}$).

The methodology for determining $k_{\text{obs}}$ was applied to other acid concentrations ([H$^+$] = 0.1 mol dm$^{-3}$; 1.0 mol dm$^{-3}$ and 3.0 mol dm$^{-3}$) at 7 mol dm$^{-3}$ total NO$_3^-$ with 0.001 mol dm$^{-3}$ < $[\text{NH}]_{\text{Total}}$ < 0.07 mol dm$^{-3}$. In these conditions, the solutions consist of a mixture HNO$_3$-LiNO$_3$ but there is no data in the literature on the acid dissociation for high concentration of nitrate ions. It was therefore decided to use an arbitrary constant value of dissociation of the nitric acid, which adjusts the free acidity data available in the literature.$^{39,40}$ An acidity constant of 12.9 was used. From these kinetic results the value of $k_{\text{obs}}$ can be deduced for each acidic solution containing different concentration of total hydrazine.

The variation of $k_{\text{obs}}$ in function of the free acidity is shown in Figure 7. This variation of $k_{\text{obs}}$ solves the equation (27) and determines the kinetic constants $k_{\text{N}_2\text{H}_5^+}$ and $k_{\text{N}_2\text{H}_6^{2+}}$ and $K_a^2$.

According to the observed kinetics it is found that $k_{\text{N}_2\text{H}_5^+} = 2.9 \pm 0.9 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$, $k_{\text{N}_2\text{H}_6^{2+}} = 1.3 \pm 0.3 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$, and $K_{a_2} = 10 \pm 4$. The value of the $K_{a_2}$ in the literature is 11.2 for hydrazinium protonation which is close to that found here by measuring the kinetics in different solutions.$^{27}$
Figure 7. Variation of experimental $k_{\text{obs}}$ with free acid concentration for a medium containing deaerated solution of 7 mol dm$^{-3}$ total NO$_3^-$; (40 Gy pulse$^{-1}$). The data are fitted (solid line) from modelling calculations and dotted lines are uncertainty.
CONCLUSIONS

The detailed decay mechanism of NO$_3^-$ has been determined through a combination of experiment and calculation for 7 mol dm$^{-3}$ solutions of deaerated aqueous LiNO$_3$ and HNO$_3$, in the absence and presence of hydrazine. In the absence of hydrazine, the predominant NO$_3^-$ decay pathways are strongly dependent upon the pH of the solution. For neat neutral pH LiNO$_3$ (7 mol dm$^{-3}$) solutions, NO$_3^-$ is rapidly consumed by OH$^-$ (37%), H$_2$O (37%), NO$_2^-$ (17%), and NO$_2$ (17%). As the acidity increase with increasing HNO$_3$ fraction, there is a greater degree of undissociated HNO$_3$ which strongly influences the NO$_3^-$ decay pathways. For neat HNO$_3$ (7 mol dm$^{-3}$) solutions, NO$_3^-$ is rapidly consumed by HNO$_2$ (15%) and NO$_2$ (80%).

In the presence of hydrazine, NO$_3^-$ is rapidly consumed by N$_2$H$_5^+$, and N$_2$H$_6^{2+}$, once again exhibiting a pH dependence. The rate constants were found to be $k_{N_2H_5^+} = 2.9 \pm 0.9 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$, $k_{N_2H_6^{2+}} = 1.3 \pm 0.3 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$.

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Notes:

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