CHAPTER 3

RESULTS AND DISCUSSION
CHAPTER- 3

RESULTS AND DISCUSSION

3.1 RADIOLYSIS OF AQUEOUS SOLUTIONS OF SODIUM NITRATE:

3.1.1 Results:

The gamma radiolysis of nitrate ions in aqueous solutions was carried out as a function of the dose absorbed at various concentration of nitrate ions in aerated as well as de-oxygenated solutions. The concentration of the products formed during the gamma radiolysis namely nitrite and hydrogen peroxide were estimated spectrophotometrically. The yields of nitrite and hydrogen peroxide formed as a function of the dose absorbed in aerated and de-oxygenated solutions at different concentrations of nitrate are shown in Figs. 3.1, 3.2 and Fig 3.3 respectively. The curves being quite linear, it was possible in most cases to extrapolate to small intercepts for nitrite formation, to the extent of 0.05 to 0.01 μM depending upon the initial concentration of nitrate. The situation is similar to that reported by Allen and Halroyd$^{90}$ as well as by Daniels and Wigg.$^{50}$ Johnson and Weiss$^{91}$ had also observed similar results in the radiolysis of nitrate solutions using the Ce(IV) reduction method for the estimation of the nitrite
Fig. 3.1: Radiolysis of aerated aqueous solutions of sodium nitrate.
Fig. 3.2: Radiolysis of de-oxygenated sodium nitrate solution.
Fig. 3.3(a): Formation of H$_2$O$_2$ in the radiolysis of sodium nitrate solution in the presence of oxygen.
Fig. 3.3 (b): Formation of $\text{H}_2\text{O}_2$ in the radiolysis of sodium nitrate aqueous solution in the presence of oxygen.
Fig. 3.3© - Formation of \( \text{H}_2\text{O}_2 \) in the radiolysis of sodium nitrate solutions in de-oxygenated samples.
The G-values of nitrite and hydrogen peroxide were calculated from the slopes of the linear plots and are recorded in the Table 3.1 from which it may be seen that the G(NO$_2^-$) increases with the concentration of nitrate. Further, the de-oxygenated samples show higher G-values of nitrate as compared to those observed in the aerated solutions at all the concentrations studied. The nitrite yields obtained in the present investigation are found to be in close agreement with the values reported by Daniels and Wigg, for aerated samples. However, there is a considerable disagreement regarding the G(NO$_2^-$) values reported in the literature by different workers. Faraggi et al. find no differences in the G-values of nitrite between aerated and de-oxygenated solutions. Though the G-values of nitrite reported in the present work agree reasonably well in the case of aerated solutions, they differ from the values reported by Faraggi et al. in the case of de-oxygenated solutions.

The G(H$_2$O$_2$) yields given in the Table 3.1 also show an increasing trend with the concentration of nitrate ions. Yields in de-oxygenated solutions are found to be higher as compared to those obtained in aerated solutions at all the
Table 3.1: G-values of products obtained in the aerated and de-oxygenated aqueous solutions of nitrate at neutral pH

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>G(NO$_2^-$) Aerated</th>
<th>G(NO$_2^-$) De-oxygenated</th>
<th>G(H$_2$O$_2$) Aerated</th>
<th>G(H$_2$O$_2$) De-oxygenated</th>
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<tr>
<td>1.0</td>
<td>0.26</td>
<td>0.28</td>
<td>0.50</td>
<td>0.60</td>
</tr>
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<td>2.5</td>
<td>0.36</td>
<td>0.58</td>
<td>0.54</td>
<td>0.68</td>
</tr>
<tr>
<td>5.0</td>
<td>0.42</td>
<td>0.72</td>
<td>0.58</td>
<td>0.69</td>
</tr>
<tr>
<td>10</td>
<td>0.51</td>
<td>0.89</td>
<td>0.62</td>
<td>0.75</td>
</tr>
<tr>
<td>50</td>
<td>0.59</td>
<td>0.94</td>
<td>0.64</td>
<td>0.78</td>
</tr>
<tr>
<td>100</td>
<td>0.67</td>
<td>1.04</td>
<td>0.68</td>
<td>0.80</td>
</tr>
<tr>
<td>200</td>
<td>0.72</td>
<td>1.14</td>
<td>0.70</td>
<td>0.85</td>
</tr>
<tr>
<td>500</td>
<td>0.73</td>
<td>1.16</td>
<td>0.75</td>
<td>0.89</td>
</tr>
</tbody>
</table>
concentrations of nitrate ions studied. Daniels and Wigg had also investigated the radiation chemistry of nitrate and reported the hydrogen peroxide yields \( [G(H_2O_2)] \) in the nitrate ion concentration range of 1 to 500 mM. The \( G(H_2O_2) \) values were found to vary between 0.65 to 0.85 irrespective of whether the samples were aerated or de-oxygenated. The yields of hydrogen peroxide observed in the present work (Table 3.1) vary from 0.60 to 0.89 in de-oxygenated samples which are in good agreement with the above mentioned values. The corresponding \( G(H_2O_2) \) values in the aerated samples are found to increase from 0.50 to 0.75 over a similar concentration range (1-500 mM) of nitrate solutions. Faraggi et al. have obtained almost a constant G-value of 0.75 for the formation of hydrogen peroxide in all samples with no effect of concentration and de-oxygenation contrary to our observations.

3.1.2 Discussion:

It is well known that water upon radiolysis yields reducing species such as \( e^-_{aq} \) and H and oxidizing species like OH, HO\(_2\) and H\(_2\)O\(_2\). These primary radiolytic products (DRP) of water react with dissolved solutes leading to the reduction or oxidation of solute depending on its nature and the electrode potential.
In the radiolysis of aqueous solutions one has to consider two effects: (i) the absorption of radiation by the solute ions leading directly to the formation of products and (ii) an indirect effect due to the absorption of radiation energy by the solvent molecules and the interaction of resulting products with the solute ions. In dilute solutions, the former effect is negligible. The radiation chemical behaviour of any dissolved substance at low concentrations will thus be determined by the sequence of reactions that these species can enter into. While the behaviour of the molecular products can be well predicted; the nature of radical products formed depends on several factors. Though many kinetic studies have been made on the determination of the rate of reactions of hydrated electrons, hydroxyl radical and hydrogen atoms with several organic and inorganic compounds present as solutes, data in regard to the reaction mechanism have been scanty. For an understanding of the mechanisms a knowledge of the chemical behaviour of \( e^-_{aq} \), H and OH radicals is very relevant and indispensable for predicting the possible radiolytic fate of any given solute at low concentrations.

The radiolysis of nitrate ion solutions has been studied in aerated as well as de-oxygenated solutions wherein the nitrate ion gets reduced to nitrite. Apart from
the nitrite ions, hydrogen peroxide is also produced in the radiolysis of nitrate solutions. Quantitative results on the formation of nitrite\textsuperscript{53,58,59} and hydrogen peroxide\textsuperscript{53,58-59} reported by different investigators are not in accord amongst themselves. Most probably the divergences are due to differences in the analytical procedures adopted by the different workers. As an example, we find that widely different values for $G(\text{NO}_2^-)$ have been reported at pH 7; varying from 2-3\textsuperscript{56} to 5-8\textsuperscript{32}. These observations are difficult to reconcile with well established values of $G(\text{H}_2\text{O})$ of water.

With a view to resolving the discrepancies, the present study was undertaken especially in respect of yields of products reported in literature and if possible to arrive at a reaction mechanism involved in the radiolysis of nitrate solutions. For this purpose, an extensive series of measurements of nitrite production was made over a wide range of nitrate concentrations from 1 mM to 500 mM in a neutral medium. Particular emphasis was placed on neutral solutions because even though extensive studies have been reported in such solutions, there have been no agreed quantitative data.
3.1.2.1 The Yield of Nitrite in Oxygen-free Solutions:

The formation of nitrite in the radiolysis of de-oxygenated solutions can be explained on the basis of following sequence of reactions.

\[
\begin{align*}
\text{NO}_3^- + e_{aq}^- & \rightarrow \text{NO}_2^- \quad \text{---(3.1)} \\
\text{NO}_3^- + H & \rightarrow \text{HNO}_2^- \quad \text{---(3.2)} \\
\text{NO}_2^- + H_2O^+ & \rightarrow \text{HNO}_2^- + H_2O \quad \text{---(3.3)} \\
\text{HNO}_2^- & \rightarrow \text{NO}_2^- + OH^- \quad \text{---(3.4)}
\end{align*}
\]

Reaction (3.1) proceeds with a rate constant $1.1 \times 10^{10}$ M$^{-1}$s$^{-1}$ while the Reaction (3.2) takes place with a rate constant of $1.4 \times 10^7$ M$^{-1}$s$^{-1}$. Thus, the hydrated electron reacts almost 785 times faster than the hydrogen radical and hence it may be concluded that the concentration of NO$_3^-$ required to scavenge the e$_{aq}^-$ completely is much lower than that required for the total consumption of H radicals. The HNO$_2^-$ formed in Reactions (3.2 and 3.3) disappears by Reaction (3.4) forming NO$_2$. The NO$_2$ thus formed immediately reacts with water by disproportionation reaction giving nitrite as a stable product according to the following reaction

\[
2\text{NO}_2 + H_2O \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2H^+ \quad \text{---(3.5)}
\]

The nitrite formed in the above reaction may disappear by reacting with the hydroxyl radical, the rate constant being
$6.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for this reaction.

\[
\text{NO}_2^- + \text{OH} \rightarrow \text{NO}_2 + \text{OH}^- \quad (3.8)
\]

This NO$_2$ formed in the above reaction further undergoes Reaction (3.5) and finally leading to the formation of the product, nitrite.

The dependence of radiolytic reduction of nitrate on its initial concentration shows that it is not able to scavenge all the pro of water at low concentrations. As we increase the concentration of nitrate more and more hydrated electrons and hydrogen atoms get scavenged thereby giving greater decomposition of nitrate to nitrite ions. The consumption of higher and higher fraction of reducing species with the concentration of nitrate is confirmed$^{50,59}$ by the corresponding decrease observed in G-values of H$_2$ whose precursor is the hydrogen atom. This increasing trend occurs up to a certain concentration and beyond that the $G(\text{NO}_2^-)$ attains almost a constant value. The limiting $G(\text{NO}_2^-)$ value obtained by extrapolation of the plot of $G(\text{NO}_2^-)$ versus concentration of nitrate (Fig. 3.4) are found to be 0.72 and 1.14 for aerated and de-oxygenated solutions respectively. The value of 0.72 for the formation of nitrite ions in aerated solutions is not in agreement with the value reported by Faraggi et al.$^{50}$ Further, the limiting $G(\text{NO}_2^-)$ observed in de-oxygenated solutions is found to be higher in
Fig. 3.4 - Dependence of $G(\text{NO}_2^-)$ on the concentration of nitrate ions in the radiolysis of sodium nitrate.
the present work than that reported by Daniels and Wigg\textsuperscript{59} in He-swept samples.

According to the mechanism postulated, the reducing species $e_{aq}^-$ and H reduce one equivalent of nitrate ion each generating thereby the transient species, $\text{NO}_3^-$ and $\text{HNO}_3^-$ respectively. These transients decay to tetravalent nitrogen ($\text{NO}_2$) which in turn disproportionates forming nitrite. It is evident from the above reaction sequence that two $e_{aq}^-$ or two H-atoms are required for the formation of one nitrite ion as a final stable product, as two $\text{NO}_2$ species participate in the disproportionation reaction (Reaction 3.5). Therefore, the $\text{G(}\text{NO}_2^-\text{)}$ yield should be equivalent to half of the summation of $\text{G(}e_{aq}^-\text{)}$ and $\text{G(H)}$. Besides this, out of the total number of nitrite ions formed some of them get consumed by OH radicals via Reaction (3.6). From the above mentioned reactions it is clear that two hydroxyl radicals are responsible for the disappearance of one nitrite ion. Assuming the complete scavenging of $e_{aq}^-$ and hydrogen atoms by the nitrate ions (Reactions 3.1 and 3.2) as well as to the removal of OH radical by $\text{NO}_2^-$ (Reaction 3.6), the overall material balance equation for the formation of nitrite in de-oxygenated solutions is given by the expression

$$\text{G(}\text{NO}_2^-\text{)} = \frac{1}{2} [\text{G(}e_{aq}^-\text{)} + \text{G(H)} - \text{G(OH)}] \quad ----(I)$$

However, the limiting G-value in de-oxygenated solutions
using the above equation comes out to be 0.41 which is lower than the value of 1.14 observed in the present study. The higher limiting value of \( G(\text{NO}_2^-) \) indicates that OH radicals are partially consumed by the nitrite ions and hence equation (I) needs to be rewritten as

\[
G(\text{NO}_2^-) = \frac{1}{2} \left[ G(e_{aq}^-) + G(H) - f(G(\text{OH})) \right] \quad -----(II)
\]

The fraction \( f \) of OH which combines with \( \text{NO}_2^- \) forming nitrite ion appears to be 0.42 giving limiting \( G(\text{NO}_2^-) \) value of 1.15 for de-oxygenated solutions.

3.1.2.2 Yields of Nitrite in Aerated Solutions:

Apart from Reactions that take place in de-oxygenated nitrate solutions giving nitrite, the dissolved oxygen in aerated solutions also brings about an additional reactions being an efficient scavenger of hydrated electrons and hydrogen atoms. This leads to the initiation of the following course of reactions.

\[
e_{aq}^- + O_2 \rightarrow O_2^- \quad -----(1.18)
\]

\[
H + O_2 \rightarrow \text{HO}_2^- \quad -----(1.17)
\]

\[
\text{HO}_2^- \rightarrow H^+ + O_2^- \quad -----(1.44)
\]

\( O_2^- \) thus formed, may either react with \( \text{NO}_2^- \) formed in the Reactions (3.4) and (3.6),

\[
O_2^- + \text{NO}_2^- \rightarrow \text{NO}_2^- + O_2 \quad -----(1.64)
\]
or may disappear as follows

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The increasing trend in the $G(\text{NO}_2^-)$ values with concentration of nitrate can be explained on similar lines as described for oxygen-free solutions. The limiting G-value of nitrite in aerated solutions obtained from the extrapolation method is found to be 0.72. However, we could not establish the material balance equation for the formation of nitrite in aerated solutions because of the uncertainty in the extent of the occurrence of Reactions (1.64, 1.84, 1.16 and 1.47) involving $O_2^-$ as one of the reactants.

The observed trend of lower G-values of nitrite in aerated nitrate solutions compared to those in de-oxygenated samples (Table 3.1) can be attributed to the presence of oxygen in the aerated solution which competes with nitrate ions to scavenge hydrated electrons via Reaction (1.18). Hence fewer hydrated electrons are available for nitrate ions to scavenge than actually produced. Among the subsequent reactions initiated by $O_2^-$ the extent of Reaction (1.64) producing NO$_2^-$ appears to be quite low. Unfortunately the rate constant between NO$_2^-$ and O$_2^-$ is not known in

$$2O_2^- + 2H^+ \rightarrow H_2O + O_2 \quad \text{----(1.84)}$$

$$O_2^- + HO_2^- \rightarrow HO^- + O_2 \quad \text{----(1.18)}$$

$$O_2^- + O_2^- \rightarrow H_2O \rightarrow HO^- + O_2 + OH^- \quad \text{----(1.47)}$$
literature. It appears that a large fraction of $O_2^-$ is consumed by Reactions (1.84, 1.84, 1.16 and 1.47) which do not contribute directly or indirectly to the formation of nitrite ions. When the oxygen in the sample is removed completely, the reducing species are left to be scavenged solely by the nitrate ions and thereby yielding higher G-values in the de-oxygenated solutions than in the aerated samples as observed.

It is worthwhile to compare the data of nitrite observed in aerated nitrate solutions obtained in the neutral medium in the present investigations with those reported by Patil et al$^{93}$ for the basic medium at pH 12. It was found that the G-values of nitrite in aerated nitrate solutions are much higher in a basic medium than in a neutral medium. The enhancement in the yield of nitrite at pH 12 is attributed by them to the occurrence of following additional reactions. In the basic medium OH radicals get ionized to $O^-$ which in turn reacts with nitrate ions leading to the formation of nitrite.

\[
\begin{align*}
    NO_3^- + O^- + H_2O & \rightarrow NO_3^+ + 2OH^- \quad (3.7) \\
    2NO_3^- & \rightarrow 2NO_2^- + O_2 \quad (3.8) \\
    2NO_2^- + H_2O & \rightarrow NO_3^- + NO_3^- + 2H^+ \quad (3.5)
\end{align*}
\]
3.1.2.3 The $\text{H}_2\text{O}_2$ Formation:

The increase in the yield of hydrogen peroxide with concentration of nitrate solutions (aerated and de-oxygenated) could be attributed to the occurrence of radical-radical recombination of hydroxyl radicals (Reaction 1.6) and perhydroxyl radicals (Reaction 1.15). Moreover, the excited water molecules in the spur which diffuse out into the bulk of solution may be interacting with nitrate ions in the solution rather than undergoing dimerization or radical production reactions resulting in the formation of hydrogen peroxide and nitrite ions.

$$\text{H}_2\text{O}^* + \text{NO}_3^- \rightarrow \text{H}_2\text{O}_2 + \text{NO}_2^- \quad \text{(3.9)}$$

Therefore, it is clear that as the nitrate concentration increases the Reaction (3.9) occurs more frequently along with Reactions (1.6) and (1.15) eventually reflecting on the yield of hydrogen peroxide.

3.2 Radiolysis of Aqueous Solutions of Nitrate - Alcohols:

When aqueous solutions of nitrate and alcohols are subjected to gamma radiolysis the \textit{prf} of water interact with the reactants in a manner depending upon their reactivities. The reducing species expected to react with nitrate ions
while the oxidizing species like hydroxyl radical will be consumed by the alcohol added to the solution. The hydrogen atoms also react with the alcohols in a similar way as \( \text{OH} \). However, the rate constant of reaction of H-atom with most of the alcohols is of the order of \( 10^8 \text{ M}^{-1}\text{s}^{-1} \) which is quite low as compared to that with nitrate \( (1.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}) \). Therefore, the consumption of H-atoms by alcohol is negligible in binary solutions. As mentioned earlier (Section 3.1.2.1), the \( \text{e}_{aq}^- \) and H atoms reduce one equivalent of nitrate ion each leading to the formation of transients \( \text{NO}_2^- \) and \( \text{NO}_2^- \). In the absence of alcohol these intermediates finally disappear to produce nitrite ions. On the other hand, the \( \text{NO}_3^- \) and \( \text{NO}_2^- \) in the presence of alcohol prefer to react with the alcohol radicals which are formed from the attack of \( \text{OH} \) yielding nitrite and aldehyde as their corresponding products of nitrate and alcohol. Keeping this idea in mind, we have selected typical systems containing nitrate ions acting as an efficient scavenger for the reducing species and alcohols (methyl, ethyl, 1-propyl, 1-butyl, iso-propyl, iso-butyl and ter-butyl) which selectively scavenge the hydroxyl radicals. The products formed as nitrite, hydrogen peroxide and aldehydes resulting from above systems were estimated. Further, the study was extended to investigate the effect of pH on the radiolysis.
of nitrate-alcohol systems. The neutral, basic (pH 12) and acidic (pH 3.5) media were chosen for the study.

Two sets of experiments were carried out for the radiolysis of each nitrate-alcohol system selected; one in presence of air and the other in which the oxygen present in the solution was removed by replacing it with nitrogen for all the pHs of the solutions.

The effect of concentration of nitrate and alcohol of interest on the yield of the radiolytic products was also examined. The concentration of one reactant was kept constant while that of the other was varied. In a typical set of experiments the concentration of nitrate in synthetic solutions was changed from 1 mM to 100 mM while that of the alcohol was kept constant. In another set of experiments the concentration of the nitrate was kept constant and that of the alcohol was changed from 1 mM to 100 mM.

For the sake of convenience, the results obtained in nitrate-alcohol systems at neutral, basic and acidic media are presented separately. The interpretation of the results obtained in each medium is provided thereafter.
3.2.1 RADIOLYSIS OF AQUEOUS SOLUTIONS OF NITRATE-ALCOHOLS IN THE NEUTRAL MEDIUM:

3.2.1.1 Results:

The radiation chemistry of nitrate and alcohols (methyl, ethyl, 1-propyl, 1-butyl, iso-propyl, iso-butyl and tert-butyl) in the aqueous solutions at neutral pH is carried out for various combinations of concentrations of the reactants at different absorbed doses. The results of the formation at nitrite in aerated and de-oxygenated solutions of neutral pH containing nitrate and alcohol of interest with dose absorbed are depicted in Figs.3.5, 3.8, 3.11, 3.14, 3.17, 3.19 and 3.22. The corresponding yields of hydrogen peroxide with the absorbed dose in the above systems are presented in Figs. 3.6, 3.9, 3.12, 3.15, 3.18, 3.20 and 3.23 while the variation of the formation of aldehyde concentration with absorbed dose are recorded in Figs. 3.7, 3.10, 3.13, 3.16 and 3.21.

A critical examination of Figs. 3.5 to 3.23 as well as Figs. 3.1 to 3.3 representing the results of nitrate solution alone and Tables 3.1 to 3.8 leads to the following important observations in the radiolysis of nitrate+alcohol systems.
Fig. 3.5: Yield of nitrite in the presence of methanol at neutral pH.
Fig. 3.6: Yield of $\text{H}_2\text{O}_2$ in the presence of methanol at neutral pH.
Fig 3.7: Yield of formaldehyde in the presence of methanol at neutral pH.
Fig. 3.8: Variation in the yield of nitrite with absorbed dose in the binary mixture of nitrate - ethanol at neutral pH.
Fig 3.9: Variation in the yield of $\text{H}_2\text{O}_2$ in the binary solutions of nitrate-ethanol in netural medium.
Fig. 3.10: Variation in the yield of acetaldehyde with absorbed dose in the binary solutions of nitrate–ethanol at neutral pH.
Fig. 5-11: Variation in the yield of nitrite in the nitrate-1-propanol binary mixtures with absorbed dose.
Fig 3.12: Variation in the yield of hydrogen peroxide in the nitrate-1-propanol binary mixtures with absorbed dose.
Fig. 7.13: Variation in the yield of propionaldehyde in the nitrate-1-propanol binary mixtures with absorbed dose.
Fig. 3.14: Yield of nitrite in the presence of 1-butanol at neutral pH.
Fig. 3.15: Dependence of yield of \( \text{H}_2\text{O}_2 \) in the nitrate-1-butanol solutions with absorbed dose at neutral pH.
Fig. 3.16: Yield of butyraldehyde in the presence of nitrate–1–butanol solutions at neutral medium.
Fig. 3.17: Dependence of nitrite yield in the presence of isopropanol with dose absorbed at neutral pH.
Fig. 3.18: Dependence of yield of $\text{H}_2\text{O}_2$ in the presence of iso-propanol with absorbed dose at neutral pH.
Fig 3.19: Variation of nitrite formed in binary mixtures as a function of dose absorbed.
Fig. 320: Variation of aldehyde formed in binary mixtures with dose absorbed.
Fig. 3.2: Amount of hydrogen peroxide formed in binary mixtures with dose absorbed.
Fig. 3.22: Dependence of yield of nitrite with absorbed dose in the binary solution of nitrate-ter-butanol at neutral pH.
Fig. 3.23: Dependence of yield of H₂O₂ in the nitrate-ter-butanol solutions with absorbed dose at neutral pH.
Table 3.2: Yield of nitrite, hydrogen peroxide and formaldehyde in the binary solutions of nitrate + methanol at neutral pH

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>[MeOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO$_2^-$) G(H$_2$O$_2$) G(-CHO)</td>
<td>G(NO$_2^-$) G(H$_2$O$_2$) G(-CHO)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.09</td>
<td>2.23</td>
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<tr>
<td>1</td>
<td>100</td>
<td>1.18</td>
<td>2.56</td>
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<tr>
<td>100</td>
<td>1</td>
<td>1.61</td>
<td>1.50</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.12</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Table 3.3: Effect of concentrations of nitrate and ethanol on the yield of nitrite, hydrogen peroxide and acetaldehyde on the radiolysis of nitrate + ethanol binary solutions at neutral pH

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>[EtOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO$_2^-$) G(H$_2$O$_2$) G(-CHO)</td>
<td>G(NO$_2^-$) G(H$_2$O$_2$) G(-CHO)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.89</td>
<td>1.88</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.06</td>
<td>2.51</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.19</td>
<td>1.43</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.53</td>
<td>1.93</td>
</tr>
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Table 3.4: Variation in the yield of nitrite, hydrogen peroxide and 1-propionaldehyde with concentration of nitrate as well as 1-propanol in the binary mixture of nitrate-1-propanol at neutral pH.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[1-PrOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
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<td>2.08</td>
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</tr>
<tr>
<td>100</td>
<td>1</td>
<td>2.41</td>
<td>1.98</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.75</td>
<td>2.15</td>
</tr>
</tbody>
</table>

Table 3.5: Dependence of yields of NO₂⁻, H₂O₂ and CH₃CH₂CH₂CHO on the nitrate and butanol concentrations at neutral pH.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[1-BuOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.96</td>
<td>1.94</td>
</tr>
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<td>1.24</td>
<td>2.05</td>
</tr>
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<td>100</td>
<td>1</td>
<td>1.73</td>
<td>1.75</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.45</td>
<td>1.84</td>
</tr>
</tbody>
</table>
Table 3.6: Values of the yields of nitrite, hydrogen peroxide the radiolysis of binary solutions of nitrate containing iso-propanol at neutral pH.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[Iso-ProH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
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<td>1</td>
<td>1.10</td>
<td>2.07</td>
</tr>
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<td>100</td>
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</tr>
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<td>1</td>
<td>1.76</td>
<td>1.63</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.14</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Table 3.7: Influence of the change in the concentration of nitrate and iso-butanol in their binary aqueous solutions on the radiation chemical yields of nitrite, hydrogen peroxide and iso-butyraldehyde at neutral pH.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[Iso-BuOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.43</td>
<td>2.48</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.61</td>
<td>2.35</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>2.24</td>
<td>1.84</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.57</td>
<td>1.65</td>
</tr>
</tbody>
</table>
Table 3.8: G-values of nitrite and hydrogen peroxide in the presence of nitrate-ter-butanol binary solutions at neutral pH.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[ter-BuOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.50</td>
<td>1.94</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.56</td>
<td>2.46</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>2.12</td>
<td>1.45</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.40</td>
<td>1.88</td>
</tr>
</tbody>
</table>
1. The radiolytic formation of nitrite in different aqueous solutions of nitrate-alcohol is found to increase linearly with the dose absorbed.

2. When we compare the yields of products in aerated and de-oxygenated solutions, nitrite yields are found to be higher in the de-oxygenated solutions as compared to those observed in the aerated counterparts. However, the yields of aldehyde and hydrogen peroxide are greater in aerated solutions than those found in the de-oxygenated medium.

3. The G-values of nitrite as well as of respective aldehydes increases with increase in the concentration of nitrate as well as of the alcohol added in both aerated and de-oxygenated solutions. For example, G-values of nitrite increases from 1.24 to 2.41 as the concentration of nitrate is changed from 1 to 100 mM in aerated solutions containing a constant (1 mM) concentration of 1-propanol while the corresponding values of the yield of nitrite in deoxygenated solutions increases from 1.58 to 2.42 for the same combination of reactant concentrations. Similarly, the G(NO$_2^-$) increases from 2.41 to 2.75 if we changed the concentration of 1-propanol from 1 to 100 mM at a constant concentration of nitrate (100 mM) in aerated solutions. The G(NO$_2^-$) also found to
vary from 2.42 to 2.81 at a constant concentration of nitrate (100 mM) and that of the 1-propanol is changed from 1 to 100 mM in de-oxygenated solutions.

4. The hydrogen peroxide yield increases with the concentration of 1-propanol and decreases with increase in the nitrate concentration in aerated solutions. On the other hand, an opposite trend in the G(H₂O₂) is observed in the de-oxygenated solutions. For example, at a fixed concentration of nitrate (100 mM), the G(H₂O₂) rises from 1.98 to 2.15 in aerated solutions as the concentration of 1-propanol increased from 1 to 100 mM. However, the G(H₂O₂) value decreases from 2.06 to 1.98 in aerated solutions as the concentration of nitrate is changed from 1 to 100 mM keeping the concentration of 1-propanol constant at 1 mM. However, the change in the G(H₂O₂) values from 1.06 to 0.57 in de-oxygenated solution is observed when the concentration of 1-propanol is increased from 1 mM to 100 mM at 100 mM concentration of nitrate.

5. A comparison of the G-values of nitrite and hydrogen peroxide in plain nitrate solutions with those observed in the nitrate-alcohol solutions reveals that the yields of nitrite and hydrogen peroxide in the latter are higher than in the former. For instance, in the aerated
solutions containing 100 mM of nitrate and 1 mM of 1-propanol, the G-values observed were 1.98 and 2.41 for hydrogen peroxide and nitrite respectively in contrast to the corresponding values of 0.68 and 0.67 in pure nitrate of same concentration (Tables 3.1 and 3.4). The corresponding G-values of H$_2$O$_2$ and nitrite in de-oxygenated solutions containing same proportions of nitrate-1-propanol were found to be 1.08 and 2.42 as against the values of 0.80 and 1.04 respectively in de-oxygenated nitrate solution (100 mM).

6. From the Tables 3.2 to 3.5, it is observed that there is no definite correlation between the yields of the products with the chain length of the alcohols studied. However, the branched alcohols such as iso-propyl, iso-butyl and ter-butyl alcohols give slightly higher yields of the products in both aerated and de-oxygenated samples in relation to those found in the solutions containing linear alcohols.

3.2.2 Discussion:

One of the most widely used methods to determine the scavengable yield of $e^-_{aq}$ has been to measure $G(\text{NO}_2^-)$ in the de-oxygenated aqueous solutions containing nitrate ion as an electron scavenger and formate$^{83,93,94}$ as a hydroxyl
radical scavenger. In the present case, the radiolysis of nitrate-alcohol solutions was carried out in the neutral medium. The observed yields of the products are discussed below in detail.

The nitrate ions on radiolysis get reduced to nitrite as mentioned earlier, that is, via Reactions (3.1 to 3.4). However, in aqueous solutions of NO$_3^-$-alcohols additional reactions occur involving the alcohol, its radical and intermediates resulting from interactions with nitrate ions. The alcohols R--OH (R = CH$_3$, CH$_2$CH$_2$, CH$_3$(CH$_2$)$_2$, CH$_3$(CH$_3$)$_2$, (CH$_3$)$_2$CH, (CH$_3$)$_2$CHCH$_2$, (CH$_3$)$_3$C groups) scavenge hydroxyl radicals thereby producing the respective hydroxyalkyl radicals (CH$_2$OH, CH$_3$CHOH, CH$_3$CH$_2$CHOH, CH$_3$(CH$_2$)$_2$CHOH, (CH$_3$)$_2$COH, (CH$_3$)$_2$CHCHOH and CH$_2$(CH$_3$)$_2$COH). The formation of radical in general is represented by following reactions.

$$R$$-$$OH + OH \rightarrow R$$-$$OH + H_2O \quad ---(3.12)$$

$$R$$-$$OH + H \rightarrow R$$-$$OH + H_2 \quad ---(3.13)$$

These alcohol radicals react with NO$_3^-$ and NO$_2^-$ formed in Reaction (3.1 - 3.4) as follow

$$R$$'-$$OH + NO$_3^-$ \rightarrow R$$-$$CHO + NO$_2^-$ + OH$^- \quad ---(3.14)$$

$$R$$'-$$OH + NO$_2$ \rightarrow R$$-$$CHO + NO$_2^-$ + H$^+$ \quad ---(3.15)$$

giving nitrite and aldehyde. Apart from these, the alcohol radicals may also react with oxygen present in the aerated
solutions leading to the following reactions as

\[
R'\cdot\cdot\cdot OH + O_2 \rightarrow O_2 R'\cdot\cdot\cdot OH \quad (3.18)
\]

\[
2O_2 R'\cdot\cdot\cdot OH \rightarrow 2\text{R'\cdot\cdot\cdot CHO} + H_2 O_2 + O_2 \quad (3.17)
\]
or
\[
O_2 R'\cdot\cdot\cdot OH + HO_2(O^-) \rightarrow \text{R'\cdot\cdot\cdot CHO} + H_2 O_2 + O_2 \quad (3.18)
\]

The above reactions occur predominantly as long as the reactive species (NO_3^-, NO_2) and oxygen are present. The unreacted alcohol radicals undergo disproportionation or dimerization reactions as

\[
2\text{R'\cdot\cdot\cdot OH} \rightarrow \text{R'\cdot\cdot\cdot CHO} + \text{R\cdot\cdot\cdot OH} \quad (3.19)
\]

\[
2\text{R'\cdot\cdot\cdot OH} \rightarrow \text{R(OH)(OH)R} \quad (3.20)
\]

The above sequence of reactions operating during the radiolysis of binary aqueous solutions of nitrate-alcohol is illustrated below with reference to a typical system, viz. nitrate+1-propanol, aerated as well as de-oxygenated.

Hydroxyl radical reacts with 1-propanol via abstraction of hydrogen atom from a \(\alpha\)-carbon atom giving hydroxypropyl radical, the rate constant of this reaction being 2.65 x 10^6 M^{-1} s^{-1}.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CHOH} + \text{H}_2\text{O} \quad (3.21)
\]

While the OH radicals left unscavenged in the absence of sufficient amount of alcohol, recombine to give hydrogen peroxide via Reaction (1.6).
The H-atom also undergoes hydrogen abstraction reactions with 1-propanol but at a slower rate. The rate constant of the Reaction (3.22) is of the order of $10^7$ M$^{-1}$ s$^{-1}$.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{H} \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2 \quad (3.22)$$

The hydroxypropyl radical thus formed in turn reacts with NO$_3^-$ and NO$_2$ in the binary mixture reducing them to nitrite ions and getting itself oxidized to propionaldehyde.

$$\text{CH}_3\text{CH}_2\text{CHO} + \text{NO}_3^- \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{NO}_2^- + \text{OH}^- \quad (3.23)$$

$$\text{CH}_3\text{CH}_2\text{CHO} + \text{NO}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{NO}_2^- + \text{H}^+ \quad (3.24)$$

The remaining hydroxypropyl radicals disappear according to the following reaction

$$2\text{CH}_3\text{CH}_2\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad (3.25)$$

$$2\text{CH}_3\text{CH}_2\text{CHO} \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad (3.26)$$

In aerated nitrate + 1-propanol solutions, following additional reactions occur

$$\text{CH}_3\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHOHCH}_3 \quad (3.27)$$

$$2\text{CH}_3\text{CH}_2\text{CHO} \rightarrow 2\text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}_2 + \text{O}_2 \quad (3.28)$$

or $$\text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}_2 (\text{O}_2^-) \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O}_2 + \text{O}_2^- \quad (3.29)$$

Based on the extent of the occurrence of these reactions in the radiolysis, the observed trend in the yields of the different products can be explained.
Lower G-values of nitrite in aerated solutions than those observed in de-oxygenated ones are explained by considering the competition reactions of oxygen with nitrate ions to scavenge the hydrogen radical and hydrated electrons via Reaction (1.17 and 1.18). Hence less number of $e_{aq}^-$ are available in the presence of oxygen, for reducing the nitrate ions, thereby yielding lower G-values in oxygenated solutions.

The increasing trend in the G-values of nitrite in both aerated and de-oxygenated solutions with concentration of alcohol or nitrate keeping one of them constant can be explained on the basis of the probability of the occurrence of Reactions (3.1-3.5) and (3.23 and 3.24). For example, as we increase the concentration of nitrate at a fixed concentration of 1-propanol, more and more $\text{NO}_2^-$ and $\text{NO}_3^-$ species are generated and consequently the efficiency of nitrite formation via Reactions (3.23) and (3.24) increases giving higher nitrite yield (Table 3.4). On the other hand, when the concentration of alcohol increases keeping that of the nitrate constant, more number of hydroxypropyl radicals are produced and are available for the reaction with transients ($\text{NO}_3^-$ or $\text{NO}_2^-$). This also leads to the formation of higher concentration of nitrite resulting in higher yields (Table 3.4)
The higher \( G(H_{2}O_{2}) \) values observed in aerated binary mixtures as compared to the de-oxygenated samples keeping all other experimental conditions constant can be interpreted in terms of the reactions of \( O_{2} \) with hydrogen atoms and hydrated electrons (Reactions 1.17 and 1.18) as well as with hydroxypropyl radicals (Reaction 3.27) which finally lead to the formation of hydrogen peroxide through Reactions (3.28 and 3.29). In the de-oxygenated solutions Reaction (3.27) and hence Reactions (3.28 and 3.29) do not occur and therefore, hydrogen peroxide formed in these solutions as observed are only via Reaction (1.6) and therefore, lower yield of the hydrogen peroxide is obtained in de-oxygenated solutions as compared to the aerated samples (Tables 3.2 to 3.8).

The dependance of propionaldehyde yield on the concentration of both the reactants in aerated and de-oxygenated solutions can be interpreted in the same way as provided for the variation in the nitrite formation. It is seen that the propionaldehyde is formed in the Reactions (3.23, 3.24, 3.26, 3.28 and 3.29) which are governed by the concentration of species whose formation depends on either alcohol or on nitrate ion concentrations.
The branched alcohols such as iso-propanol, iso-butanol and ter-butanol also undergo hydrogen abstraction reactions. The corresponding hydroxyalkyl radicals thus generated interact with NO$_3^-$ and NO$_2$ giving nitrite, hydrogen peroxide and acetone or iso-butyraldehyde. We could not determine the concentration of acetone resulting from the radiolysis of iso-propanol and ter-butanol due to lack of facilities. Simple chemical methods did not yield reproducible results.

To illustrate the formation of acetone the nitrate -iso-propanol system is chosen wherein following reactions occur.

\[
\begin{align*}
(CH_3)_2CHOH + OH & \rightarrow (CH_3)_2COH + H_2O \quad \text{(3.30)} \\
(CH_3)_2CHOH + H & \rightarrow (CH_3)_2COH + H_2 \quad \text{(3.31)}
\end{align*}
\]

The NO$_3^-$ and NO$_2$ formed from nitrate reacts with the above mentioned alcohol radicals producing acetone and nitrite as

\[
\begin{align*}
(CH_3)_2COH + NO_3^- & \rightarrow (CH_3)_2CO + NO_2^- + OH^- \quad \text{(3.32)} \\
(CH_3)_2COH + NO_2 & \rightarrow (CH_3)_2CO + NO_2^- + H^+ \quad \text{(3.33)}
\end{align*}
\]

The unreacted hydroxyisopropyl radicals alternatively undergo disproportionation or dimerization reaction as follows

\[
\begin{align*}
2(CH_3)_2COH & \rightarrow (CH_3)_2CO + (CH_3)_2CHOH \quad \text{(3.34)} \\
2(CH_3)_2CHOH & \rightarrow (CH_3)_2COHOHCO(CH_3)_2 \quad \text{(3.35)}
\end{align*}
\]
In the presence of dissolved oxygen the hydroxyisopropyl radicals react with oxygen giving acetone and hydrogen peroxide

\[(\text{CH}_3)_2\text{COH} + \text{O}_2 \longrightarrow \text{O}_2\text{COH} (\text{CH}_3)_2 \]  
\[2\text{O}_2\text{COH} (\text{CH}_3)_2 \longrightarrow 2(\text{CH}_3)\text{CO} + \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(3.36)}\]

or \[2\text{O}_2\text{COH} (\text{CH}_3)_2 + \text{HO}_2 (\text{O}^-) \longrightarrow 2(\text{CH}_3)\text{CO} + \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(3.38)}\]

It may be noted that the Reactions (3.36 to 3.38) do not occur in the de-oxygenated solutions.

The enhancement in the yield of nitrite in these solutions with nitrate and iso-propanol concentrations (Table 3.6) can be explained by considering the Reactions (3.32 and 3.33) along with Reactions (3.1-3.5).

The other product, hydrogen peroxide follows a somewhat different pattern in solutions containing branched alcohols. The yield of hydrogen peroxide in aerated solutions increase with the concentration of iso-propanol at a fixed concentration of nitrate, while it decreases with the concentration of nitrate at a constant alcohol concentration (Table 3.6). This type of variation in the formation of hydrogen peroxide with the concentration of both the reactants may qualitatively be explained by considering the extent of the occurrence of reactions. It
appears that, at higher concentration of alcohol especially in aerated solutions, the alcohol radical follows Reaction (3.36-3.38) along with the (Reaction- 1.8) more frequently than those taking place at lower concentrations thereby affecting the yield of $\text{H}_2\text{O}_2$. On the other hand, at higher concentrations of nitrate, the alcohol radicals prefer to react with the transients resulting from nitrate ions rather than with oxygen. Moreover, as the oxygen present in the solution scavenges the hydrated electrons, the chances of $\text{O}_2$ reacting with alcohol radical decreases giving a lower yield of $\text{H}_2\text{O}_2$ at higher concentration of nitrate. In the de-oxygenated solutions Reactions (3.36-3.38) are completely eliminated and only the dimerization of OH radicals occur and hence the lower yields are observed in the de-oxygenated samples.

In nitrate + ter-butanol solutions, the ter-butanol molecule does not have any $\alpha$-hydrogen atom but six $\beta$-hydrogen are available for the attack of hydroxyl and hydrogen radicals. Therefore, any one of them will be removed by hydroxyl and hydrogen radicals thereby generating the corresponding alcohol radical. Typical reactions are given below
These ter-butyl alcohol radicals further interact with the intermediates and oxygen yielding nitrite, hydrogen peroxide and acetone in the similar way as has been given for the isopropanol since the reaction pattern is more or less similar, though the reaction rates may differ.
3.2.2 RADIOLYSIS OF NITRATE/ALCOHOL SYSTEMS IN BASIC MEDIUM (AT pH 12):

3.2.2.1 Results:

To examine the influence of basic pH on the extent of radiolysis, all the solutions were prepared by adding sodium hydroxide solutions in such a way that the resultant solution gave a pH of 12. After gamma irradiation, the solution was first neutralized and the products were analysed by a suitable technique as mentioned in the second chapter. The variation of the yields of the products formed in the presence of different alcohols with dose absorbed for different combinations of concentrations of reactants, are shown graphically in Figs. 3.24 to 3.34. The G-values of nitrite, hydrogen peroxide and aldehydes in aerated and de-oxygenated solutions are presented in the Tables 3.9 to 3.15.

The important observations drawn from these studies are summarized below:

1. The G-values of nitrite (Tables 3.9 to 3.15) are found to be higher at pH 12 than those obtained in neutral solutions in all the systems studied both in aerated and de-oxygenated solutions.
Fig. 3.24: Yield of nitrite with absorbed dose in the binary solution of nitrate–methanol at pH 12.
Fig. 3.25: Yield of nitrite in nitrate ethanol aqueous solutions at pH 12.
Fig. 3.26: Yield of formaldehyde with absorbed dose in the nitrate-methanol binary solutions in basic medium.
Fig. 3.27: Yield of acetaldehyde in the presence of nitrate-ethanol binary solutions at pH 12.
Fig. 3.28: Effect of de-oxygenation on the yield of
(A) nitrite  (B) n-propionaldehyde in the
nitrate-n-propanol in basic medium.
Fig. 3.29: Effect of de-oxygenation on the yield of (A) nitrite and (B) n-butyraldehyde in the nitrate-n-butanol solutions at pH 12.
Fig. 3.30: Variation in the yield of A nitrite and B H$_2$O$_2$ in the radiolysis of nitrate-isopropanol solution at pH 12.
Fig. 3.31: Variation in the yield of nitrite in the radiolysis of nitrate-iso-butanol solution at pH 12.
Fig 3.32 - Variation in the yield of iso-butyraldehyde in the presence of nitrate-iso-butanol solutions at pH 12.
Fig. 3.33: Yield of (A) nitrite and (B) \( \text{H}_2\text{O}_2 \) in the presence of nitrate-ter-butanol binary solutions at pH 12.
Fig. 3.34: Estimation of H₂O₂ in the binary mixtures containing (A)-nitrate-methanol and (B)-nitrate-ethanol at pH 12.
Fig. 3.34: Estimation of $\text{H}_2\text{O}_2$ in the binary solutions of nitrate containing iso-butanol at pH 12.
Fig. 3.35: Yield of nitrite in the presence of nitrate-methanol binary solutions at pH 3.5.

\[
\begin{align*}
\text{Aerated} & \quad \left[ \text{NO}_3^- \right]/\text{mM} : \left[ \text{MeOH} \right]/\text{mM} \\
\odot & \quad 1 : 1 \\
\triangle & \quad 1 : 100 \\
\square & \quad 100 : 1 \\
\times & \quad 100 : 100 \\
\end{align*}
\]
Table 3.9: Yield of nitrite, hydrogen peroxide and formaldehyde in the binary solutions of nitrate + methanol at pH 12.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[MeOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
<td>G(-CHO)</td>
</tr>
<tr>
<td>1</td>
<td>0.80</td>
<td>2.05</td>
<td>1.84</td>
</tr>
<tr>
<td>1</td>
<td>0.89</td>
<td>2.25</td>
<td>4.13</td>
</tr>
<tr>
<td>100</td>
<td>1.36</td>
<td>2.22</td>
<td>1.78</td>
</tr>
<tr>
<td>100</td>
<td>1.85</td>
<td>2.31</td>
<td>2.89</td>
</tr>
</tbody>
</table>

Table 3.10: Effect of concentrations of nitrate and ethanol on the yield of nitrite, hydrogen peroxide and acetaldehyde on the radiolysis of nitrate + ethanol binary solutions at basic pH.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[EtOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
<td>G(-CHO)</td>
</tr>
<tr>
<td>1</td>
<td>0.74</td>
<td>1.61</td>
<td>1.78</td>
</tr>
<tr>
<td>1</td>
<td>0.79</td>
<td>1.73</td>
<td>3.21</td>
</tr>
<tr>
<td>100</td>
<td>1.48</td>
<td>1.77</td>
<td>1.56</td>
</tr>
<tr>
<td>100</td>
<td>1.59</td>
<td>1.85</td>
<td>2.68</td>
</tr>
</tbody>
</table>
Table 3.11: Variation in the yield of nitrite, hydrogen peroxide and 1-propionaldehyde with concentration of nitrate as well as 1-propanol in the binary mixture of nitrate+1-propanol at pH 12.

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>[1-PrOH]/mM</th>
<th>Aerated ( G(\text{NO}_2^-) )</th>
<th>( G(H_2O_2) )</th>
<th>( G(-\text{CHO}) )</th>
<th>De-oxygenated ( G(\text{NO}_2^-) )</th>
<th>( G(-\text{CHO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.80</td>
<td>0.90</td>
<td>1.38</td>
<td>2.41</td>
<td>1.88</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.96</td>
<td>1.10</td>
<td>2.49</td>
<td>2.78</td>
<td>2.33</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.20</td>
<td>1.26</td>
<td>1.20</td>
<td>3.88</td>
<td>1.60</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.60</td>
<td>1.48</td>
<td>2.17</td>
<td>4.68</td>
<td>2.33</td>
</tr>
</tbody>
</table>

Table 3.12: Dependence of yields of NO$_2^-$, H$_2$O$_2$ and and CH$_3$CH$_2$CHO on the nitrate and butanol concentrations at pH 12.

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>[1-BuOH]/mM</th>
<th>Aerated ( G(\text{NO}_2^-) )</th>
<th>( G(H_2O_2) )</th>
<th>( G(-\text{CHO}) )</th>
<th>De-oxygenated ( G(\text{NO}_2^-) )</th>
<th>( G(-\text{CHO}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.90</td>
<td>0.80</td>
<td>1.35</td>
<td>2.61</td>
<td>1.30</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.05</td>
<td>0.90</td>
<td>1.89</td>
<td>3.01</td>
<td>1.47</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.93</td>
<td>1.03</td>
<td>1.03</td>
<td>3.61</td>
<td>1.11</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.11</td>
<td>1.30</td>
<td>1.86</td>
<td>4.01</td>
<td>1.34</td>
</tr>
</tbody>
</table>
Table 3.13: Values of the yields of nitrite, hydrogen peroxide the radiolysis of binary solutions of nitrate containing iso-propanol at pH 12.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[Iso-PrOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.76</td>
<td>1.07</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.85</td>
<td>1.47</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.41</td>
<td>1.14</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.61</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Table 3.14: Influence of the change in the concentration of nitrate and iso-butanol in their binary aqueous solutions on the radiation chemical yields of nitrite, hydrogen peroxide and iso-butyaldehyde at pH 12.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[Iso-BuOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂) G(-CHO)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.88</td>
<td>0.60 1.33</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.00</td>
<td>0.65 2.73</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.48</td>
<td>0.67 1.20</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.67</td>
<td>0.75 1.73</td>
</tr>
</tbody>
</table>
Table 3.15: G-values of nitrite and hydrogen peroxide in the presence of nitrate-ter-butanol binary solutions at pH 12.

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>[ter-BuOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO$_2^-$)</td>
<td>G(H$_2$O$_2$)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.78</td>
<td>1.20</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.03</td>
<td>1.36</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.42</td>
<td>1.20</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.64</td>
<td>1.41</td>
</tr>
</tbody>
</table>
2. $G(\text{NO}_2^-)$ and $G(\text{H}_2\text{O}_2)$ increase with the concentration of nitrate in aerated and de-oxygenated solutions at constant alcohol concentration (Tables 3.9 to 3.15). For example, in the aerated solutions containing 100 mM concentration of iso-butanol, $G(\text{NO}_2^-)$ increases from 1.00 to 1.67 as the nitrate concentration is changed from 1 to 100 mM (Table 3.14). Similarly when the alcohol concentration is increased from 1 to 100 mM and that of the nitrate was kept constant at 100 mM, the $G(\text{NO}_2^-)$ rises from 1.48 to 1.67 (Table 3.14) in the aerated solutions.

3. The important results brought out in the present investigation are in regard to the absence of the formation of hydrogen peroxide in the radiolysis of basic solutions of all the combinations of concentrations of nitrate and alcohol in de-oxygenated solutions.

4. The formation of aldehyde (Tables 3.9-3.12 and 3.14) shows a somewhat different trend. For a given set of solutions the G-values of aldehyde increase with the concentration of a given alcohol for a fixed concentration of nitrate in aerated as well as in de-oxygenated solutions. On the contrary if the nitrate concentration is increased keeping that of the alcohol constant, the G-values of aldehyde exhibit a decreasing trend. For instance, the $G(\text{iso-butyraldehyde})$ enhances from 1.33 to 2.73 as the
iso-butanol concentration increases from 1 to 100 mM keeping the nitrate concentration constant (1 mM). On the other hand, the G(iso-butyraldehyde) decreases at a fixed concentration of iso-butanol (100 mM) from 2.73 to 1.73 as the nitrate concentration changed from 1 to 100 mM in the solutions.

5. The G(aldehyde) is found to be lower in the de-oxygenated solutions than in the aerated samples under identical conditions of experiments (Tables 3.9 to 3.12 and 3.14).

3.2.2.2 Discussion:

It is known that the yield of pre produced during radiolysis varies with pH and solute concentration in solution. On the basis of these observations two hypothesis have been postulated to explain the observed variations in the primary yields with pH and the concentration of the solute. Dainton\textsuperscript{94} and co-workers explained the changes in the radical yields due to reaction of excited water molecules with H\textsuperscript{+}, OH\textsuperscript{-} or added solutes.

\[
\begin{align*}
H_2O^* + H^+ & \longrightarrow H + OH + H^+ \quad \text{——(3.41)} \\
H_2O^* + OH^- & \longrightarrow H + OH + OH^- \quad \text{——(3.42)} \\
H_2O^* + S & \longrightarrow \text{Intermediates and free radicals} \quad \text{——(3.43)}
\end{align*}
\]

In the absence of excess H\textsuperscript{+}, OH\textsuperscript{-} (i.e. in neutral water) or
at low concentration of added solute, it is assumed that energy of excited water is dissipated without the formation of free radicals.

Hayon\textsuperscript{35} has proposed a different hypothesis in which he considers that in the regions of high radical concentration present in the radiolysis of aqueous systems a certain fraction of primary species recombine to give back water. The extent of the recombination reaction becomes less when H\textsuperscript{+}, OH\textsuperscript{-} or other solutes are added to the water. This diminishing of recombination reaction is explained on account of following proposed reactions.

\begin{align*}
e^- + H^+ &\rightarrow H \quad \text{(3.44)} \\
OH + OH^- &\rightarrow O^- + H_2O \quad \text{(1.45)} \\
e^- + S &\rightarrow S_{\text{red}} \quad \text{(3.46)} \\
OH + S &\rightarrow S_{\text{ox}} \quad \text{(3.47)}
\end{align*}

Among the primary radical products, the hydroxyl radical behaves as a weak acid in equilibrium with its anion, O\textsuperscript{-}, the relative properties of acid and the anion depend on the pH of the solution. The radical is also reactive so that the reaction with solute may precede to the establishment of the acid-base equilibrium. In basic solutions it is more convenient to regard hydroxyl ion and solute as competing for hydroxyl radical than to treat the
OH as a weak acid; the hydroxyl ion – hydroxyl radical reaction is

\[ \text{OH} + \text{OH}^- \rightarrow \text{O}^- + \text{H}_2\text{O} \]  \hspace{1cm} \text{(1.37)}

The rate constant of above reaction \((1.2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1})\) is very high. Thus, in strongly basic medium OH radical gets ionized to its counter ion, \(\text{O}^-\) which is reactive towards many inorganic compounds. Unfortunately, values of few rate constants are available in literature for reactions of the oxide radical ion, \(\text{O}^-\) with different solutes. Similarly, the H-atoms also get converted into hydrated electrons according to Reaction (1.25) with a rate constant of \(2.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}\).

In addition to the above reactions \(\text{O}^-\) formed in Reaction (1.37) initiates following reactions.

\[ \text{NO}_3^- + \text{O}^- + \text{H}_2\text{O} \rightarrow \text{NO}_2^+ + 2\text{OH}^- \]  \hspace{1cm} \text{(3.48)}

\[ 2\text{NO}_3^- \rightarrow 2\text{NO}_2 + \text{O}_2 \]  \hspace{1cm} \text{(3.49)}

The \(\text{NO}_2\) thus formed gives nitrite in the presence of water.

Further, alcohol present in the binary solution, for example, iso-butanol undergoes following reactions in basic medium.

\[ (\text{CH}_3)_2\text{CHCH}_2\text{OH} + \text{OH} \rightarrow (\text{CH}_3)_2\text{CHCHOH} + \text{H}_2\text{O} \]  \hspace{1cm} \text{(3.50)}

\[ (\text{CH}_3)_2\text{CHCH}_2\text{OH} + \text{H} \rightarrow (\text{CH}_3)_2\text{CHCHOH} + \text{H}_2 \]  \hspace{1cm} \text{(3.51)}

The hydroxyisobutyl radical formed in the above reactions reacts with \(O_2\) if present in solution.
\[
\text{(CH}_3\text{)}_2\text{CHCH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{CHOHCH(CH}_3\text{)}_2 \quad (3.52)
\]

\[
\text{2CH}_2\text{CHOHCH(CH}_3\text{)}_2 \rightarrow 2\text{(CH}_3\text{)}_2\text{CHO} + \text{H}_2\text{O}_2 + \text{O}_2 \quad (3.53)
\]

\[
\text{2CH}_2\text{CHOHCH(CH}_3\text{)}_2 + \text{HO}_2(\text{O}_2^-) \rightarrow 2\text{(CH}_3\text{)}_2\text{CHO} + \text{H}_2\text{O}_2 + \text{O}_2 \quad (3.54)
\]

The nitrate transients, NO$_2^-$ or NO$_2$ formed in the radiolysis of nitrate-alcohol solutions instead of decaying in their own way prefer to react with the hydroxyisobutyl radicals producing thereby nitrite and isobutyraldehyde:

\[
\text{(CH}_3\text{)}_2\text{CHCHOH} + \text{NO}_2^- \rightarrow \text{(CH}_3\text{)}_2\text{CHCHO} + \text{NO}^- + \text{OH}^- \quad (3.55)
\]

\[
\text{(CH}_3\text{)}_2\text{CHCHOH} + \text{NO}_2 \rightarrow \text{(CH}_3\text{)}_2\text{CHCHO} + \text{NO}_2^- + \text{H}^+ \quad (3.56)
\]

Alternatively, hydroxyisobutyl radicals can undergo dimerization or disproportionation reactions yielding glycol or isobutyraldehyde respectively.

The hydrated electrons and O$_2^-$ (formed in Reaction 1.37) react with O$_2$ leading to the formation of O$_2^-$ and O$_3^-$ respectively in basic medium:

\[
e^- \text{aq} + \text{O}_2 \rightarrow \text{O}_2^- \quad (1.18)
\]

\[
\text{O}_2^- + \text{O}_2 \rightarrow \text{O}_3^- \quad (1.38)
\]

The existence of O$_3^-$ species in the solution has been confirmed by Czapaski and Dorfman$^{97}$ by recording the absorbance at 430 nm which is a characteristic of O$_3^-$, the rate constant of the reaction being $2.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. O$_3^-$ formed (Reaction 1.38) in turn reacts with NO$_2$ giving back nitrate.

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\[ O_3^- + NO_2 \longrightarrow O_2 + NO_3^- \quad \text{---(3.57)} \]

The reaction sequence is completed by \( O_2^- \) reacting with \( HO_2 \) radical (rate constant, \( 4.4 \times 10^7 M^{-1} s^{-1} \)),

\[ O_2^- + HO_2 \longrightarrow HO_2^- + O_2 \quad \text{---(1.18a)} \]

The lower \( G(NO_2^-) \) in aerated solutions can now be explained well on the basis of reactions operating in nitrate-iso-butanol system as mentioned above. In deoxygenated solutions the nitrite yield is higher and is attributed to the elimination of Reactions (1.18, 1.38 and 3.57) which are mainly responsible for the reduction in the nitrite yield. Therefore, it may be stated that the higher yield of nitrite in de-oxygenated solutions is mainly governed by the hydrated electrons and the species \( O_3^- \).

As the concentration of alcohol increases one would expect that the aldehyde yield should increase, and indeed, the expectation was borne out in the case of iso-butyraldehyde in aerated solutions. Surprisingly, however, the aldehyde yield was found to decrease with the increasing concentration of nitrate in de-oxygenated solutions. The increasing yield of aldehyde can be explained on the basis of Reactions (3.50, 3.51, 3.55 and 3.58), all together. In addition, since the solution contained dissolved oxygen, Reactions (3.52-3.54) also favour
increased yield of iso-butyraldehyde in aerated solutions. As a result of the above mentioned reactions it is clear that, as the concentration of iso-butanol increases, more alcohol radicals are generated and hence the reactions which give rise to aldehyde dominate resulting in a higher yield of isobutyraldehyde. However, the decrease in the yield of aldehyde in the binary aerated solution with increasing concentration of nitrate is difficult to explain on the basis of reaction sequence proposed. Some reactions involving the nitrate ions may be taking place which affect the aldehyde yield adversely.

Lower yields of iso-butyraldehyde observed in the de-oxygenated solutions are attributed to the absence of Reactions (1.18, 3.52-3.54) which occur only in the aerated solutions. Therefore, the isobutyraldehyde is formed only via Reactions (3.55 and 3.56) and consequently lowering the overall yield of aldehyde. On the contrary, the aldehyde yield shows a very interesting behavior in the nitrate-straight chain alcohol systems. The yield decreased from methanol to 1-butanol in aerated solutions as observed for the hydrogen peroxide. A similar trend was also obtained in de-oxygenated solutions except at 100:100 mM combination of nitrate-1-propanol solutions. This decrease in the aldehyde production in the simple alcohols in aerated and
de-oxygenated solutions may be understood in terms of percentage abstraction probabilities and the reactivity of the alcohol radicals produced with the nitrate transients, NO$_3^-$ and NO$_2$ which finally leads to the formation of the product, aldehyde.

The increasing trend in hydrogen peroxide yield with the concentration of nitrate as well as with that of the alcohol in aerated solutions is attributed to the probable reaction of perhydroxyl radical with the alcohol of interest thereby giving corresponding hydroxyalkyl radicals and hydrogen peroxide. For example, in iso-butanol, the HO$_2$ radical attacks iso-butanol giving isobutyraldehyde and hydrogen peroxide according to following reaction

$$\text{HO}_2 + (\text{CH}_3)_2\text{CHCH}_2\text{OH} \rightarrow (\text{CH}_3)_2\text{CHCHOH} + \text{H}_2\text{O}_2 \quad ---(3.58)$$

Alternatively, perhydroxyl radicals may disappear via dimerization reaction forming hydrogen peroxide again with somewhat low rate constant, $0.25 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$.

$$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad ---(1.15)$$

Further, Reactions (3.53 and 3.54) and Reaction (1.6) also contribute towards the yield of hydrogen peroxide. At higher concentrations of iso-butanol, Reaction (3.58) yields more H$_2$O$_2$. Therefore, it is clear from the
above explanations that the existence and the occurrence of Reactions (3.58, 1.15 and 1.8) are mainly responsible for the formation of hydrogen peroxide.

The fact that the $G(H_2O_2)$ produced is in negligible amount in de-oxygenated solutions indicates that the hydrogen peroxide formed must be consumed by the protons of water, one such probable reaction is

$$\text{O}^- + H_2O_2 \longrightarrow H_2O + O_2^- \quad (3.59)$$

the rate constant being $5.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. It is thought that the Reaction (3.59) is mainly responsible for the diminishing yield of hydrogen peroxide in de-oxygenated solutions.

Values of $G(\text{NO}_2^-)$ obtained in the presence of branched alcohols, as iso-propanol, iso-butanol and ter-butanol found to be more or less constant for all possible combinations of nitrate and alcohol in aerated solutions. The constant nitrite yield observed in the above systems (for branched alcohols) can be attributed to the the reactivity of the hydroxyalkyl radical generated from alcohol-hydroxyl and/or H-radical reactions which are responsible for the formation of nitrite. In de-oxygenated solutions, the nitrite yield is found to be higher in all
the systems of nitrate/branched alcohol as compared to nitrate/straight chain alcohol. The G-value of nitrite is found to be lower in the \( \text{NO}_3^-/\text{ter-butanol} \) as compared to the \( \text{NO}_3^-/\text{iso-propanol} \). Results obtained in \( \text{NO}_3^-/\text{iso-butanol} \) system can be explained on the basis of the percentage abstraction of hydrogen atom. In ter-butanol there is no \( \alpha \)-hydrogen as such, and hence \( \beta \)-hydrogen is removed from the alcohol. The hydroxyterbutyl radical thus formed appears to have lower reactivity than the corresponding alcohol radicals of iso-propanol and iso-butanol.

In straight chain alcohols, (as methanol, ethanol, 1-propanol and 1-butanol), we do not find any correlation between the yields of nitrite with the chain length of the alcohols. However, the yield of hydrogen peroxide decreases with the chain length of the alcohol in aerated solutions. This trend can be attributed to the the percentage abstraction of \( \alpha \)-hydrogen atom from methanol to 1-butanol. The probability of \( \alpha \)-hydrogen abstraction decreases from methanol to 1-butanol. Therefore it affects the total production of corresponding hydroxyalkyl radicals which is mainly governed by the hydroxyl radicals. In other words, more OH radicals get consumed by methanol as compared to ethanol, 1-propanol and 1-butanol and thereby affecting the Reaction (1.6). Eventually the yield decreases as one goes
3.2.3 RADIOLYSIS OF NITRATE IONS CONTAINING ALCOHOLS IN ACIDIC MEDIUM (pH 3.5):

3.2.3.1 Results:

After studying the radiolysis of nitrate—alcohol solutions in neutral and basic media it is thought of interest to examine the yield of different products formed in these solutions in acid medium. The solutions of desired concentrations of nitrate and the chosen alcohols were prepared in sulphuric acid and the pH was adjusted to 3.5. The solutions thus prepared were subjected to gamma irradiation, after which the samples were first neutralised by alkali solution and then further analysis was carried out for the final stable products namely nitrite, hydrogen peroxide and aldehyde.

The effect of different alcohols as well as their concentrations on the product yields at this pH have been investigated. The same alcohols (methanol, ethanol, 1-propanol, 1-butanol, iso-propanol, iso-butanol and ter-butanol) which were chosen for earlier studies are selected for this purpose. Similar sets of experiments were performed; keeping initial concentrations of nitrate ions (1
or 100 mM) constant and changing that of the alcohol from 1 to 100 mM and vice versa in both aerated as well as in de-oxygenated solutions.

As the study covers the variation of more or less same parameters as mentioned earlier on the yield of products formed, a certain amount of repetition in describing the results may have remained though an attempt has been made to minimise the same.

The experimental findings of yields of nitrite, hydrogen peroxide and aldehydes at various concentrations of both the reactants with absorbed dose are presented graphically in Figs. 3.35 to 3.53 and the G-values of various products calculated from the slopes of linear plots are recorded in the Tables 3.16 to 3.22.

Some of the important observations from these investigations in the acidic medium are summarised below:

1. The nitrite yield was found to be lower in the acidic pH than that observed in neutral and basic media for all the concentrations of nitrate and alcohols chosen.

2. From the Tables 3.16-3.22 it is seen that the $G(\text{NO}_2^-)$ varies with the concentration of either of the reactants, the other one being kept constant. For example, $G(\text{NO}_2^-)$
Fig. 3.36: Yield of $\text{H}_2\text{O}_2$ in the nitrate–methanol binary solutions at pH 3.5.
Fig. 3.37: Yield of formaldehyde in the nitrate-methanol binary solutions at pH 3.5.
Fig. 3.38: Variation in the yield of nitrite with dose absorbed in the binary solutions of nitrate-ethanol at pH 3.5.
Fig. 3.39: Variation in the yield of $\text{H}_2\text{O}_2$ with absorbed dose in the binary solutions of nitrate–ethanol at pH 3.5.
Fig. 3.40: Variation in the yield of acetaldehyde with absorbed dose in nitrate-ethanol solutions in the acidic medium.
Fig. 3.41: Variation of $\text{NO}_2^-$ yield with dose solutions absorbed in the nitrate-n-propanol solutions at pH 3.5.
Fig. 3.42: Variation in the yield of H$_2$O$_2$ with dose absorbed in the nitrate-n-propanol solutions at pH 3.5.
Fig. 3.43: Variation in the yield of $\text{H}_2\text{O}_2$ in the nitrate-n-propanol solutions at pH 3.5.
Fig. 3.44: Yield of nitrite in the nitrate-n-butanol binary solutions at pH 3.5.
Fig. 3.45: Yield of $\text{H}_2\text{O}_2$ in the binary solutions of nitrate-n-butanol at pH 3.5.
Fig. 3.46: Yield of n-butyraldehyde in the nitrate-n-butanol binary solutions at pH 3.5.
Fig. 3.47: Yield of nitrite in the radiolysis of nitrate-iso-propanol solution at pH 3.5.
Fig. 3.48: Yield of H$_2$O$_2$ in the radiolysis of nitrate-iso-propanol solutions at pH 3.5.
Fig. 3.49: Yield of nitrite in the radiolysis of nitrate-iso-butanol solutions at pH 3.5.
Fig. 3.50: Yield of $\text{H}_2\text{O}_2$ in the radiolysis of nitrate-iso-butanol solutions at pH 3.5.
Fig. 3.51: Yield of iso-butyraldehyde in the radiolysis of nitrate-iso-butanol solutions at pH 3.5.
Fig. 3.52: Formation of nitrite with absorbed dose at pH 3.5 in nitrate-ter-butanol solutions.
Fig.3.53: Yield of H\(_2\)O\(_2\) with dose absorbed at pH 3.5 in nitrate-ter-butanol solutions.
Table 3.16: Yield of nitrite, hydrogen peroxide and formaldehyde in the binary solutions of nitrate = methanol at pH 3.5.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[MeOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.77</td>
<td>0.46</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.95</td>
<td>0.42</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.51</td>
<td>0.31</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.13</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Table 3.17: Effect of concentrations of nitrate and ethanol on the yield of nitrite, hydrogen peroxide and acetaldehyde on the radiolysis of nitrate-ethanol binary solutions at acidic medium (at pH 3.5).

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[EtOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO₂⁻)</td>
<td>G(H₂O₂)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.00</td>
<td>1.98</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.08</td>
<td>1.88</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.47</td>
<td>0.80</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.17</td>
<td>0.74</td>
</tr>
</tbody>
</table>
Table 3.18: Variation in the yield of nitrite, hydrogen peroxide and 1-propionaldehyde with concentration of nitrate as well as 1-propanol in the binary mixture of nitrate-1-propanol at pH 3.5.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[1-PrOH]/mM</th>
<th>Aerated G(NO₂⁻) G(H₂O₂) G(-CHO)</th>
<th>De-oxygenated G(NO₂⁻) G(H₂O₂) G(-CHO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.75 1.96 2.23</td>
<td>0.41 0.69 1.67</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.51 1.90 2.43</td>
<td>1.12 0.50 1.83</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.86 1.08 2.74</td>
<td>2.31 0.64 2.15</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.05 0.98 3.13</td>
<td>2.74 0.62 2.32</td>
</tr>
</tbody>
</table>

Table 3.19: Dependence of yields of NO₂⁻, H₂O₂ and CH₃CH₂CH₂CHO on the nitrate and butanol concentrations at pH 3.5.

<table>
<thead>
<tr>
<th>[NO₃⁻]/mM</th>
<th>[1-BuOH]/mM</th>
<th>Aerated G(NO₂⁻) G(H₂O₂) G(-CHO)</th>
<th>De-oxygenated G(NO₂⁻) G(H₂O₂) G(-CHO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.64 1.04 1.32</td>
<td>0.24 0.58 1.29</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.86 1.14 2.63</td>
<td>0.41 0.39 2.15</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.67 1.31 1.64</td>
<td>2.37 0.89 1.30</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.00 1.41 2.74</td>
<td>2.61 0.54 2.30</td>
</tr>
</tbody>
</table>
Table 3.20: Values of the yields of nitrite, hydrogen peroxide the radiolysis of binary solutions of nitrate containing iso-propanol at pH 3.5.

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>[Iso-ProH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO$_2^-$)</td>
<td>G(H$_2$O$_2$)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.38</td>
<td>1.04</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.43</td>
<td>1.27</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.63</td>
<td>1.71</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.83</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 3.21: Influence of the change in the concentration of nitrate and iso-butanol in their binary aqueous solutions on the radiation chemical yields of nitrite, hydrogen peroxide and iso-butyaldehyde at pH 3.5.

<table>
<thead>
<tr>
<th>[NO$_3^-$]/mM</th>
<th>[Iso-BuOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>G(NO$_2^-$)</td>
<td>G(H$_2$O$_2$)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.21</td>
<td>1.23</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.41</td>
<td>1.20</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.37</td>
<td>0.98</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.77</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Table 3.22: G-values of nitrite and hydrogen peroxide in the presence of nitrate-ter-butanol binary solutions at pH 3.5.

<table>
<thead>
<tr>
<th>[NO\textsubscript{3}][/M]</th>
<th>[ter-BuOH]/mM</th>
<th>Aerated</th>
<th>De-oxygenated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G(NO\textsubscript{2}\textsuperscript{-})</td>
<td>G(H\textsubscript{2}O\textsubscript{2})</td>
<td>G(NO\textsubscript{2}\textsuperscript{-})</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.35</td>
<td>1.16</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0.39</td>
<td>1.43</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1.30</td>
<td>1.88</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1.61</td>
<td>2.13</td>
</tr>
</tbody>
</table>
values are found to be 0.95 and 2.13 for the aerated solutions containing constant concentration of methanol (100 mM) and varying amount of nitrate (1 and 100 mM). Similarly, the nitrite yield increases from 1.51 to 2.13 as the methanol concentration is changed from 1 to 100 mM keeping that of the nitrate constant (100 mM) in the aerated solutions.

3. The G(NO₂⁻) values in the de-oxygenated solutions are higher in the presence of methanol, ethanol or ter-butanol than those observed in the corresponding aerated samples. Other alcohols show a different behaviour towards radiolysis. The higher G-values of nitrite is observed in de-oxygenated solutions containing 1-propanol and 1-butanol than in the aerated samples only at higher concentration of nitrate (100 mM) (Tables 3.18 and 3.19). However, a reverse trend in G(NO₂⁻) is found in these solutions containing above mentioned alcohols at lower concentration of nitrate (1 mM). While the solutions containing iso-butanol and iso-propanol follow an entirely different pattern. The mixtures containing nitrate (1 mM) and alcohols (1 and 100 mM) in the de-oxygenated solutions showed a negligible amount of nitrite formation beyond the detection limit but starts forming more with increasing rate at 100 mM nitrate.
concentrations.

4. The hydrogen peroxide yield in terms of their G-values in the aerated solutions decreases with the concentrations of nitrate and alcohols (especially methanol, ethanol and 1-propanol). On the other hand, the use of 1-butanol and ter-butanol along with nitrate showed an increase in $G(H_2O_2)$ with concentrations of both reactants. In the case of de-oxygenated solutions, no definite trend in $G(H_2O_2)$ is observed in the binary solutions.

5. The aldehydes formed during the radiolysis were estimated in all the alcohol-nitrate solutions except those containing iso-propanol and ter-butanol. The aldehyde yield (Tables 3.16-3.19 and 3.21) increases with increase in the concentrations of nitrate and of some alcohols (methanol, ethanol and 1-propanol) in both the aerated and de-oxygenated solutions. In general, the $G$(aldehyde) is found to be lower in the de-oxygenated solutions as compared to the aerated samples.

3.2.3.2 Discussion:

A survey of the literature reveals that there is almost no data on the radiolysis of aqueous nitrate-alcohol solutions in the acidic medium. Hence, the mechanism of the radiolysis in these solutions is incompletely understood.
Hence, the results in the present investigations are only qualitatively explained under various conditions of experiments.

At low pH, it is known that the $e_{aq}^-$ is rapidly scavenged by the hydrogen ions in acidic solutions forming hydrogen atom as

$$e_{aq}^- + H^+ \rightarrow H$$  \hfill (1.27)

Consequently this reduces the concentration of $e_{aq}^-$ in acidic medium. The H-atoms formed in the Reaction (1.27) are consumed by nitrate ions at a relatively lower rate and hence only a smaller fraction of hydrogen atoms is utilized in the formation of nitrite. In contrast to this, the H-atom in the basic medium gets converted into hydrated electrons which in turn produce nitrite at much higher rate yielding thereby higher G-values of nitrite as observed.

Methanol for example, in de-oxygenated binary solutions scavenges the hydrogen and hydroxyl radicals which lead to the formation of methanol radical via hydrogen abstraction reaction

$$\text{CH}_3\text{OH} + H \rightarrow \text{CH}_2\text{OH} + \text{H}_2 \quad \hfill (3.60)$$

$$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O} \quad \hfill (3.61)$$

The alcohol radicals thus produced (Reactions 3.60
and 3.61) react with the transient species, mainly with $\text{NO}_2$ leading to the formation of formaldehyde as a stable product

$$\text{CH}_2\text{OH} + \text{NO}_2 \rightarrow \text{HCHO} + \text{NO}_2^- + \text{H}^+ \quad (3.62)$$

In the absence of these species, the hydroxymethyl radicals disappear producing either formaldehyde or glycol

$$2(\text{CH}_2\text{OH}) \rightarrow \text{HCHO} + \text{CH}_3\text{OH} \quad (3.63)$$

$$2(\text{CH}_2\text{OH}) \rightarrow (\text{CH}_2\text{OH})_2 \quad (3.64)$$

Apart from these reactions, the following reactions also take place in the aerated solution and need to be considered while explaining the results.

$$\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad (1.17)$$

$$\text{HO}_2 \rightarrow \text{H}^+ + \text{O}_2^- \quad (1.44)$$

$$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (1.15)$$

$$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{O}_2\text{CH}_2\text{OH} \quad (3.65)$$

followed by the reactions

$$2\text{O}_2\text{CH}_2\text{OH} \rightarrow 2\text{HCHO} + \text{H}_2\text{O}_2 + \text{O}_2 \quad (3.66)$$

or

$$\text{O}_2\text{CH}_2\text{OH} + \text{HO}_2(\text{O}_2^-) \rightarrow \text{HCHO} + \text{H}_2\text{O}_2 + \text{O}_2^- \quad (3.67)$$

When a comparison of $G$-values of various products is made between the straight chain (propanol and butanol) and their branched alcohols (iso-propanol, iso-butanol and ter-butanol) one finds some interesting observations. $G(\text{NO}_2^-)$ values are higher in 1-propanol as compared to iso-propanol in both aerated and de-oxygenated solutions. Similarly, the
yield of nitrite obtained in nitrate/1-butanol, nitrate/iso-butanol and nitrate/ter-butanol systems in aerated solutions follows the following order

\[ G_{\text{NO}_2}^{\text{(1-propanol)}} > G_{\text{NO}_2}^{\text{(iso-propanol)}} \text{ and } G_{\text{NO}_2}^{\text{(1-butanol)}} > G_{\text{NO}_2}^{\text{(iso-butanol)}} > G_{\text{NO}_2}^{\text{(ter-butanol)}} \]

except at the 1 mM concentration of nitrate and iso-butanol.

The higher yields in straight chain alcohols compared to those in branched alcohols are attributed to the reactivities of the corresponding hydroxyalkyl radicals produced during the radiolysis. From these results, it seems that the hydroxyalkyl radicals generated from straight chain alcohols are more reactive than the corresponding ones resulting from branched alcohols thereby affecting adversely the yield of nitrite. Further, the G-values of iso-butyraldehyde is found to be higher than the G(iso-butyraldehyde) formed in aerated nitrate/1-butanol and nitrate/iso-butanol solutions respectively. A comparison between the yields of propionaldehyde and acetone resulting from the 1-propanol and iso-propanol respectively could not be made as it was not possible to estimate the acetone formed.

Unfortunately, in straight chain alcohols we do not find any correlation with the chain length of the alcohols.
used. The yields of nitrite, aldehyde and hydrogen peroxide are found to vary from alcohol to alcohol. This may be due to the differences in the stabilities of the respective alcohol radicals formed which influence the product yields.

The striking observation is of a lower yield of nitrite in de-oxygenated solutions in the case of 1-propanol and 1-butanol as well as its total absence in the iso-propanol and iso-butanol containing 1 mM of nitrate ions as compared to the aerated samples. From these results it appears that the nitrite formed in the presence of these alcohols at lower concentration of nitrate gets converted into nitrate again by some unknown reactions.

The increase in the $G(\text{NO}_2^-)$ values with the concentration of nitrate as well as methanol in the binary solutions is attributed to the occurrence of Reactions (3.2) and (3.4) and hence Reaction (3.5) along with the Reaction (3.62). As the concentration of methanol increases, more and more alcohol radicals are produced, as a consequence the frequency of occurrence of Reaction (3.62) increases thereby producing higher nitrite yield as observed. The observation of higher yield of nitrite in de-oxygenated solutions as compared to aerated one for all the combinations of concentration of both the reactants can be accounted for in
a similar way as discussed earlier in explaining the results in neutral and basic media.

Similar to the results obtained in neutral and basic media, the yield of aldehyde increases with the concentrations of both the reactants in aerated as well as in de-oxygenated systems. The results are best discussed by taking a specific example of the nitrate/methanol system. The hydroxyl radical removes α-hydrogen atom from methanol producing hydroxymethyl radicals. These radicals subsequently react with NO$_2$ species yielding formaldehyde as a stable product via Reaction (3.62). With increasing concentration of methanol the extent of the occurrence of Reaction (3.62) increases and therefore enhances the formaldehyde yield.

The higher G(H$_2$O$_2$) values found in aerated binary mixtures as compared to the de-oxygenated solutions can be understood in terms of the contribution of Reactions (3.66) and (3.67) in the formation of hydrogen peroxide in aerated solutions apart from Reaction (1.6). In de-oxygenated solutions only Reaction (1.6) occurs and all other reactions involved in H$_2$O$_2$ formation (Reactions- 3.66 and 3.67) are totally excluded. The influence of the concentration of nitrate and alcohol on the yield of hydrogen peroxide is
explained by considering the extent of the occurrence of reactions which are responsible for the formation of hydrogen peroxide.

In conclusion, there are several results which are found to be anomalous in nitrate + alcohol systems in acidic medium. As mentioned earlier, the data in this area being limited, the reactivities of the various transients formed could not be predicted and hence we could not explained the abnormal results obtained in aerated and de-oxygenated solutions especially for 1-propanol, 1-butanol and their branched forms of isomers. Much more work is required to be done to understand the radiolytic processes taking place in the acidic medium.