CHAPTER IV
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STUDY FOLLOWING THE DISSOLUTION OF \(\gamma\)-IRRADIATED ALKALI HALIDES IN AQUEOUS NITRATE SOLUTIONS

This chapter deals with the results obtained on dissolution of \(\gamma\)-irradiated alkali halides in sodium nitrate solutions.

The experimental procedure in short involved the exposure of a fixed amount of alkali halide to \(\gamma\)-radiation. This was followed by dissolution of the irradiated samples in 10 ml aqueous solution of sodium nitrate, whose concentration was between 0.05 to 0.2 M. The \(\text{NO}_2^-\) was one of the products formed in nitrate solutions which was detected and estimated by using diazo method.

The \(\text{NO}_2^-\) yield thus formed was studied by varying the different parameters such as, \(\gamma\)-dose given to the salt, mesh size of the salt, amount of the salt and concentration of nitrate solutions. The effect of scavengers such as \(\Gamma^-\), MeOH and CO\(_2\) on the formation of \(\text{NO}_2^-\) has also been studied.

Results

The \(\text{NO}_2^-\) formed, as one of the products, varied following the dissolution of NaCl (30 and 200 mesh) exposed to increasing \(\gamma\)-dose in aqueous sodium nitrate solutions. Such variation of
Graph. 4.1 - $\left[ \text{NO}_2^- \right]$ yield as a function of $\gamma$-dose given to 30 and 200 mesh NaCl
Graph 4.2 - Yields of \([\text{NO}_2^-]\) formed following the dissolution of increasing amount of 200 mesh \(\gamma\)-irradiated alkali halids in 0.05 sodium nitrate solution.
Concentration of sodium nitrate solution in mole $\text{lit}^{-1}$

Graph 4.3 - Variation in $\left[\text{NO}_2^-\right]$ yield with concentration of sodium nitrate solution, NO$_2$ being formed following the dissolution of 2g (200 mesh) alkali halides $\gamma$-irradiated (6 Mrads) in nitrate solutions.
Graph 4.4 - Effect of scavengers (I\textsuperscript{-}, MeOH and CO\textsubscript{2}) present, on the yield of [NO\textsubscript{2}\textsuperscript{-}] formed following the dissolution of increasing amount of 200 mesh γ-irradiated NaCl to 6 Mrads in 0.05 M sodium nitrate solutions.
NO$_2^-$ yield as a function of γ-dose given to the salt is shown in Graph 4.1. Initially the increase in the yield is sharp but attains a plateau at higher γ-doses. The Graph also shows the effect of mesh size of the salt on the variation in NO$_2^-$ yield, being higher for 200 mesh as compared to 30 mesh.

Graph 4.2 shows the effect of variation of amount added of 200 mesh alkali halides irradiated to fixed γ-dose (6 Mrads) on the yield of NO$_2^-$ . With increasing amount of the addition of irradiated NaCl, the NO$_2^-$ formed increases regularly. For other alkali halides the NO$_2^-$ yield reaches a maximum corresponding to the addition of ~1.5 to 2.0 g after which the yield falls down.

Graph 4.3 shows the variation in the NO$_2^-$ yield with the nitrate concentration, corresponding to the dissolution of 2 g alkali halide samples irradiated to 6 Mrads (fixed γ-dose). The trend in the variation of NO$_2^-$ yield is not regular.

Graph 4.4 represents the variation in NO$_2^-$ yield with the increasing amount of 200 mesh NaCl γ-irradiated to 6 Mrad dissolved in 0.05 M nitrate solution and those containing the scavengers I$^-$, MeOH and CO$_2$. The NO$_2^-$ yield is more in presence of I$^-$ as a scavenger as compared to the pure nitrate. While the NO$_2^-$ yield is less when MeOH and CO$_2$ are present in nitrate solutions.
**Discussion**

Arnikar et al.\(^2\) while studying the aquoluminescence observed a total quenching in nitrate solutions. Similar observations were made by Atari\(^3\) and others\(^4\). They have explained the quenching of aquoluminescence on the basis of abstraction of \(e_{aq}^-\) by \(NO_3^-\).

\[
NO_3^- + e_{aq}^- \rightarrow NO_3^{-2} + aq
\]

However the \(NO_3^{-2}\) intermediate leading to the product formation was not studied by them. Hence we had undertaken the study of dissolution of \(\gamma\)-irradiated alkali halides in nitrate solutions to find out the products formed. We had succeeded in detecting the formation of \(NO_2^-\) as one of the products with the help of diazo method. The \(NO_2^-\) formed has been explained on the basis of mechanisms proposed by others\(^5-7\) in their studies on \(\gamma\)-radioysis and photolysis of neutral nitrate solutions.

Anbar and Hart\(^5\), suggested the formation of \(NO_2^-\) during the \(\gamma\)-radioysis of neutral nitrate solutions to be through the \(NO_3^-\). Ottlenghi and Rabani\(^6\) from the photolytic studies on nitrate solutions suggested the mechanism for the \(NO_2^-\) formation to be through \(NO_3^{-2}\) which gives rise to \((NO_2)_{aq}\). The \((NO_2)_{aq}\) further disproportionates to give \(NO_2^-\).

\[
e_{aq}^- + NO_2^- \rightarrow NO_3^{-2}
\]

\[
NO_3^{-2} \xrightarrow{H^+} (NO_2)_{aq} + 2 OH^-
\]

\[
2(NO_2)_{aq} \rightarrow NO_3^- + NO_2^- + 2H^+ \quad .. \ 4.1
\]
The $\text{NO}_2^-$ formation via $(\text{NO}_2)_aq$ as an intermediate was favoured on the basis of recording a transient spectrum which resembled the gas phase spectrum of $\text{NO}_2$ with same molar extinction coefficient ($\varepsilon_N = 100 \text{ M}^{-1} \text{ cm}^{-1}$).6

The formation of $(\text{NO}_2)_aq$ as an intermediate also comes from the scavenger studies made by Hyder.7 According to Hyder the presence of $I^-$ enhanced the $\text{NO}_2^-$ yield while the presence of $\text{O}_2$ as a scavenger decreased the $\text{NO}_2^-$ yield as compared to that obtaining in pure nitrate solution.

The enhancement of $\text{NO}_2^-$ yield also due to the presence of $I^-$ was possible only if $I^-$ directly reduced the $(\text{NO}_2)_aq$.

$$2I^- + 2(\text{NO}_2)_aq \rightarrow 2\text{NO}_2^- + I_2 \quad \text{(4.2)}$$

On the other hand, the role of $\text{O}_2$ as a scavenger resulting in the decrease in $\text{NO}_2^-$ yield has been explained, on the basis of back reaction of $\text{NO}_2^-$ to $\text{NO}_3^-$ by oxidation of $\text{NO}_2$ as

$$2\text{NO}_2^- + \text{O}_2 \rightarrow 2\text{NO}_3^-$$

Finally the formation of $(\text{NO}_2)_aq$ as an intermediate also comes from the oxidation of $\text{Fe(CN)}_6^{4-}$ to $\text{Fe(CN)}_6^{3-}$.6

Thus in the present work, the formation of $\text{NO}_2^-$ can be said to be through $(\text{NO}_2)_aq$ formation.
The NO$_2^-$ yield in the present work need not be solely through e$_{aq}$$. Since other intermediate species like ($^\cdot$OH)$_{aq}$ have also been proposed to be formed$^8$ apart from e$_{aq}$, following the dissolution of $\gamma$-irradiated alkali halides in aqueous medium.

Therefore NO$_2^-$ may also be forming by the interaction of ($^\cdot$OH)$_{aq}$ with NO$_3^-$ as follows:

\[
X^* \longrightarrow (X^-)_{aq} + H^+_{aq} + (^\cdot$OH)$_{aq}
\]

\[
2NO_3^- + 2(^\cdot$OH)$_{aq} \longrightarrow 2(NO_2^-)_{aq} + 2(\cdotOH)^-_{aq} \quad \cdots \text{4.3}
\]

\[
2(NO_3^-)_{aq} \longrightarrow 2NO_2 + O_2 \quad \cdots \text{4.1}
\]

\[
2(NO_2^-)_{aq} \longrightarrow NO_2^- + NO_3^- + 2H^+
\]

The NO$_3^-$ to (NO$_2^-$) formation by ($^\cdot$OH)$_{aq}$ has earlier been proposed by Challenger and Masters$^9$ in their $\gamma$-radiolytic studies.

The nitrate reduction leading to NO$_2^-$ formation takes place due to the colour centres from $\gamma$-irradiated alkali halides. Therefore any variation in the concentration of colour centres should affect the NO$_2^-$ yield. Indeed in the present work this variation in NO$_2^-$ yield has been obtained, when a fixed amount of NaCl exposed to increasing dose of $\gamma$-radiations was dissolved in nitrate solution. This NO$_2^-$ yield is shown as a function of $\gamma$-dose given to (30 and 200 mesh)
in Graph 4.1. The curves in Graph 4.1 indicate increasing trend in the $\text{NO}_2^-$ yield, which resemble F centre growth-curve as reported by Gordon and Novick\textsuperscript{10}, indicating the involvement of F centres in the $\text{NO}_2^-$ formation. The $\text{NO}_2^-$ yield increase is initially somewhat sharp but latter attain a plateau supporting the fact that F centres are involved in the $\text{NO}_2^-$ formation and formed from two different processes. In the first stage $\text{NO}_2^-$ is formed due to F centres produced from defects inherently present in the salts prior to irradiation. In the second stage the $\text{NO}_2^-$ is formed due to the F centres originating from generation of defects by radiation.

Similar theory for F centre formation has been reported by (1) Rabin and Klick\textsuperscript{11} and other workers\textsuperscript{12-16}.

Graph 4.1 also shows the effect of mesh of $\gamma$-irradiated NaCl on the $\text{NO}_2^-$ yield. The higher yield of $\text{NO}_2^-$ was obtained for 200 mesh as compared to that of 30 mesh salt. This effect may be attributed to the introduction of more defects in the salt due to grinding prior to irradiation\textsuperscript{17}. Similar mesh effect was observed by Epstein\textsuperscript{18} in his work on $\gamma$-radiolysis of KCl followed by its dissolution in aqueous iodide which yielded free iodine. The yield of iodine liberated following the dissolution of $\gamma$-irradiated KCl of fine mesh was found to be more consistent. Of course, no concrete explanation has been offered by him.
The mesh effect may alternatively be explained on the basis of explanation given by Gordon and Novick\(^\text{10}\) about the formation of colour centres in \(\gamma\)-irradiated alkali halide crystals. According to them, in a single crystal of alkali halide, the colour centres formed are maximum at the surface and minimum at the centre of the crystal, decreasing exponentially. Therefore probably, due to grinding of the alkali halide crystal to fine powder, more surface is exposed to \(\gamma\)-radiations yielding more colour centres. Hence in the present work the \(\text{NO}_2^-\) formed from F centres are found to be more for 200 mesh salt than that recorded for 30 mesh salt.

The concentration of colour centres can also be varied by varying the amount of salt of a particular mesh exposed to fixed \(\gamma\)-dose. In the present work, this is reflected by obtaining higher \(\text{NO}_2^-\) yields for \(\gamma\)-irradiated (200 mesh) alkali halides dissolved in nitrate solutions. Graph 4.2 represents this result. As can be seen from Graph 4.2 that the \(\text{NO}_2^-\) yield increases continuously for irradiated NaCl. But in case of irradiated KCl, KBr and NaBr a maximum corresponding to 2.0 g of the salts is obtained after which the \(\text{NO}_2^-\) yield decreases. At present, we have no explanation to offer for this observation.

Graph 4.2 also shows the higher \(\text{NO}_2^-\) yield due to irradiated chlorides than for bromides. This may be due to
the formation of more colour centres in irradiated chlorides than in bromides, which are available for the reaction. For instance Chaure\textsuperscript{19} reported higher F centre concentration in irradiated NaCl \((2 \times 10^{19} \text{ mol}^{-1})\) than that in NaBr \((0.9 \times 10^{19} \text{ mol}^{-1})\).

**Effect of nitrate concentration on NO\textsubscript{2}\textsuperscript{-} yield**

Graph 4.3 shows the effect of nitrate concentration on the NO\textsubscript{2}\textsuperscript{-} yield. As is apparent that there is no regular trend found in the NO\textsubscript{2}\textsuperscript{-} yield. This can be explained on the basis of F centre release, which is a bulk process\textsuperscript{12}. There is a complete conversion of F centre into \(e_{aq}^-\) during their release in the aqueous medium. Since \(e_{aq}^-\) formation is a bulk process it is quite likely that not all \(e_{aq}^-\) is taken up by NO\textsubscript{3}\textsuperscript{-} to give NO\textsubscript{2}\textsuperscript{2-} but some may be lost by reactions such as dimerisation\textsuperscript{20}.

\[
2e_{aq}^- \rightarrow H_2 + 2OH^- 
\]

Therefore this may be probable reason for the trend observed in the present work (Graph 4.3).

**Effect of scavengers**

Graph 4.4 shows the extent of NO\textsubscript{2}\textsuperscript{-} formation in 0.05 M nitrate, in presence of I\textsuperscript{-}, MeOH and CO\textsubscript{2} as scavengers. As is apparent from the Graph 4.4 that the NO\textsubscript{2}\textsuperscript{-} yield is enhanced
in presence of I⁻ as scavenger. This may be explained on the basis of the direct reduction of (NO₂)ₐq by I⁻ as

\[ 2(NO₂)_{aq} + 2I^- \rightarrow 2NO_2^- + I_2 \]

\[ I_2 + I^- \rightarrow I^- \]

In this case NO₂⁻ is produced at the expense of (NO₂)ₐq instead by disproportionation theory forward in case of pure nitrate (Eq. 4.1).

The presence of MeOH as a scavenger lowers the NO₂⁻ yield (Graph 4.4). This may probably be due to the reaction of (NO₂)ₐq with MeOH.

\[ 2(NO₂)_{aq} + CH_3OH \rightarrow CH_3NO_2 + HNO_3 \quad \ldots \quad 4.4 \]

Thus the (NO₂)ₐq concentration is lowered because of the reaction (Eqn. 4.4) and therefore the probability of (NO₂)ₐq disproportionation leading to NO₂⁻ formation is lowered.

The CO₂ gas acting as a scavenger decreased the NO₂⁻ yield, as shown in Graph 4.4. This decrease may be attributed to the abstraction of e⁻ₐq by CO₂ in competition with NO₃⁻, since the rate of e⁻ₐq reaction with CO₂ and NO₃⁻ are of the same order \( \approx 10^{10} \) M sec⁻¹. This results in the lowering of the concentration of e⁻ₐq reacting with NO₃⁻ in turn leading to lesser NO₂⁻ yield. The (CO₂ + e⁻ₐq) resulting
in \( \text{CO}_2^- \) subsequently dimerises\(^\text{23}\) to give \( \text{C}_2\text{O}_4^{2-} \).

\[
\begin{align*}
\text{CO}_2^- + e_{\text{aq}}^- & \rightarrow \text{CO}_2^- \\
2\text{CO}_2^- & \rightarrow \text{C}_2\text{O}_4^{2-}
\end{align*}
\]
References