

Gamma Radiolysis of Anhydrous & Hydrated Thorium Nitrates

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The γ -ray induced decomposition of anhydrous and hexahydrated thorium nitrates has been studied using ^{60}Co γ -source in the dose range of 38-550 kGy. The $G(\text{NO}_2^-)$ values decrease somewhat exponentially with the dose. Gamma-radiolysis of 0.05 and 0.1 M aqueous solutions has also been studied at 45 kGy.

Decomposition of alkali metal and many other nitrates induced by γ -radiation has been investigated by several workers¹⁻⁸. Baberkin and Proskurnin⁹ have observed that $G(\text{NO}_2^-)$ are higher in some hydrated nitrates than those in the corresponding anhydrous crystals. Previous works^{1,4-6} from our laboratory on the γ -radiolysis of mono-, bi-, and trivalent metal nitrates have shown that the nature of outer cation and water of crystallisation affect the $G(\text{NO}_2^-)$ values considerably. Herein we report the results of γ -radiolysis of both anhydrous and hexahydrated thorium nitrates at an absorbed dose of 38-550 kGy. Preliminary results of γ -radiolysis of 0.05 and 0.1 M aqueous solutions of thorium nitrate are also reported.

All chemicals used were of AR grade and solutions were prepared in doubly distilled water. Samples in dried Corning glassware were irradiated at room temperature in cobalt-60 gamma chamber at a dose rate of 1.90 kGy hr⁻¹. Gamma dose was measured with Fricke dosimeter using $G(\text{Fe}^{3+}) = 15.6$. The damage product, nitrite was estimated spectrophotometrically at 540 nm employing a Beckman model DU-2 spectrophotometer and following the diazo colour reaction of Shin¹⁰ as modified by Kershaw and Chamberlin¹¹. The G -values were calculated on the basis of the total dose absorbed without any further correction. Blank correction was found to be quite significant in both the cases.

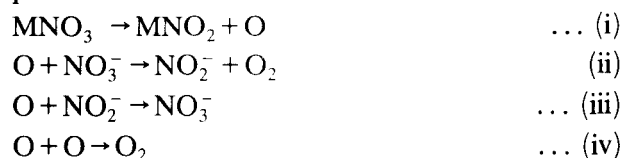
The plots of growth of damage nitrite, $[\text{NO}_2^-]$ with dose (in the range of 38 to 550 kGy) for both anhydrous and hexahydrated thorium nitrate samples are linear and pass through the origin at low doses (<0.1 MGy). At higher doses such plots, though linear, show sharp breaks and the

rate of production of $[\text{NO}_2^-]$ becomes slow. It follows a first order rate equation (1)

$$[\text{NO}_2^-] = kD + C \quad \dots (1)$$

where D is the absorbed dose and k and C are constants. At low doses (<0.1 MGy) C vanishes and the rate of decomposition is very fast. The $G(\text{NO}_2^-)$ values for both the samples decrease almost exponentially with increase in dose. Yields of NO_2^- and $G(\text{NO}_2^-)$ at an absorbed dose of 4.5 Mrads for both the samples as well as in aqueous solutions (0.05 M and 0.1 M) of thorium nitrate are given in Table 1.

Chen and Johnson¹² have postulated the mechanism, shown in Scheme 1, for nitrate decomposition.



Scheme 1

However, recent studies have indicated that the reaction mechanism is complex and the formation of NO , NO_2 , NO_3^{2-} and NO_2^{2-} including some excited species has been also proposed^{13,14}. The decomposition of nitrates has been shown to be complex with dependence on lattice parameters, linear energy transfer, temperature and pressure¹⁵.

The predominance of either of reactions, (ii), (iii) and (iv) may make the decomposition a fast or slow process. Probably at higher doses when all the water molecules have been consumed, recombination processes (iii) and (iv) may be taking place, or the whole lattice may be getting disturbed so that the production of NO_2^- becomes slow. It is further observed that the rate of production of NO_2^- is higher for hydrated form as

Table 1 - Yield of NO_2^- and $G(\text{NO}_2^-)$ Values for Thorium Nitrate at an Absorbed Dose of 45 kGy.

Sample	Conc. of NO_2^- (ppm)	$G(\text{NO}_2^-)$
$\text{Th}(\text{NO}_3)_4$ (solid)	356 ± 10	1.55 ± 0.04
$\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ (solid)	457 ± 9	2.10 ± 0.07
$\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, (0.05 M aq soln)	63.0 ± 0.1	0.22 ± 0.01
$\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, (0.1 M aq. soln)	77.8 ± 0.2	0.36 ± 0.01

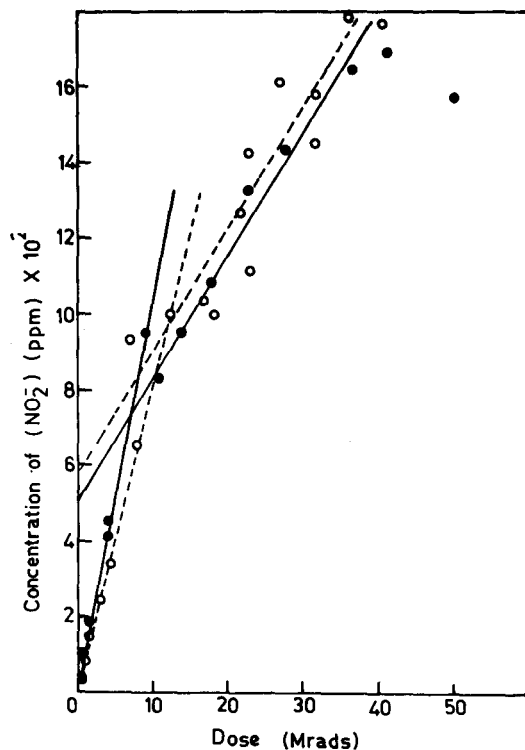


Fig. 1 – Yield of nitrite ion formation with absorbed dose in hydrated (●) and anhydrous (○) thorium nitrate samples.

compared to that for the anhydrous compound. It is expected that only one NO_3^- is available in the case of nitrates of monovalent cations while increasing number of nitrate ions are available for the decomposition of nitrates of multivalent cations. Thus $G(\text{NO}_2^-)$ is bound to be higher for nitrates of higher valent cations. The presence of six water molecules in $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ may facilitate the decomposition as was observed in the case of mercuric nitrate⁶. In both the cases $G(\text{NO}_2^-)$ values decrease with dose almost in an exponential manner, though slowly in the case of anhydrous salt. In case of anhydrous form variation of $G(\text{NO}_2^-)$ versus dose is not smooth but several breaks are observed. This type of behaviour may possibly be due to phase transformation or some other microcrystalline changes taking place in the crystals. Baberkin and Proskurnin⁹ have postulated a reverse reaction of the type (iii) for anhydrous calcium nitrate. In hydrated salt, either the rate of this reaction is slowed down or the reaction is completely stopped presumably due to structural interferences from water molecules. The presence of water molecules of crystallisation might accelerate the process of radiolytic decomposition because of species such as H_3O^+

and OH^- which are likely to be formed in the lattice itself¹.

It may also be noted from Fig. 1 that the role of water of crystallization in the radiolysis is only at the initial doses up to about 0.1 MGy. Beyond this dose, $G(\text{NO}_2^-)$ values are almost similar for anhydrous and hydrated thorium nitrate samples. It implies that all the water molecules of crystallization get radiolysed at <0.1 MGy upto which production of NO_2^- is accelerated. After this, however, the production of NO_2^- becomes slower because of non-availability of other participating species.

In aqueous solution of $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, the rate of production of NO_2^- is considerably slowed down (Table 1) and resultant $G(\text{NO}_2^-)$ values are also low. With increase in thorium nitrate concentration, the yield of (NO_2^-) and $G(\text{NO}_2^-)$ both increase but not in the same proportion. In this case, major part of energy is likely to be shared by the solvent molecules and only a fraction is available for radiolytic decomposition of the nitrate salt. Also the large number of oxidising species so formed may be combining to retard the formation of NO_2^- .

Further investigations are in progress to pinpoint the role of water of crystallization or of solvent.

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