Notes

Effect of Radiation Dose on Formation & Annealing of Different Damage Fragments in Potassium Nitrate

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It is observed that at all absorbed doses (0.05 to 2.00 MGy), the concentration of equivalent nitrite, $(NO_2^-)'$ is higher than that of nitrite, NO_2^- in γ-irradiated potassium nitrate. With increasing dose, though the initial damage induced in the crystals increases, G-values and the fraction annealed (φ) for the species decrease.

Despite extensive work[1-8] on the radiolytic decomposition of alkali metal nitrates[1-11], wherein NO_2^-, O and O_2 are the primary radiolytic products, a clear cut mechanism is yet to be established. It is seen that oxygen remains trapped[5,9] in the lattice as molecular oxygen upto about 22% decomposition on irradiation at room temperature. Further the G-value for the decomposition of potassium nitrate varies with temperature and also with % decomposition at a particular temperature[1,4,9]. The slope of the plot of nitrite ion formation as a function of dose changes abruptly at some point below 2% decomposition[1] and upto 22% decomposition, the yield of the nitrite ion is independent of the intensity but dependent upon the amount of nitrate present. Many workers[2,4,8,10,11] have reported an increase in apparent nitrite yield, determined by ceric method of analysis as compared to that determined by conventional Shinn method. This discrepancy is attributed to the presence of small amount of reducing species other than NO_2^-. The present note deals with the effect of radiation dose on the formation and thermal recovery of total reducing species, $(NO_2^-)'$ and nitrite, NO_2^- in γ-irradiated potassium nitrate.

Crystals of potassium nitrate (AR, BDH) were dried at 383K and stored over phosphorus pentoxide before use. Glass ampoules containing the samples and sealed in vacuo were irradiated with Co-60 γ-rays at room temperature. The dose rate was 0.102 MGy hr^{-1}, as determined[12] using Fricke dosimeter, taking $G(Fe^{3+})$ = 15.5. Crystals were exposed to different doses between 0.05 and 2.00 MGy.

Nitrite was estimated by the diazo colour reaction of Shinn[13] as modified by Kershaw and Chamberlin[14]. In ceric analysis, irradiated crystals were dissolved in 2 $\times 10^{-4} M$ Ce^{4+} in 0.4 M H_2SO_4 and the absorbance at 330 nm was compared with that of a reagent blank
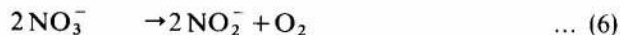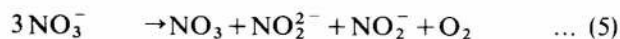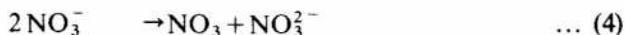
containing the unirradiated nitrate at the same concentration. Isothermal recovery was carried out at 423K in an oil-bath thermostatically regulated to ±0.1K of the desired temperature.

The colours of the crystals were not much affected even at high irradiation doses and at all absorbed doses the nitrite yield i.e. the equivalent nitrite, $(NO_2^-)'$ as estimated by its ability to reduce the ceric ion, is higher than the nitrite, i.e. NO_2^- determined colorimetrically after diazotisation and coupling. The difference, $\Delta(NO_2^-)$ may be attributed to presence of non-nitrite reducing species[2,8,15-18], such as NO, NO_2, NO_3, O^-, O_2^-, O_3 and e_t^-, generated by irradiation. The suggested mode of radiolysis are as follows:

At room temperature irradiation, nitrite ion and oxygen are the primary radiolytic products[15] (Eq. 1) followed by reactions (2) and (3).

$$NO_3^- \rightarrow NO_2^- + O \qquad \ldots (1)$$

$$NO_3^- + O \rightarrow NO_2^- + O_2 \qquad \ldots (2)$$

$$NO_2^- + O \rightarrow NO_3^- \qquad \ldots (3)$$

According to Cunningham[2], NO_3^- decomposes to give either $NO + O_2^-$ or $NO + O^- + O$. The presence of ozonide ion (NO_3^-) in irradiated crystals have been suggested by Zdansky and Sroubek[16] and the species may be formed as a result of reaction: $NO_3^- + NO_3 \rightarrow N_2O_3 + O_3^-$. Din Muhammad and Maddock[8] suggested the following modes of decomposition (Eq. 4-7):

$$2NO_3^- \rightarrow NO_3 + NO_3^{2-} \qquad \ldots (4)$$

$$3NO_3^- \rightarrow NO_3 + NO_2^{2-} + NO_2^- + O_2 \qquad \ldots (5)$$

$$2NO_3^- \rightarrow 2NO_2^- + O_2 \qquad \ldots (6)$$

$$NO_3^- \rightarrow NO_3 + e_t^- \qquad \ldots (7)$$

The difference in yield cannot be attributed[2] to surface effects, particle size or prior treatment of the salt.

The growth of damage fragments with dose is graphically shown in Fig. 1. The plots are linear upto 0.30 and 0.50 MGy respectively for $(NO_2^-)'$ and NO_2^-, beyond which deviations occur. Slopes of the initial linear parts correspond to $G(NO_2^-)' = 1.53$ (lower than the value[8] 1.7) and $G(NO_2^-) = 1.3$ [lower than the reported values[2,5,8,17-20], 1.70, 1.60, 1.61, 1.57 but in good agreement with the data (1.25), obtained by Chen and Johnson[3]]. As lattice changes[1,3] occur in potassium nitrate at a dose of about 0.66 MGy, G-values for the entities decrease with increase in dose and at doses of 0.05 and 2.00 MGy, $G(NO_2^-)' = 1.49$ and 1.00; and $G(NO_2^-) = 1.37$ and 0.95 respectively.
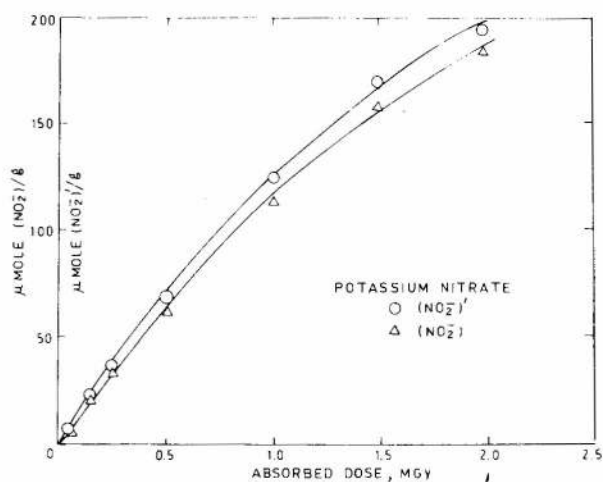
Fig. 1—Growth of total reducing species, $(NO_2^-)'$ and nitrite, NO_2^- with dose in γ-irradiated potassium nitrate at 300K
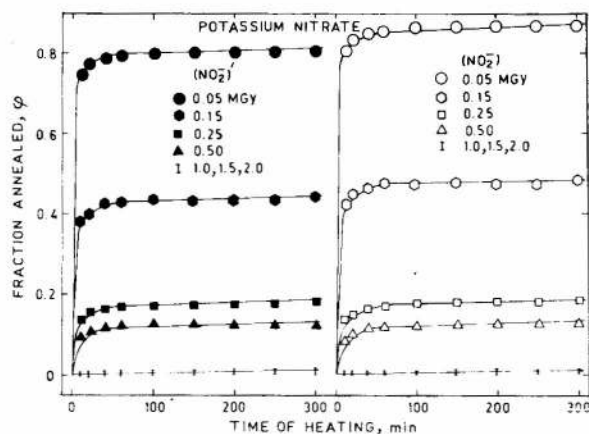

Fig. 2—Annealing of total reducing species, $(NO_2^-)'$ and nitrite, NO_2^- in potassium nitrate irradiated with different doses

The recovery data (Fig. 2) are a combination of fast phase change annealing[21-23] and thermal annealing processes. The annealing isotherms show that there is an abrupt recovery of the damage followed by a pseudo-plateau. The fraction of the damage fragments $(NO_2^-)'$ and NO_2^- recombine rapidly[22-24] (found in $t=0$ axis) due to crystal transition followed by a limited amount of annealing. Lattice mobility also plays an important role in determining the reactions in crystalline solids during phase change by liberating the neutral damage species, possibly O_2^- and O, a proportion of which rapidly recombines with NO_2^- to give the target material[22-24]. As the crystal transformation leads to loss of most of the damage O_2 from the lattice, very little further annealing can occur. The data show that though the extent of recovery of the fragments increases with increase in the period of heating, it decreases with increase in dose of γ-rays and is practically insignificant at high doses, e.g. at 1.00-2.00 MGy (Fig. 2).

Under the present experimental conditions, the species present[15,19,22] in appreciable concentration are NO_2^-, O_2 and O. At low and moderate doses[1,3], molecular oxygen remains trapped in the crystal lattice whereas at high doses it diffuses out of the lattice due to high percentage of decomposition, and radical[2] concentration reach saturation where recovery process involves secondary radicals or non-radicals predominently. The suggested mechanisms for fast phase change annealing, first and second order processes are as follows:

The fast phase change recovery and the first order annealing may be due to rapid reaction of NO_2^- and O pairs.

$$NO_2^- + O \rightarrow NO_3^- \qquad \ldots (8)$$

whilst the more significant second order process is

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad \ldots (9)$$

Potassium nitrate undergoes lattice expansion[1,25,26] during irradiation resulting in an increase in free space where second order reaction (Eq. 9) is more favoured over the first order process (Eq. 8). But with increasing dose, more and more molecular oxygen, diffuses out of the crystal lattice resulting retardation in the recovery process and at sufficiently high doses, e.g. at 1.00 to 2.00 MGy, almost no annealing is observed.

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