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Reduction of Nitrate during release of Stored Energy from Gamma Irradiated Crystalline Potassium Fluoride in Aqueous Nitrate Solution

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ABSTRACT

Reduction of nitrate takes place when the stored energy in the form of colour centres is released during dissolution of g-irradiated crystalline potassium fluoride in aqueous potassium nitrate solution. Various parameters like dose, amount and storage time of irradiated potassium fluoride which control the yield of nitrite have been studied. Similarly, the effect of concentration of potassium nitrate has been investigated. The energy transfer parameter has been determined as the ratio of G/NO_2^- obtained by the addition of irradiated crystalline potassium fluoride on the basis of reduction of nitrate

Key words: Reduction, Nitrate, Gamma Irradiation, KF and F-centre.

INTRODUCTION

Crystalline Potassium fluoride on exposure to ionizing radiation produce F centres and hole centres. Dissolution of such crystals in water results in the formation of hydrated electrons.

$$\text{F centre crystal} \rightarrow e^-_{aq}$$

Recombination of hydrated electrons with the hole centres at the water- solid interphase during the dissolution process lead to the emission of visible light termed as aqua luminescence /AL/[1].

$$F_2 + e^-_{aq} \rightarrow [F^-_{aq} + / F_{aq} \ / * \ ] \rightarrow 2F^-_{aq} + hv \ /AL/$$

On the other hand the solution of crystalline potassium fluoride in aqueous nitrate[2,3] and their mixtures[4,5] induces oxidation and reduction reactions respectively. The present paper deals with the effect of dose, storage time of irradiated crystalline potassium fluoride and on the concentration variation of potassium nitrate.

EXPERIMENTAL

AnalaR grade polycrystalline potassium fluoride were dried under an IR lamp, 3.5 g of potassium fluoride was sealed in a glass envelop and wrapped in black paper.This sample was irradiated to dose of 41 kGy using a ^{60}Co source, whose dose rate measured by Fricke dosimeter was 30.24 kGy/h. The irradiated crystalline potassium fluoride was dissolved in 0.1M potassium nitrate solution. The dissolution of irradiated crystalline potassium fluoride was carried out in a freshly prepared 10 cm^3 aqueous potassium nitrate solution of known concentration under constant stirring and in total darkness. The yield of nitrite in the sample solution as well as in blank was estimated by Shinn's method [6] measuring the absorbance of a diazo-complex at 540nm on Hitachi spectrophotometer.

Fig.1 shows the yield of nitrite as a function of the amount of irradiated KF added. The yield of nitrite increases with increase in amount of irradiated KF added before it levels of above 3.0 g. Freshly irradiated samples of 3.5 g KF were stored for various periods and then dissolved in 10cm^3 of 0.1 M KNO_3 solution.

Fig. 2 shows the yield of nitrite as a function of storing time of irradiated KF. The yield of nitrite becomes independent of storage time after three hours.

The yield of nitrite as a function of dose absorbed by crystalline KF is shown in fig.3. The yield of nitrite increases initially with dose and becomes independent of dose above 40 kGy. The plot of yield of nitrite as a function of concentration of aqueous potassium nitrate solution is shown in fig.4. The yield of nitrite increases with increasing concentration of the salt. However, the nature of the concentration dependence curve of KNO_3 reveals that in the first step of concentration range (10^{-4} to 5×10^{-2}) M of KNO_3 the yield of nitrite is very slow. A sharp increase in the yield of nitrite is observed in the second step above 0.01M of nitrite. However, the yield of nitrite remains constant at about 10^0 M of nitrite in the third step.

DISCUSSION

The dissolution of irradiated crystalline potassium fluorides in aqueous nitrate solution produces nitrite as the stable product. Therefore, the mechanism proposed for the conversion of nitrate to nitrite is based on the reaction suggested by Daniels[7], Hart[8] and Rabini [9] who explained the formation of nitrite in their radiolysis and photolysis studies. The following reactions are envisaged during the dissolution of irradiated salts in aqueous nitrate solution.

$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-}$

The NO_3^{2-} species disproportionates

$2NO_3^{2-} + H_2O \rightarrow NO_3^- + NO_2^- + 2OH^-$

and thus one nitrite ion is formed at the cost of two electrons.

Concentration dependance

The variation in the yield of nitrite as a function of concentration of aqueous potassium nitrate is shown in fig.4. The concentration curve for aqueous potassium nitrate solution shows that in the first step of concentration range (10^{-5} to10^{-2}) M potassium nitrate the yield of nitrite is very low. A sharp increase in the yield of nitrite is observed in the second step above 0.01 M nitrate. However, the yield of nitrite remains constant at about 0.5M of nitrate in the third step. The light emission process and the reduction of nitrate completes at low potassium nitrate concentrations. The net result is that a very small increment in the yield of nitrite is observed up to 10^{-3} M potassium nitrate concentration. The yield of nitrite reaches a plateau above 10^0 M potassium nitrate, indicating that this concentration of nitrate is just sufficient to remove all the F- centres released during the dissolution. The yield of nitrite increases when the concentration of potassium nitrate is in the range of 10^{-3} to 10^0 M. Similar conclusion were made by Gopinathan[10] while studying the light emission process in aqueous nitrate solution by pulse technique found (90+10)% quenching of light emission at 10^0 M potassium nitrate solution.

Effect of dose absorbed

The effect of dose absorbed by crystalline potassium fluorides on the yield of nitrite showed a rapid increase in the yield of nitrite (fig.3) up to 40 kGy followed by saturation at higher doses. According to Gordon and Nowick [11] the formation of F-centres in crystalline potassium fluorides is a two stage process. The initial fast stage is attributed to the trapping of electrons by negative ion vacancies intrinsically present in the crystal, while second stage arise due to the generation of new negative ion vacancies during irradiation, The plateau region corresponds to the slow formation of new vacancies.

The nitrite yield Vs dose curve (fig.3) clearly indicates that the vacancies created at higher doses have no effect on the yield of nitrite.

Amount and storage time of the irradiated salt

The yield of nitrite increases with the amount of the irradiated salt added up to 3.5 g of KF per10cm^3 nitrate solution (fig.1). The concentration of colour centres increase with increasing mass of the salt exposed to a fixed ã-dose. The yield of nitrite reaches a plateau at which solubility of potassium fluoride in water approaches a saturation value at room temperature. This behaviour is in accordance with the observation

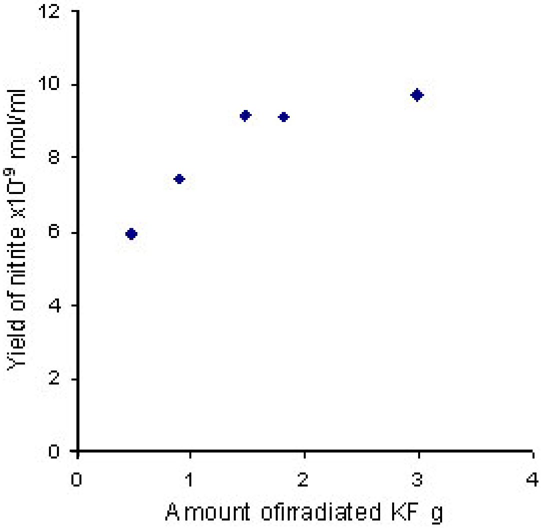

Fig. 1: The plot of the yield of nitrite as a function of amount of irradiated KF

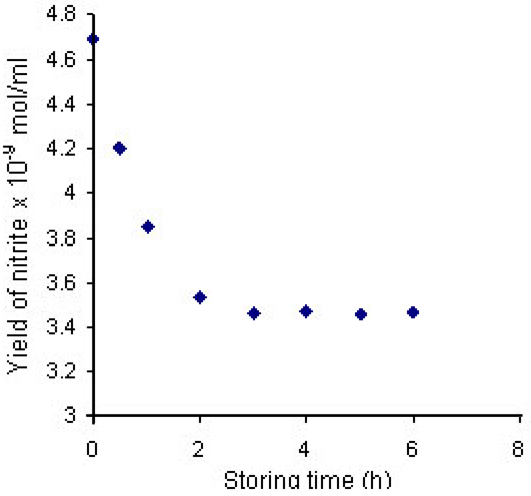

Fig. 2: The plot of the yield of nitrite as a function of storing time of irradiated KF

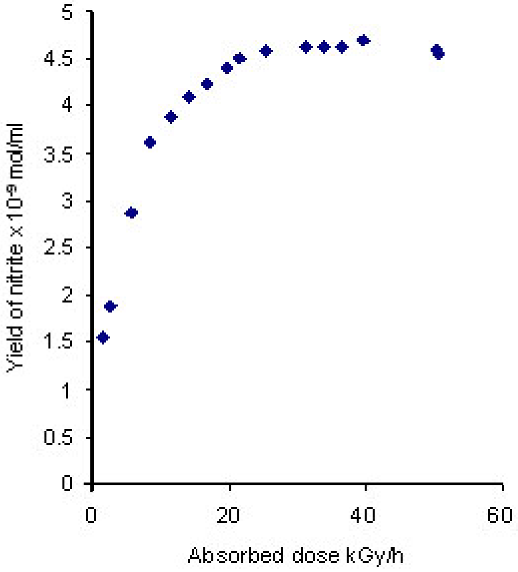

Fig. 3: The plot of the yield of nitrite as a function of dose absorbed by irradiated KF

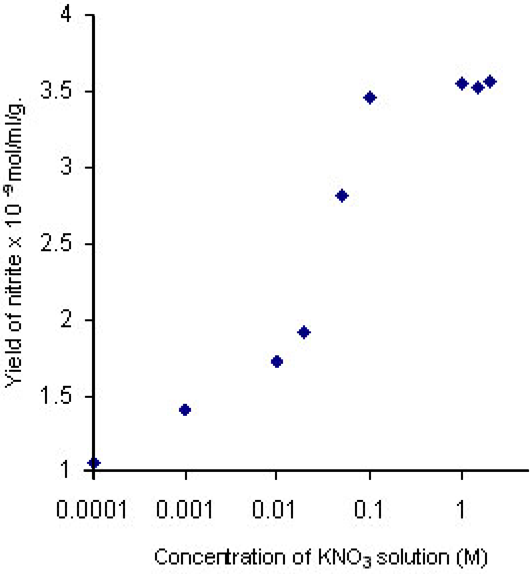

Fig. 4: The plot of the yield of nitrite as a function of concentration of KNO$_3$

made on the rate of the dissolution of the irradiated NaCl single crystal in aqueous $NaNO_3$ solution by Kalkar and Bhujbal[12]. According to them the dissolution follows preferentially diffusion controlled path than activation controlled if large amount of salt is already present in the solution.

It is well known that some of the colour centres in freshly irradiated crystalline potassium fluorides are unstable and recombine giving room temperature luminescence [6] (RTL). Once the RTL is over the stable colour centres remaining trapped in the crystal lattice are responsible for inducing chemical changes during dissolution in aqueous solution. The yield of nitrite is less for crystal in which, the RTL has completely decayed than with the freshly irradiated crystals; moreover, the RTL can be regenerated by exposure to visible light. Hence crystalline potassium fluorides are not exposed to light even during the dissolution process. The study of the yield of nitrite as a function of storage time of irradiated crystalline potassium fluorides is in good agreement with the above theory.

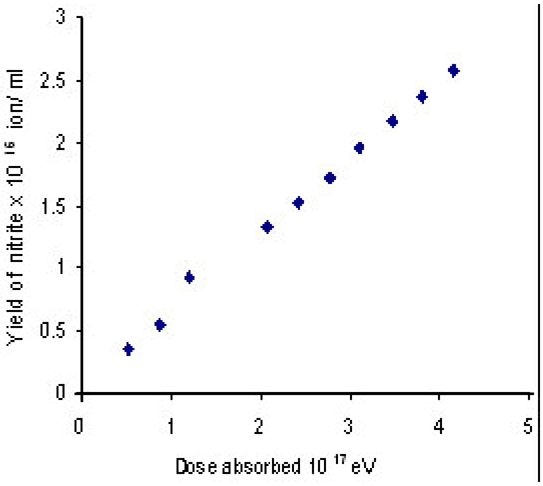

Fig. 5: Radiolysis of 1 M aqueous KNO_3 solution

Efficiency of energy transfer

In order to find out the effect of efficiency of energy transfer it is necessary to know the G-values of nitrite for direct radiolysis of aqueous potassium nitrate solution and that obtained by dissolution of irradiated crystalline potassium fluoride in nitrate. The value of $G(NO_2)$salt is maximum at 0.5 M potassium nitrate concentration. Hence G $(NO_2)^-$ as determined by radiolysis of 0.1 M potassium nitrate is 0.62. The radiolysis of aqueous 0.1 M potassium nitrate solution was carried out to evaluate G $(NO_2)^-$. The plots of the yield of nitrite Vs dose is shown in fig.5. The $G(NO_2)^-$ values

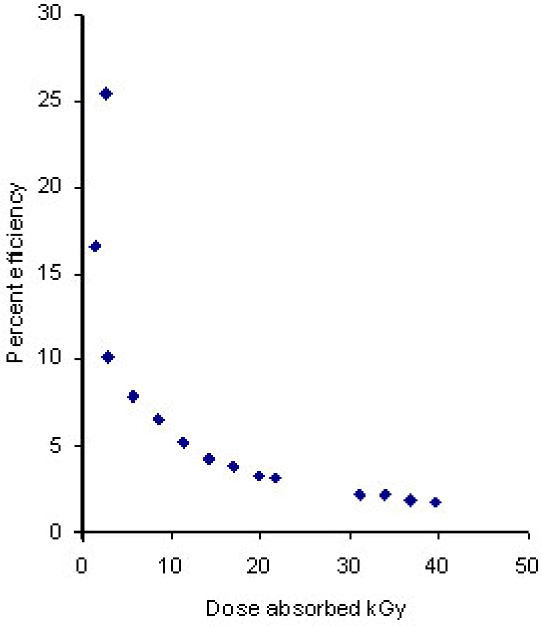

Fig. 6: The plot of percent efficiency parameter Vs dose absorbed by KF

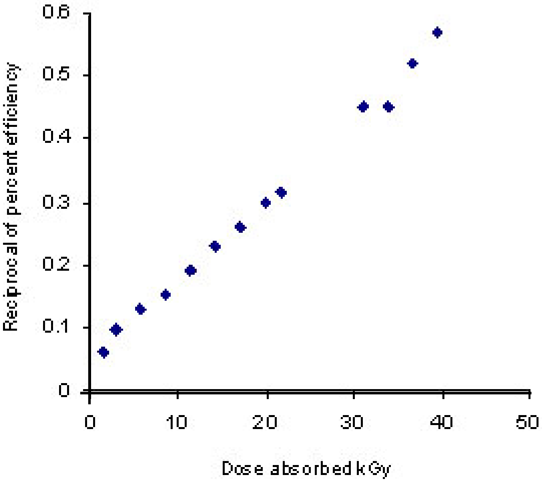

Fig. 7: The plot of reciprocal of percent parameter Vs Dose

determined from slope of linear plot is 0.62. The percentage efficiency of energy transfer (Φ) and the concentration of reducing species is determined at various doses absorbed by KF salt. The plot of percentage efficiencies Vs dose absorbed is shown in fig.6.

The (Φ) values decreases sharply up to 30 kGy dose and then become independent of absorbed dose. The radiolytic product is produced at a higher rate up to 30 kGy. Prolonged irradiation has no effect on radiolytic product of KF. Naturally the efficiency of energy transfer becomes independent of the energy stored in irradiated crystalline potassium fluoride. It is interesting to study the behaviour of KF salt with the help of variation in the percent efficiency of energy transfer with dose in which the G value obtained by γ-radiolysis remains constant. The following empiricial relation between reciprocal of percent efficiency (Φ) and absorbed dose is proposed[5] to find the limiting efficiency transfer for a particular salt or phosphor.

$$(1/\Phi) = (1/\Phi_0) + k D$$

Where Φ_0 is the limiting efficiency as the dose tends to zero, Φ is the percent efficiency at a particular dose (D) and k is a constant. The plot of the reciprocal of percent efficiency Vs dose absorbed by KF salt is shown in Fig. 7. The intercept on Y-axis give the limiting efficiency of transfer for reduction of nitrate as 19%. The low value of limiting efficiency of energy transfer indicates that all the colour centers produced in crystalline potassium fluoride are not completely utilized to produce nitrite. The colour centers are destroyed by other side reactions such as

$$O_2 + e^-_{aq} \rightarrow O2^-$$
$$H_2O + e^-_{aq.} \rightarrow H + OH^-$$

The total concentration of colour centres per mole of potassium fluoride salt was obtained from the yield of nitrite. The concentration of colour centres in singal crystal of alkali halide has been determined by physicist in the past [13]. The concentration of defects initially present in potassium fluoride salt is evaluated from the above graph by back extrapolation. The concentration of inherent colour centres are found to be 0.95×10^{17} in potassium fluoride.

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