

OXIDATION OF IODIDE DURING RELEASE OF STORED ENERGY FROM GAMMA IRRADIATED CRYSTALLINE POTASSIUM BROMIDE IN AQUEOUS IODIDE SOLUTION.

C.D. Kalkar ^a, A. B.Nikumbh^b, G. K. Kulkarni ^b.

a=Department of Chemistry, University of Pune.(M.S.).

b=P.G.Department, of Chemistry

S.S.G.M.College,Kopargaon423601(M.S.)India.

e.mail. ganeshkulkarni.1841@rediffmail.com

Abstract

The stored energy in the form of color centers is released during dissolution of γ -irradiated crystalline potassium bromide in aqueous potassium iodide solution. Various parameters like dose, amount and storage time of irradiated potassium bromide which control the yield of iodine have been studied. Similarly, the effect of concentration of potassium iodide has been investigated. The energy transfer parameter has been determined as the ratio of G/I_2 obtained by the addition of irradiated crystalline potassium bromide on the basis of oxidation of iodide.

Key words: - Irradiation, F-centre, Oxidation, Yield.

INTRODUCTION

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

F centre crystal $\rightarrow e^-_{aq}$ equation 1.

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

$Br_2 + e^-_{aq} \rightarrow [Br^-_{aq} + / Br_{aq} / *] \rightarrow 2Br^-_{aq} + hv /AL/$ equation 2.

On the other hand the dissolution of crystalline potassium bromide in aqueous iodide ^{2,3, 14,15,17} and their mixtures ^{4,5} induces oxidation and reduction reactions. The present paper deals with the effect of dose, mesh number, storage time of irradiated crystalline potassium bromide and on the concentration variation of potassium iodide.

EXPERIMENTAL

AnalaR grade polycrystalline potassium bromide was sealed in a glass envelop and wrapped in black paper. This sample was irradiated to a dose of 41 kGy using a ^{60}Co source, whose dose rate measured by Fricke dosimeter was 3.24 kGy/h. The irradiated crystalline potassium bromide was dissolved in 0.1M potassium iodide solution. The dissolution was carried out in a freshly prepared 10 cm^3 aqueous potassium iodide solution of known concentration under constant stirring and in total darkness. The yield of iodine in the sample solution as well as in blank was estimated by Shinn's method⁶ measuring the absorbance at 354nm on Hitachi spectrophotometer.

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

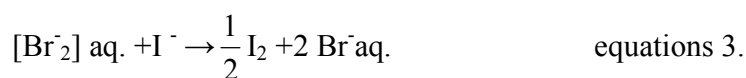
Fig.2 shows the yield of iodine as a function of storing time of irradiated KBr. The yield of iodine becomes independent of storage time after four hours. Fig.3 shows the yield of iodine as a function of mesh number of irradiated KBr. The plot shows an increasing trend with decreasing mesh number of the irradiated salt.

The yield of iodine as a function of dose absorbed by crystalline potassium bromide is shown in fig.4. The yield of iodine increases initially with dose and becomes independent of dose above 40kGy. The plot of the yield of iodine as a function of concentration of aqueous potassium iodide solution is shown in fig.5. The yield of iodine increases with increasing concentration of potassium iodide. However, the nature of the concentration dependence curve of KI reveals that in the first step of concentration range (1×10^{-4} - 1×10^{-2}) M of KI, the yield of iodine is very slow. A sharp increase in the yield of iodine is observed in the second step above 0.01 M of iodide. However, the yield of iodine remains constant at about 1 M of iodide in the third step.

DISCUSSION

The dissolution of irradiated crystalline potassium bromides in aqueous iodide solution produces iodine as the stable product. Therefore, the mechanism proposed for the conversion of iodide to iodine based on the reaction suggested by Daniels⁷, Hart⁸ and Rabini⁹ who explained the formation of iodide in their radiolysis and photolysis studies.

The following reactions are envisaged during the dissolution of irradiated salts in aqueous iodide solution.



Thus one molecule of iodine is produced at the cost of two hole centre.

CONCENTRATION DEPENDANCE

The variation in the yield of iodine as a function of concentration of aqueous potassium iodide is shown in fig.5. The concentration curve for aqueous potassium iodide solution shows that in the first step of concentration range (10^{-4} to 10^{-2}) M potassium iodide the yield of iodine is very low. A sharp increase in the yield of iodine is observed in the second step above 0.01 M iodide. However, the yield of iodine remains constant at about 1M of iodide in the third step. The light emission process and the oxidation of iodine complete at low potassium iodide concentrations. The net result is that a very small increment in the yield of iodine is observed up to 10^{-2} M potassium iodide concentration. The yield of iodine reaches a plateau above 10^0 M potassium iodide, indicating that this concentration of iodide is just sufficient to remove all the F- centers released during the dissolution. The yield of iodine increases when the concentration of potassium iodide is in the range of 10^{-3} to 10^0 M. Similar conclusion were made by Gopinathan¹⁰ while studying the light emission process in aqueous iodide solution.

EFFECT OF DOSE ABSORBED

The effect of dose absorbed by crystalline potassium bromides on the yield of iodine showed a rapid increase in the yield of iodine (fig.4) up to 40 kGy followed by saturation at higher doses. According to Gordon and Nowick¹¹ the formation of F-centers in crystalline potassium bromides 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 yield of iodine Vs dose curve (fig.4) clearly indicates that the vacancies created at higher doses have no effect on the yield of iodine.

AMOUNT, STORAGE TIME AND MESH NUMBER OF THE IRRADIATED SALT.

The yield of iodine increases with the amount of the irradiated salt added up to 3.0g of KBR/10cm³ iodide solution (fig.1). The concentration of color centers increase with increasing mass of the salt exposed to a fixed γ -dose. The yield of iodine reaches a plateau at which solubility of potassium bromide in water approaches a saturation value at room temperature. This behavior is in accordance with the observation made on the rate of the dissolution of the irradiated NaCl single crystal in aqueous NaNO₃ solution by Kalkar and Bhujbal¹². 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 color centers in freshly irradiated crystalline potassium bromide are unstable and recombine giving room temperature luminescence⁶ (RTL). Once the RTL is over the stable color centers remaining trapped in the crystal lattice are responsible for inducing chemical changes during dissolution in aqueous solution. The yield of iodine 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 bromides are not exposed to light even during the dissolution process. The study of the yield of iodine as a function of storage time of irradiated crystalline potassium bromides is in good agreement with the above theory (fig.2).

The particle size of the irradiated crystalline potassium bromide decreases on grinding. The total surface area of the salt exposed to fresh solution during dissolution process also increases with increasing mesh size of the salt. The probability of large number of color centers released instantaneously on dissolution and encountering reaction with iodide ions increases with the decreasing particle size of the salt as shown in fig.3. Similarly the density of the defect centers is greater at the surface than the bulk of the crystal. The cumulative effect is that there is a tendency of increased oxidation of iodide ions with the decreasing particle size of crystalline potassium bromide.

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 iodide for direct radiolysis of aqueous potassium iodide solution and that obtained by dissolution of irradiated crystalline potassium bromide in iodide. The value of G (I₂) salt is maximum at 0.5 M potassium iodide concentration. Hence G (I₂) as determined by radiolysis of 0.1 M potassium

iodide is 0.62. The radiolysis of aqueous 0.1 M potassium iodide solution was carried out to evaluate G (I₂). The plots of the yield of iodine Vs dose is shown in fig.6. The G (I₂) values 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 KBr salt.

The plot of percentage efficiencies Vs dose absorbed is shown in fig.7. 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 KBr Naturally the efficiency of energy transfer becomes independent of the energy stored in irradiated crystalline potassium bromide. It is interesting to study the behavior of KBr 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 empirical relation between reciprocal of percent efficiency (Φ) and absorbed dose is proposed to find the limiting efficiency transfer for a particular salt or phosphor.

$$\frac{1}{\phi} = \frac{1}{\phi_0} + kD \quad \text{Equation 4.}$$

Where Φ₀ 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 KBr salt is shown in fig.8. The intercept on Y-axis give the limiting efficiency of transfer for oxidation of iodine as 11.2 %. Low value of limiting efficiency of energy transfer indicates that all the color centers produced in crystalline potassium bromide are not completely utilized to produce iodide. The color centers are destroyed by other side reactions such as



The total concentration of color centers per mole of potassium bromide salt was obtained from the yield of iodine. The concentration of color centers in single crystal of alkali halide has been determined by physicist in the past¹³. The concentration of defects initially present in potassium Bromide salt is evaluated from the above graph by back extrapolation. The concentration of inherent color centers is found to be 1.2x10¹⁷ in potassium bromide.

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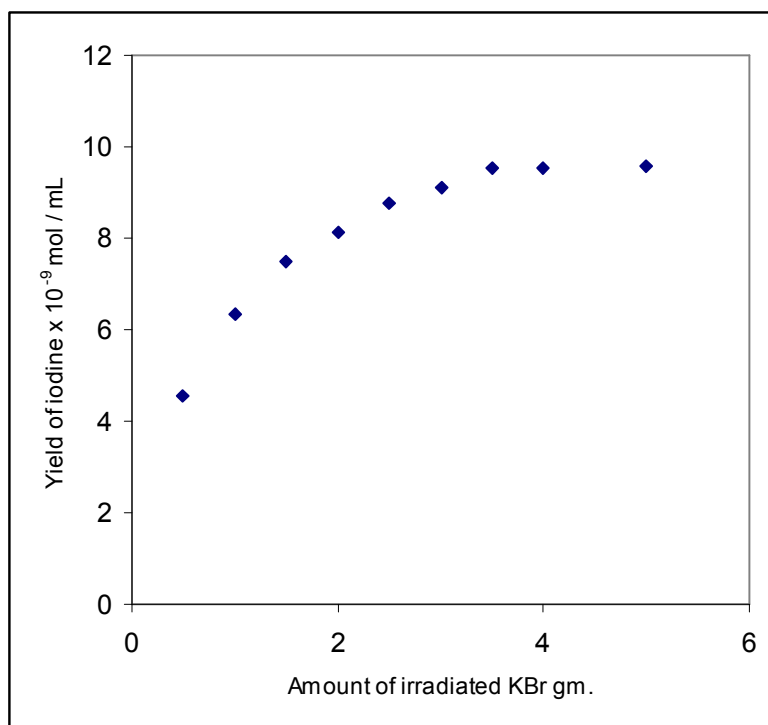
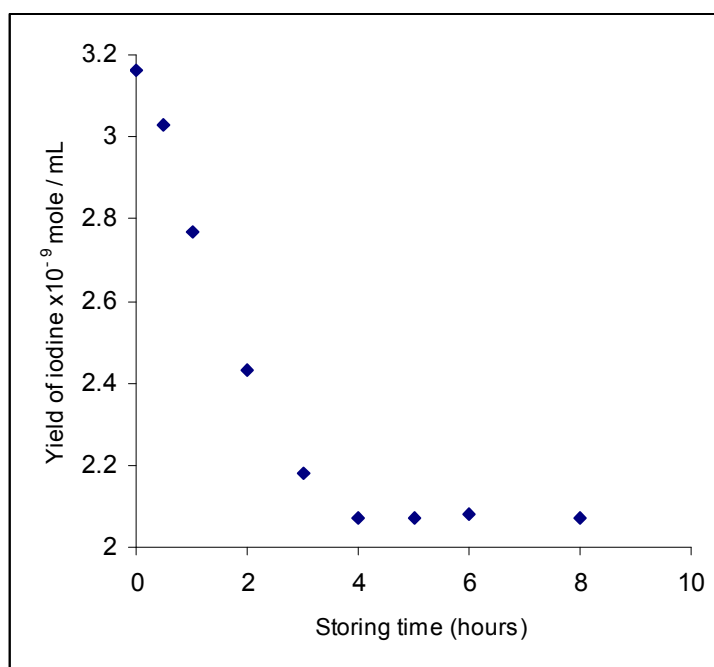
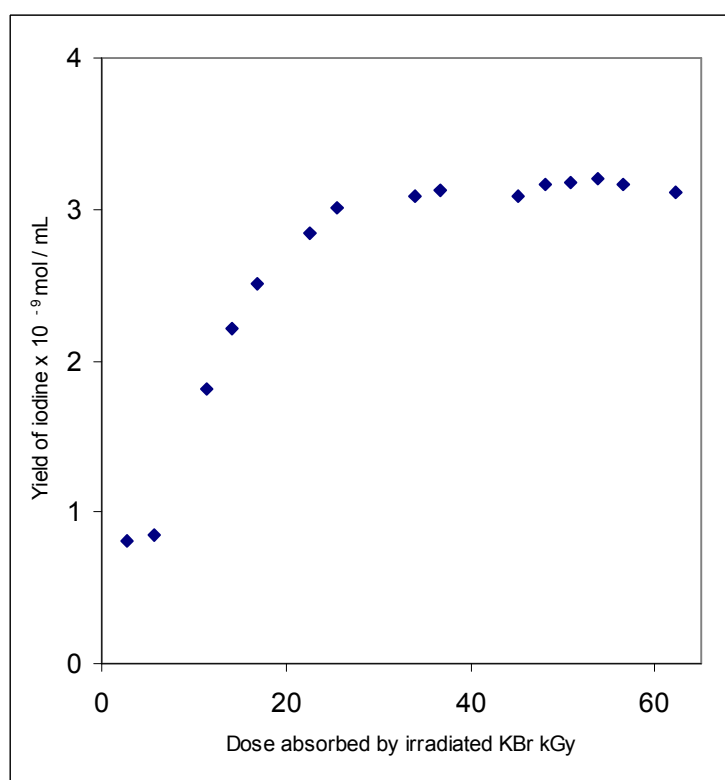
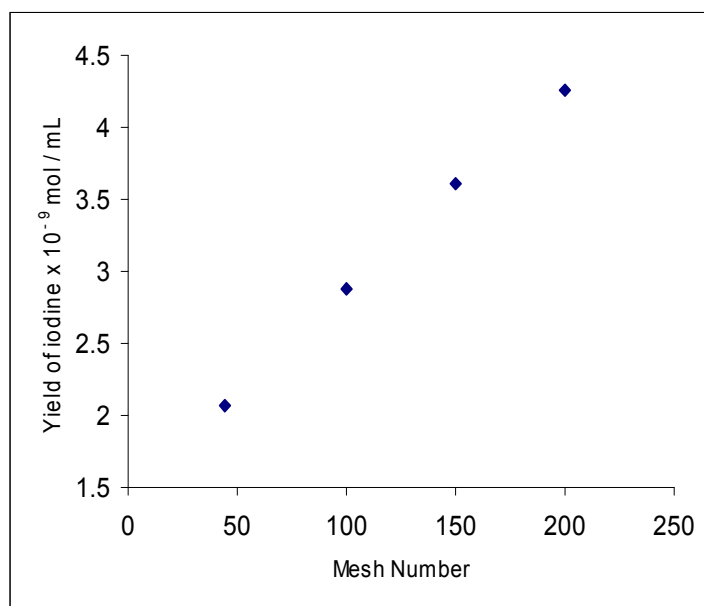
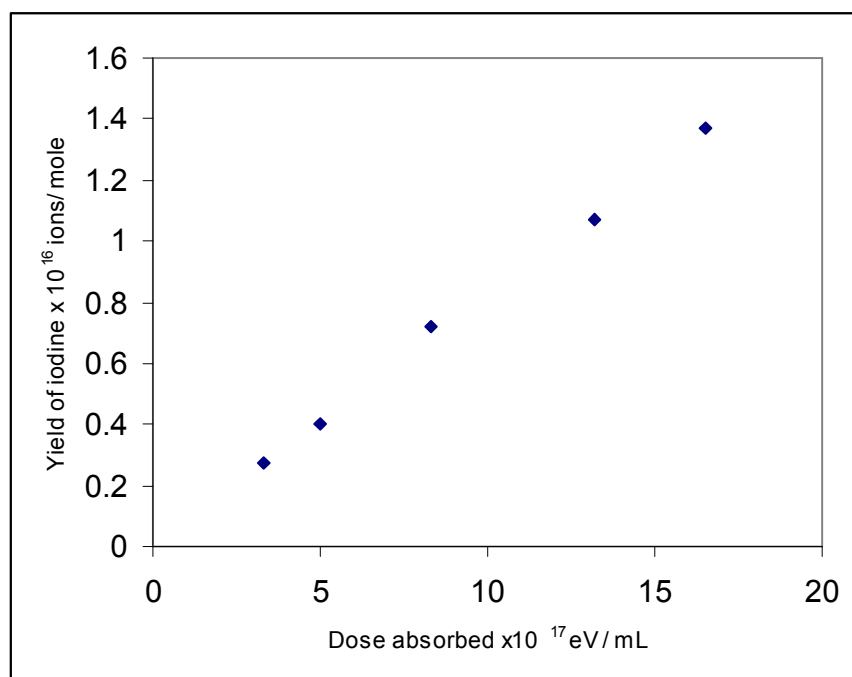
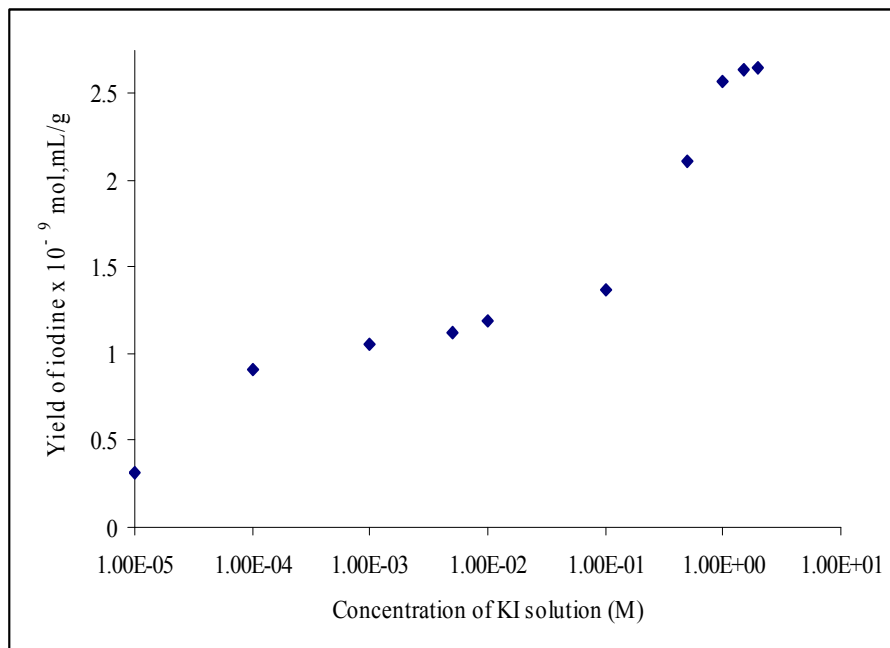


Fig. 1: The plot of the yield of iodine as a function of amount of irradiated KBr







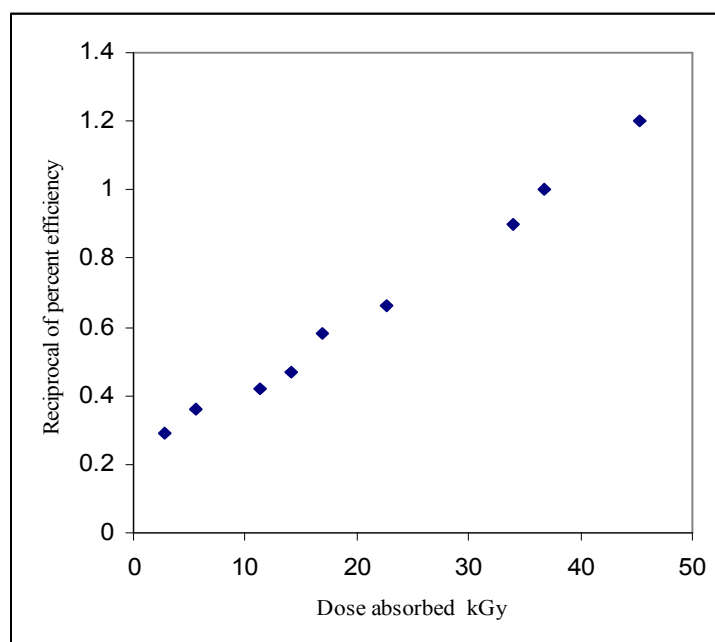
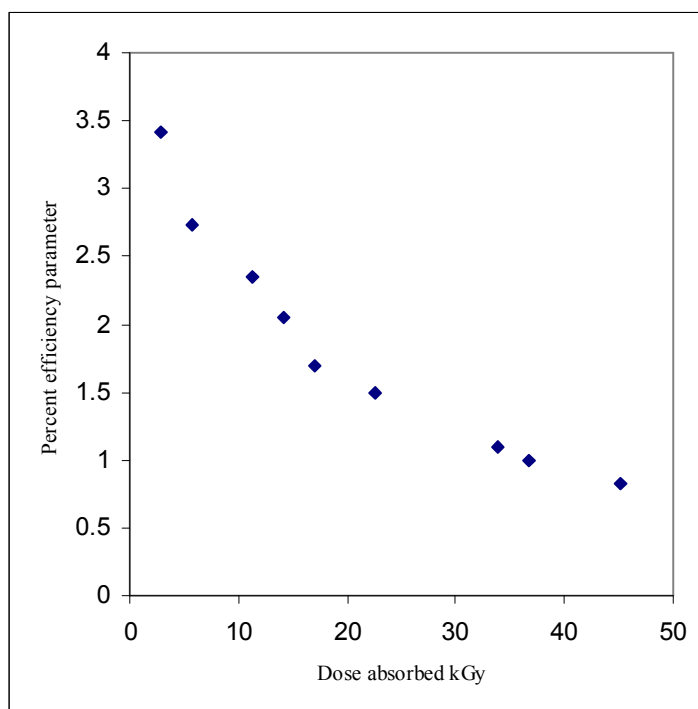


Fig. 1: The plot of the yield of iodine as a function of amount of irradiated KBr

Fig. 2: The plot of the yield of iodine as a function of storing time

of irradiated KBr.

Fig. 3: The plot of the yield of iodine as a function of mesh number of irradiated KBr.

Fig.4: The plot of the yield of iodine as a function of dose absorbed by irradiated KBr.

Fig 5:- The plot of the yield of iodine as a Function of concentration of KI solution.

Fig.6: Radiolysis of 1 M aqueous KI solution.

Fig 7:- The plot of percent efficiency parameter Vs dose absorbed by KBr.

Fig. 8: The plot of reciprocal of percent parameter Verses dose absorbed.

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