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SUMMARY

The thesis is divided into two parts. Part I deals with the radiolysis of aqueous solutions of some oxyanions and binary mixtures of these ions with alcohols. While Part II presents the results of room temperature retention of  $^{80m}\text{Br}$  and  $^{82}\text{Br}$  and subsequent isothermal annealing in organic bromo compounds.

Part I : Part I comprises of three chapters.

Chapter 1 introduces subject of radiation chemistry covering various aspects of the radiolysis of water and aqueous solutions. This is followed by a brief review of the earlier work done on the radiolysis of some systems pertaining to the present work.

The procedures used for the purification of alcohols of interest and carbon tetrachloride are described in the beginning of Chapter 2. This is followed by the description of the analytical methods employed for determining the radiolytic yields of products formed in various systems under investigation.

The results of radiolysis of pure oxyanion systems

( $\text{KIO}_3$ ,  $\text{NaIO}_4$  and  $\text{K}_2\text{S}_2\text{O}_8$ ) as well as the effect of alcohols (methyl alcohol, ethyl alcohol, propyl alcohol and butyl alcohol) on the radiolytic yields are discussed as a function of the dose in Chapter 3. The yields of the products are determined over a wide range of reactant and alcohol concentrations.

Following are some of the important observations :

- (1) The yield of the product varies linearly with the dose in pure solutions as well as in the binary mixtures over a dose range studied.
- (2) The radiolytic yields,  $G(\text{I}^-)$ ,  $G(-\text{IO}_4^-)$  and  $G(-\text{S}_2\text{O}_8^{2-})$  are found to be always higher in the presence of alcohols as compared to their yields in pure solution. For example, the limiting  $G(\text{I}^-)$  in pure solution of  $\text{KIO}_3$  is found to be 0.34 while in the binary mixture of  $\text{KIO}_3/\text{CH}_3\text{OH}$ ,  $G(\text{I}^-)$  value comes out to be 1.7.
- (3) The study of radiolysis of periodate and persulphate ions in the presence of alcohols reveals the occurrence of chain reactions. For example,  $G(-\text{IO}_4^-)$  is found to be 39 in a mixture containing equal concentration of periodate and methyl alcohol (1 mM) as against G value of 6.45 observed for the same concentration of  $\text{IO}_4^-$  ions in the absence of alcohol.
- (4) The values of  $G(\text{I}^-)$ ,  $G(-\text{IO}_4^-)$  and  $G(-\text{S}_2\text{O}_8^{2-})$  studied in all

the systems decrease with increase in molecular weight of the alcohols used under identical conditions of experiments. For instance, for a given concentration of  $[S_2O_8^{2-}]$  and methyl alcohol, 100 mM each, the  $G(-S_2O_8^{2-})$  is found to be 300, while the corresponding  $G(-S_2O_8^{2-})$  in presence of butyl alcohol is found to be 100.

As the solutions of single solute and binary mixtures used in the present work are dilute, most of the gamma photons are absorbed by water molecules and primary radiolytic products (prp) thus produced initiate the reactions. Mechanism consistent with the observed results are proposed in the systems studied. The maximum G values of the stable products on the basis of the proposed mechanisms in pure aqueous systems are given by the following expressions :

(i) Pure iodate solution,

$$G(I^-) = 1/2 [G(e_{aq}^- + H) - G(OH)]$$

(ii) Pure periodate solution,

$$G(-IO_4^-) = G(e_{aq}^- + H) + \left[ \frac{G(e_{aq}^- + H) + G(OH)}{2} \right] + G(H_2O_2)$$

(iii) Pure persulphate solution,

$$G(-S_2O_8^{2-}) = G(e_{aq}^- + H) + G(H_2O_2) + 2G(H_2) + 1/2 G(OH) + G(HO_2)$$

(iv)  $N_2O$  saturated persulphate solution,

$$G(-S_2O_8^{2-}) = G(H) + G(H_2) + G(H_2O_2) + G(HO_2) \\ + 1/2 [G(e_{aq}^- + H)]$$

The results obtained in the radiolysis of binary mixtures are explained on the basis of reactivities of prp of water with solute ions, their concentrations and the transients produced thereby. The transients are highly reactive and are responsible for the reduction of  $IO_3^-$ ,  $IO_4^-$  and  $S_2O_8^{2-}$  ions. The quantitative correlation between the G values of iodide and the primary radiolytic products of water is established in iodate-alcohol system. The high G values of the products observed in the periodate-alcohol and persulphate-alcohol systems are accounted by proposing the chain reactions in these systems. The decrease in  $G(-IO_4^-)$  or  $G(-S_2O_8^{2-})$  value with increase in molecular weight of the alcohol is attributed to the stability and hence the reactivity of the alcohol radicals.

Part II : This part is divided into three chapters (Chapters 4-6).

Chapter 4 covers the subject of hot atom chemistry. The reasons for nuclear retention and different models applied in explaining the mechanism of recoil reactions are discussed. The brief review of the work done in liquid halo compounds is

followed by the scope of the present work.

Chapter 5 consists of the experimental methods employed in the work. Methods of purification of the liquids used, preparation of some bromo compounds, neutron irradiation conditions, analytical procedure for the separation of activities into organic and inorganic fractions and activity measurements are described.

Chapter 6 deals with the results of retention and isothermal annealing of bromine isotopes ( $^{80m}\text{Br}$  and  $^{82}\text{Br}$ ) in organic bromo compounds. The effect of solvent on the organic yield of  $^{82}\text{Br}$  in different bromo compounds is also examined. The retention of  $^{80m}\text{Br}$  and  $^{82}\text{Br}$  in p-bromoacetanilide; 9-bromoanthracene; 9,10-dibromoanthracene, 2-bromobenzoic acid and 3-bromobenzoic acid is studied at various temperatures. The activation energy for the process of annealing of recoil bromine following neutron capture is determined for various systems.

Following are more important observations in the retention studies :

- (1) The retention of  $^{80m}\text{Br}$  as well as that of  $^{82}\text{Br}$  is found to be the same in a given bromo compound.
- (2) The annealing reactions are fast in the beginning and slow

down later reaching nearly a constant saturation value depending on the temperature. The annealing processes are found to obey a formal first order rate law.

(3) The rate and the extent of annealing of both the isotopes in a given compound are found to be almost same at all the temperatures studied.

(4) The pseudo-plateau value is found to be independent of the thermal prehistory of the sample.

(5) The percentage organic yield of  $^{82}\text{Br}$  varies with the nature of the solvent and the compound used.

(6) The threshold annealing temperature is found to depend on the nature of the compound.

A mechanism of isothermal annealing consistent with the observed results is proposed.