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Retention Studies in Sodium & Potassium Perchlorates & in *o*-Chlorobenzoic Acid

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Retention following radiative thermal neutron capture has been studied in sodium and potassium perchlorates and in solid *ortho*-chloro benzoic acid. On thermal annealing the percentage retention increases rapidly to a saturation value which increases with the increase in temperature. It is suggested that the annealing reaction is presumably due to the diffusion of $^{38}Cl^-$ into the unactivated sites of the parent ion.

WE have recently reported the isothermal annealing damage of the ^{128}I in $NaIO_4$ and KIO_4 (ref. 1) and of ^{80}Br and ^{80m}Br in various aromatic bromo-compounds[2]. In the present paper we have extended the work to the annealing studies of perchlorates and *ortho*-chlorobenzoic acid.

Materials and Methods

All the chemicals, viz. $NaClO_4$ (anhydrous), $KClO_4$, $AgNO_3$, etc., used were of AR grade. The sample (0·2 g) was irradiated with a ^{252}Cf fission neutron source (flux $= 2{\cdot}6\times10^9$ n s^{-1}). The chemical separation of recoil products was effected by precipitation method. The irradiated perchlorates were dissolved in water (20 ml). This was divided into two parts, of which one was used for measuring the total activity. To the other part dilute solutions (2 ml each) of sodium arsenite and sodium chloride (carrier) were added. Arsenite reduced the lower oxidizing recoil fragments of chlorine, viz. $*ClO_2^-$ and $*ClO^-$ to $*Cl^-$. All the Cl^- was precipitated as silver chloride. It was centrifuged and the precipitate was discarded. The residual activity of the filtrate containing only $*ClO_4^-$ was measured with a liquid GM counter. The neutron irradiated *ortho*-chlorobenzoic acid was dissolved in ethanol. The inorganic chlorine fragments were precipitated as silver chloride. The total activity and the residual activity before and after the separation were measured. After due corrections the percentage retention values were computed. Isothermal annealing runs were made by heating the irradiated samples in an electric furnace. In the case of *ortho*-chlorobenzoic acid an oil-bath was used.

Results and Discussion

The retention is 35% in sodium and potassium perchlorates and 47% (organic yield) in *ortho*-chlorobenzoic acid. During thermal annealing the percentage retention increases rapidly and reaches saturation (Fig. 1). These results show that the kinetics of isothermal annealing follow a first order equation[3],

$$\log \Delta R_t = \log [R_\infty - R) = kt + C$$

while ΔR_t is the fraction of the damage species remaining unannealed, R is the retention at time t, and R_∞ is the percentage retention at saturation. The plots of log $(R_\infty - R_t)$ versus time of heating are linear as seen from Fig. 2. The activation energies calculated from the plots of log k versus $1/T$ are 18·2, 39·8 and 5 kJ mol^{-1} respectively for sodium and potassium perchlorates and *ortho*-chlorobenzoic acid.

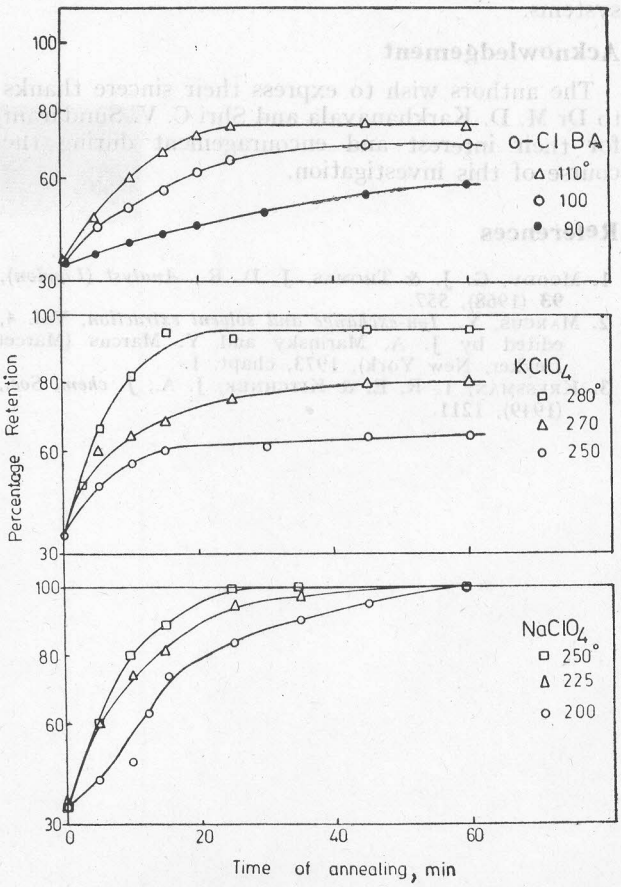

Fig. 1 — Thermal annealing of damage $^{38}Cl^-$ in $NaClO_4$, $KClO_4$ and in *ortho*-chlorobenzoic acid

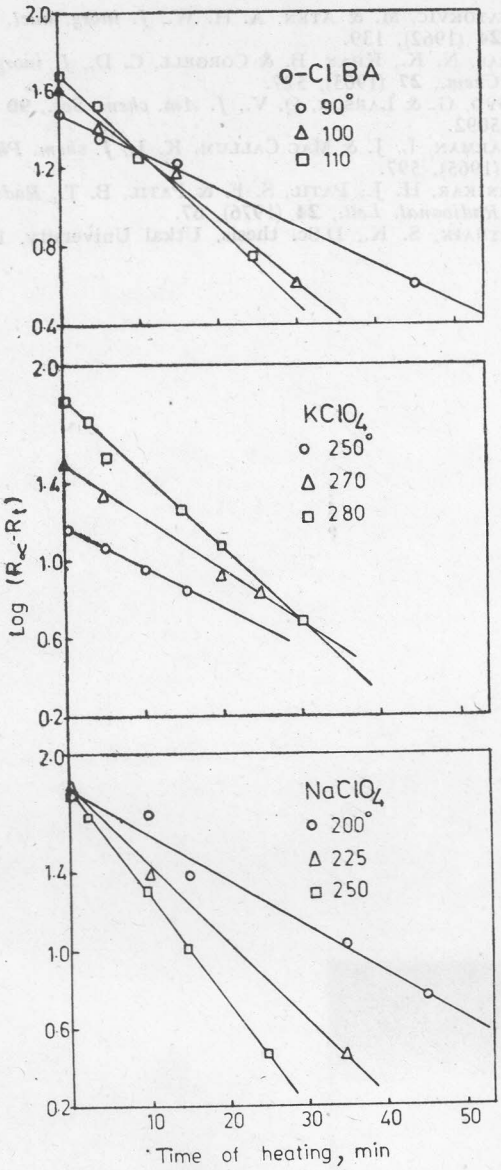

Fig. 2 — Kinetics of isothermal annealing in $NaClO_4$, $KClO_4$ and in *ortho*-chlorobenzoic acid

Mechanism of the annealing reaction — It is known that during (n, γ) irradiation perchlorate ions are degraded to various lower valency states of chlorine[4-7], viz. $*ClO_3^-$, $*ClO_2^-$ and $*Cl^-$. However, there is ample evidence to consider that $*Cl^-$ is the dominant species[4-8]. For instance, Boyd and Larsen[6] showed that 81·9% of ^{38}Cl recoils in (n, γ) reaction in $KClO_4$ is in the form of Cl^-. The annealing of the $*Cl^-$ species by stepwise oxidation to $*ClO_4^-$ would appear to be very unlikely. At the same time, as the final retention amounts to almost 100% it would imply that all the $*Cl^-$ fragments disappear during annealing. These results therefore, suggest that the annealing of $^{38}Cl^-$ is presumably by the diffusion of $^{38}Cl^-$ into unactivated sites of the parent ion by an atom transfer process[2]. The following mechanism is suggested:

$$ClO_4^- + *Cl^- \rightarrow [ClO_4*Cl]^{2-} \rightarrow Cl^- + *ClO_4^-$$

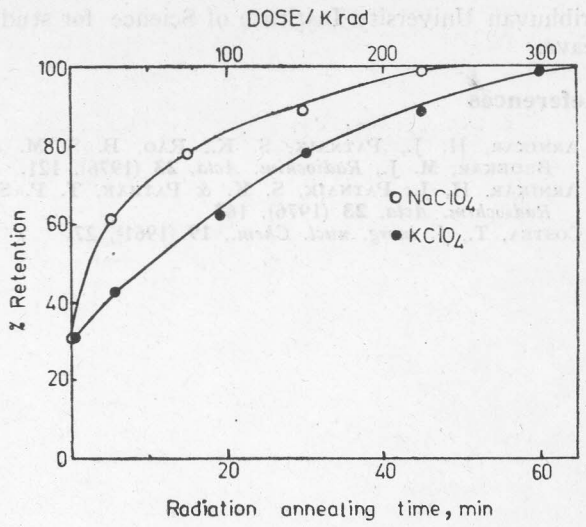

Fig. 3 — Radiation annealing in $NaClO_4$ and $KClO_4$

Such a mechanism is commonly assumed in isotope exchange or atom transfer reactions. The alternative $[ClO_4*Cl]^-$ is not considered as no free chlorine was detected in any case except at extremely high doses above 80 Mrad.

The small amounts of $*ClO^-$, $*ClO_2^-$ formed, however, anneal by reactions

$$*ClO^- + O \rightarrow *ClO_2^-$$
$$*ClO_2^- + O \rightarrow *ClO_3^-$$
$$*ClO_3^- + O \rightarrow *ClO_4^-$$

A similar process of diffusion of *Cl fragments into the unactivated sites of the parent molecule holds good in the case of *ortho*-chlorobenzoic acid as well and thereby apparent retention (organic yield) increases due to annealing, as in the case of bromo-compounds[2].

During irradiation the recoil energy is deposited in the crystals in the form of disorder. On heating this energy is released which appears to be the driving force for the annealing reaction[9]. This explains the low activation energy as obtained from corresponding Arrhenius plots.

Radiation annealing — It is also seen from Fig. 3 that the neutron irradiated perchlorate is much more susceptible to radiation annealing. In the case of sodium perchlorate 100% annealing is found within 15 min of exposure to ^{60}Co gammas, the dose rate being 5 krad/min, whereas in the case of potassium perchlorate complete annealing by radiation needs about 60 min. It is suggested that the radiation annealing occurs exclusively by an atom transfer process as discussed under the thermal annealing with the possibility that the process is accelerated in the presence of γ-rays.

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