Thermal Effects on Isotopic Exchange of $^{51}$Cr(VI) in Gamma-irradiated, $^{51}$Cr(III) Doped Sodium Chromate-Potassium Chromate Mixtures

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Transfer annealing studies on γ-irradiated $^{51}$Cr(III)-doped sodium chromate-potassium chromate mixtures, irradiated to different gamma ray doses, show that the percentage of Cr(VI) exchanged increases with increase in annealing temperature and gamma ray dose. The results have been discussed in the light of a model involving ligand and metal vacancy exchange and substitution reactions.

It has been reported that annealing of $^{51}$Cr(III) doped chromate results in oxidation of $^{51}$Cr(III) to $^{51}$Cr(VI). The effect of gamma-irradiation on oxidation of $^{51}$Cr(III) in chromate systems have been studied. Similar studies have been made in several other oxy salts and also in salts where the dopant atom is not isotopic with the central atom in the host lattice.

In the present work we have studied the effect of heating on the γ-irradiated $^{51}$Cr(III) doped Na$_2$CrO$_4$-K$_2$CrO$_4$ mixtures in order to shed more light on the mechanism of isotopic exchange and radiation damage processes in solids.

Sodium chromate was prepared and purified according to recommended methods. Potassium chromate (BDH) was used as such. The crystalline mixture of Na$_2$CrO$_4$-K$_2$CrO$_4$ was precipitated from a hot saturated solution of pure components by adding absolute ethanol, filtered washed several times with ethanol and dried at 100°C. X-ray diffraction powder pattern of this precipitated material indicated it to be a mechanical mixture of Na$_2$CrO$_4$ and K$_2$CrO$_4$ and not a true mixed salt.

Doping with $^{51}$Cr(III) was done by a co-crystallization method. For this purpose a solution (0.15 ml) of high specific activity $^{51}$Cr(III) (≈ mcCi) (Amersham, England) was added to a well-stirred, saturated aqueous solution (40 ml) of the Na$_2$CrO$_4$-K$_2$CrO$_4$ mixture at 70°C. The system was cooled for 30 min in an ice-bath after 15 sec of the addition. The crystals obtained were filtered off and washed with a saturated solution (51 ml) of sodium and potassium chromates at 0°C prior to drying invacuo. The doped mixture obtained was subjected to γ-irradiation at a dose rate of 27.12 rad/s using a Co-60 source (AEE Cairo) for appropriate irradiation times.

Solvent extraction technique was applied for the determination of the per cent exchanged. For this purpose the irradiated sample (5 mg) was dissolved in acetate buffer (20 ml, pH 5.0) at an ionic strength 0.1 M. This solution was carefully added to chloroform (20 ml) containing 1-(2 thenoyl-3,3,3 trifluoro-acetone) and dibenzylamine synergic extractants (0.05 M each). The two layers were shaken vigorously for 20 min to reach equilibrium. After separation of the phases 10 ml of each layer were withdrawn carefully and subjected to counting. Unoxidized and unexchanged $^{51}$Cr(III) in solution was extracted into the organic phase while $^{51}$CrO$_4^{2-}$ remained in the aqueous layer. The percentage exchanged was calculated from Eq.(1)

$$\gamma = \frac{\text{activity in aqueous phase}}{\text{Total activity (aqueous + organic phases)}}$$

Figure 1 shows isochronal annealing curves (2 hr) for $^{51}$Cr(III) doped Na$_2$CrO$_4$-K$_2$CrO$_4$ mixtures irradiated with different γ-ray doses together with the isochronal annealing curve for unirradiated samples. The per cent exchanged increases with increase in both γ-ray dose and annealing temperature. The oxidation of Cr(III) to Cr(VI) in the case of unirradiated sample began to occur at 60°C. The oxidation of $^{51}$Cr(III) has

![Figure 1](image-url)
been explained by a stepwise oxidation mechanism involving recombination of electronic and thermal steps. However, the formation of ligand-deficient species can result from radiation damage and solid state isotopic exchange as in the case of recoil effects\(^\text{\textsuperscript{11}}\) and the exchange can be explained on the basis of a mechanistic model involving metal and ligand vacancies exchange and substitution reactions. These considerations leads us to propose\(^\text{\textsuperscript{12a}}\) a mechanistic model as shown in Scheme 1.

\[
\begin{align*}
\text{*Cr} + \text{CrO}_4^- &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{PMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{PMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\end{align*}
\]

\[\text{(1)}\]

\[
\begin{align*}
\text{[CrO}_4^- + \text{Cr}} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{SMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{PMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\end{align*}
\]

\[\text{(2)}\]

\[
\begin{align*}
\text{[CrO}_4^- + \text{Cr}} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{PMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{SMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\end{align*}
\]

\[\text{(3)}\]

\[
\begin{align*}
\text{[CrO}_4^- + \text{Cr}} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{PMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\text{SMV} &\rightarrow \text{[CrO}_4^- + \text{Cr}} \\
\end{align*}
\]

\[\text{Scheme 1}\]

In Scheme 1, \(\square\) refers to a metal vacancy, \(\Delta\) is a ligand vacancy, \(n\), \(m\), number of ligand vacancies, PMV is a primary metal vacancy produced from direct substitution reaction between the doped atom and chromate matrix and SMV is a secondary metal vacancy produced as a result of indirect substitution reaction between PMV, chromate matrix and doped atom\(^\text{\textsuperscript{11}}\). It can be seen that the formation of \(*\text{CrO}_4^-\) and rate of isotopic exchange depend on the reaction paths (1), (2) and/or (3), i.e. recombination of deficient species formed as a result of doping with radioactive atoms and radiation damage processes in solids\(^\text{\textsuperscript{11}}\), ligand and/or metal vacancy exchange reactions and the return of the doped atom to fill the primary and secondary metal vacancies. The relative importance of reaction paths (2) and (3) will depend on whether a neighbouring molecule prefers a metal vacancy exchange or the transfer of oxygen\(^\text{\textsuperscript{13}}\).

It must be mentioned that the four graphical representations have a similar form beyond 70°C (see Fig.1), while below 70°C the three \(\gamma\)-irradiated samples show different (although similar among themselves) profiles as compared to the unirradiated sample. This is possibly due to the \(\gamma\)-irradiation effect in the solid state, which annealed out and hence did not influence the course of exchange of \(^{51}\text{Cr}\) beyond 70°C. Thermal effect may be the most important factor governing the course of exchange beyond 70°C. It may be noted that the per cent exchanged in the case of Na\(_2\)CrO\(_4\)-K\(_2\)CrO\(_4\) homogeneous mixture and those obtained for pure salts are different\(^\text{\textsuperscript{6}}\), indicating that the present data are not the average of the free components of the mixture but deserves a separate treatment.

References
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