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ON RADICALS IN GAMMA-IRRADIATED POTASSIUM TRIMETAPHOSPHATE

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The single crystal of $K_3P_3O_9$ was irradiated by gamma-rays at room temperature. The pink colored crystal (absorption maximum at around 500 nm and esr spectrum with g=2.01 and a coupling constant of 36G.) was dissolved in aqueous iodide solutions and the liberated iodine was quantitatively measured. From the product analysis, the initial G values were determined as $G(P^{4+}) \doteq G(P^{6+}) = 0.27 \pm 0.05$ at 20°C.

We have previously reported yields of radiation products in sodium metaphosphate glasses at room temperature using dissolution methods.[1)] The stable radicals in polymetaphosphates at room temperature are believed to be trapped in the longer polymer chains.[2)] So far no radiation effect on the trimetaphosphates having the ring structure has been reported. It is of interest to see whether the ring phosphates yield stable radicals as in the case of the polymeric phosphates at room temperature.

Potassium trimetaphosphate was synthesized from $Na_3P_3O_9 \cdot 6H_2O$ using the ion-exchange method.[3)] Purity of the crystal was checked by means of paper chromatography and the titration with aqueous $H_3P_3O_9$ solutions. Single crystals of potassium trimetaphosphate were grown in saturated aqueous solutions by evaporation.

The single crystal was irradiated with ^{60}Co gamma-rays to the dose of 6.7×10^{18}-7.7×10^{19} $evgr^{-1}$ (the dose rate was 6.7×10^{18} $evgr^{-1}hr^{-1}$).

The irradiated crystal took on a pink color with the absorption maximum at about 500 nm. The color center was stable up to 65°C and was relatively insensitive to visible light. The esr spectrum of the irradiated crystal was very similar to that of irradiated metaphosphate glasses[4)] as shown in Fig.1 (the g-factor of the central and the outer doublets with g=2.01 and 1.99 respectively).

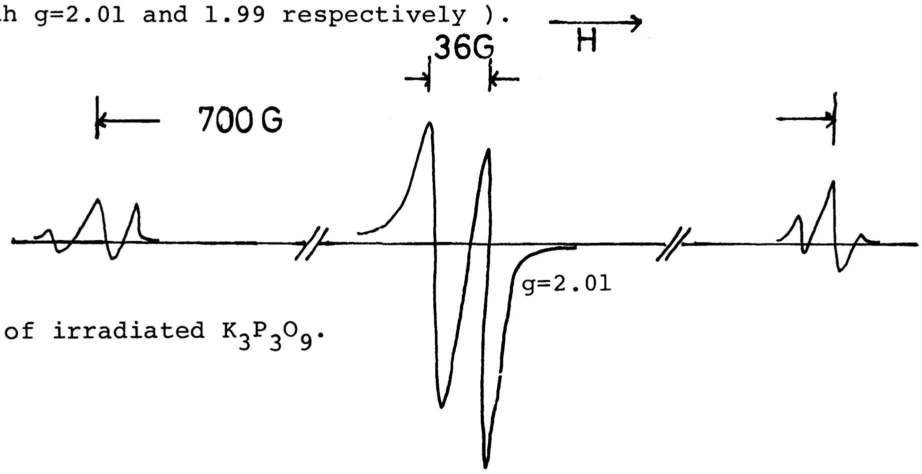
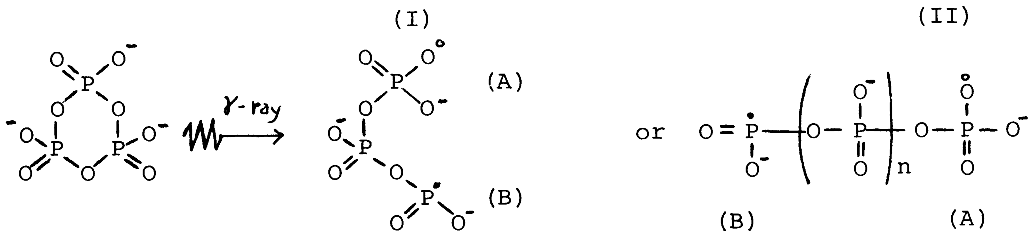


Fig.1. esr spectrum of irradiated $K_3P_3O_9$.

The irradiated trimetaphosphate was dissolved in the following aqueous solutions: (1) Aerated neutral KI solutions with varying concentrations. (2) Same as (1) with various pH's. (3) KI solutions deaerated with N_2 gas. (4) KI solutions saturated with N_2O. (5) Same as (3) with $Fe(ClO_4)_3$ and methanol added. On dissolution of the phosphate, the iodide was oxidized to liberate the I_3^- ion which absorbs at 353 nm for the aerated and acidic solutions. The formation of the triiodide ion was independent of the concentration of KI above 5×10^{-4} M, and of the acid between $10^{-2} \geq [H^+] \geq 5\times10^{-5}$ M.

The triiodide ion was not formed for the deaerated solutions. We have identified H_2O_2 as a product after dissolution of irradiated $K_3P_3O_9$ in aerated pure water, while no hydrogen gas was evolved in the solution containing alcohol and acid, nor nitrogen gas in the solutions saturated with N_2O gas. By analogy with the result of the metaphosphate glass the color center may be associated with the "trapped hole" where the valency of phosphor is $P^{6+}(PO_4^{2-})$. The possible reaction undergoing irradiation may be described as,



Site A and B correspond to the trapped hole and the counterpart "trapped electron" in which the valency of phosphor is $P^{4+}(PO_3^{2-})$.

The reaction upon dissolution may be written as in the case of metaphosphate glasses.

$$
\text{Aerated}\quad
\begin{aligned}
&P^{4+} + O_2 \longrightarrow P^{5+} + O_2^- \\
&2H^+ + O_2^- + I^- \longrightarrow I + H_2O_2 \\
&2H^+ + H_2O_2 + 2I^- \longrightarrow I_2 + 2H_2O \\
&P^{6+} + I^- \longrightarrow P^{5+} + I
\end{aligned}
$$

$$G(I_3^-) = 3/2G(P^{4+}) + 1/2G(P^{6+})$$

$$\text{Deaerated}\quad P^{4+} + P^{6+} \longrightarrow 2P^{5+} \text{ (recombination)}$$

Assuming the above reactions and the relation of G(site A) = G(site B), one may identify the yield of P^{6+} or P^{4+} with half the yield of the triiodide ion.

Figure 2 represents the yield of P^{6+} or P^{4+} so derived as a function of the absorbed dose. From the curve in Fig.2, the initial G-value is determined as 0.27.

It is interesting to note that the G-value of the color center in the irradiated potassium trimetaphosphate crystals is much lower than that in the corresponding polymetaphosphate glasses.[1)]

We also observed that the crystals of $Na_3P_3O_9{\cdot}6H_2O$, $Na_4P_4O_{12}{\cdot}10H_2O$, $K_4P_4O_{12}{\cdot}2H_2O$, $(NH_4)_3P_3O_9$, and $(NH_4)_4P_4O_{12}$ did not have color or esr centers after irradiation at room temperature.

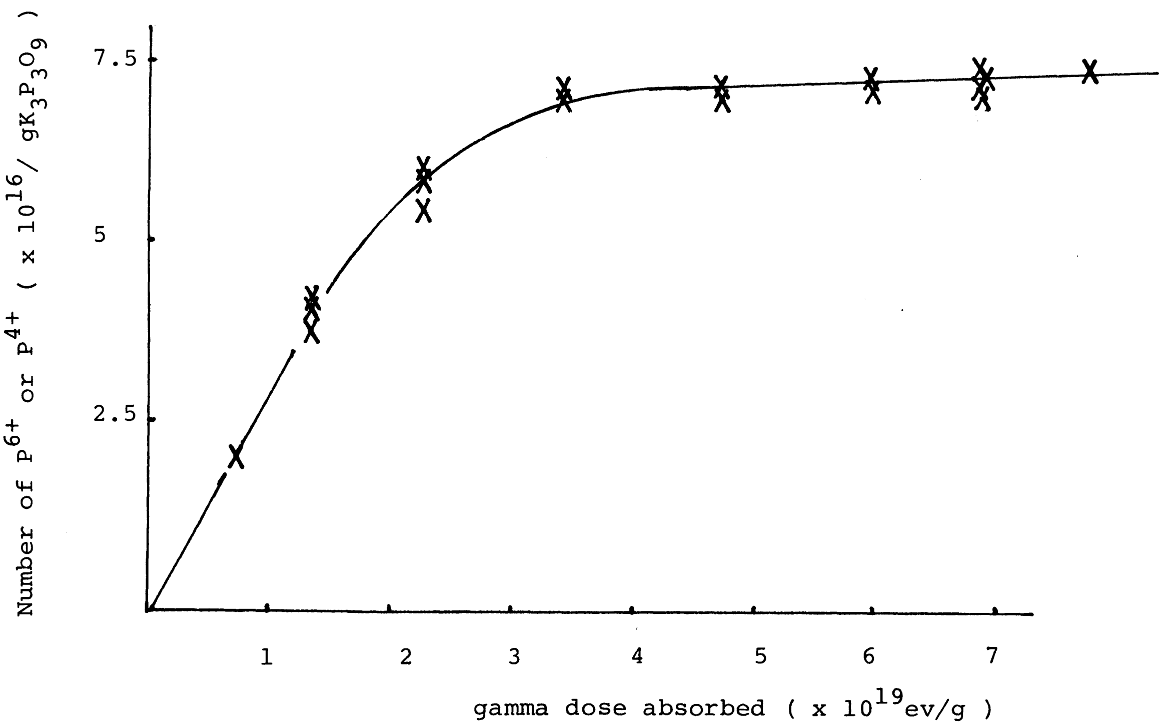


Fig.2. Formation curve of P^{6+} or P^{4+} as a function of dose.

References

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