NOTES

The Influence of pH on Mercuric Chloride Reduction under Ionising Radiations

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The post-irradiation effects in the mercuric chloride - sodium oxalate reduction system under X, β, γ- and ultraviolet radiations have been shown earlier by the present author.[1] The present study will report data on the influence of pH on the radiation-induced reduction of the above system in the presence and in the absence of oxygen.

The aerated and H_2-saturated Eder's solutions (mercuric chloride - sodium oxalate) were prepared as described earlier.[1] The pH values were altered by the addition of pure concentrated hydrochloric acid and were determined by a Beckmann pH meter. These solutions of different pH values were then exposed to radiations from (1) an ultraviolet source (a quartz Hg vapour lamp run at 220 V. 0.12 amp. from a distance of 10 cm.), (2) 112 pkV. $-$X rays (5×10^5 r/hr.), and (3) 1 MeV. electrons (2×10^7 r/hr.), for 20 min. at 30.5°C; the amount of mercurous chloride formed was calculated by titrating it against standard potassium iodate (using Jamieson's[2] procedure).

It may be seen from the figure that, in aerated solutions, the yields of mercurous chloride diminish with decreasing pH values and that at pH$\leqslant$1.9 the reduction is completely inhibited under ultraviolet, at pH$\leqslant$1.78, under X-rays, and at pH$\leqslant$1.62, with 1 MeV. electrons. It is significant that, in the presence of molecular H_2, the reduction is not completely inhibited.

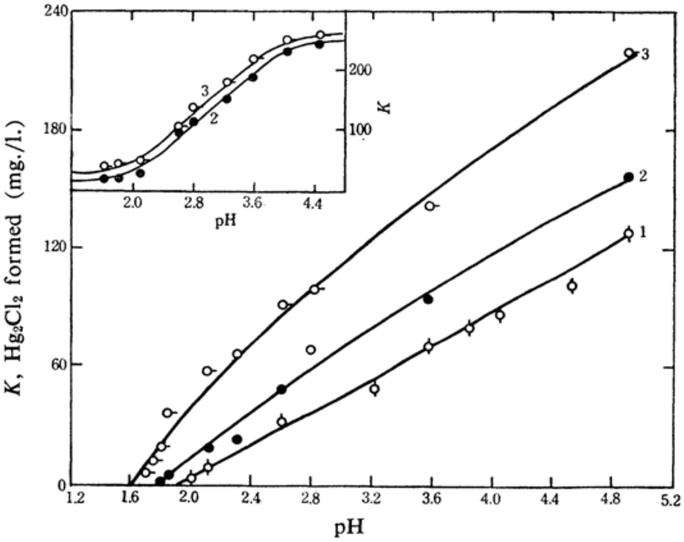

Fig. 1. Plots of K vs. pH in the presence of O_2 and saturated with H_2 (inset).
1, UV 2, X-rays 3, 1 MeV. electrons

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[1] P. S. Rao, *Z. physik. Chem.*, **19**, 226 (1959).

[2] A. I. Vogel, "A Text Book of Quantitative Inorganic Chemistry" (1961), p. 377.

The rate law[3] can be written as:

$$\frac{K_1\,[Hg_2Cl_2(C_2O_4)^{2-}]\,I}{P_1\,[1/pH]}$$

where K_1 is the rate of formation of $Hg_2Cl_2(K)$ in the absence of acid (in this system, at pH 4.9) ; I is the intensity of the ionising radiation, and P_1 is the critical value of pH when $K=0$. The near linearity of the K vs. reciprocal acidity (pH) plots and the diminution of p, with I follows from the above relationship.

It is well known[4] that the complex Hg_2Cl_2-$(C_2O_4)^{2-}$ formed by mercuric chloride and oxalate decomposes to mercurous chloride under both ultraviolet and ionising radiations as follows: $2Hg_2Cl_2(C_2O_4)^{2-}+h\nu \rightarrow 2HgCl+2Cl+2(C_2O_4)^-$ with $C_2O_4^-$ and probably Hg^+ acting as chain carriers. At high acid concentrations and under ultraviolet, it can be assumed that the chain carrier $C_2O_4^-$ is destroyed:

$$H^+ + C_2O_4^- \rightarrow HC_2O_4$$

Under ionising radiations, H atoms are produced by the disruption of H_2O molecules:[5]

$$H_2O \rightsquigarrow H+OH$$

These can be removed in the presence of O_2 or by the O_2 formed by the interaction of OH radicals.

$$2OH \rightarrow H_2O+O$$

and $$2O \rightarrow O_2$$

Thus, at high acid concentrations,

$$H+O_2 \rightarrow HO_2$$

$$HO_2+Hg^+ \rightarrow Hg^{2+}+HO_2^-$$

which might result in an inhibition of the reaction.

In the presence of molecular H_2, the possibility of H atoms exerting an oxidising effect on the present system can be shown if one assumes the formation of hydrated hydrogen molecular ions in the solution.[6]

$$H+H^+(\text{hydra.}) \leftrightarrows H_2^+(\text{hydra.})$$

The H_2^+ ion has been shown to have an oxidising effect in the $FeSO_4$ system.[7]

Thus, the back reaction,

$$Hg^+ + H_2^+(\text{hydra.}) \rightarrow Hg^{2+}+H_2$$

might account for the observed inhibition of the reduction.

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[4] G. H. Cartledge and S. L. Goldheim, *J. Am. Chem. Soc.*, **55**, 3583 (1933).

[5] G. Stein, J. Weiss and R. Watt, *Trans. Faraday Soc.*, **48**, 1030 (1952).

[6] J. Weiss, *Nature*, **165**, 728 (1950).

[7] T. Rigg, G. Stein and J. Weiss, *Proc. Roy. Soc.*, **A211**, 377 (1952).