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V. G. FIRSOV

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Abstract

Full Text

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THE INHIBITING ACTION OF THE URANYL ION ON THE RADIATION-CHEMICAL OXIDATION OF FERROUS IRON

(Presented by Academician A. I. Alikhanov on 23 I 1961)

In papers ([1,2]) it was shown that the uranyl ion inhibits the radiation oxidation of solutions of tetravalent uranium; moreover, the kinetics of inhibition can be quantitatively described by using the model of an irradiated solution proposed by Allen. In this connection it seemed important to investigate the inhibiting action of the uranyl ion on the well-studied process of radiation oxidation of ferrous iron.

Experiment. Thoroughly deaerated sulfuric-acid solutions of ferrous iron mixed with uranyl sulfate were placed in quartz ampoules with a ground-glass stopper in the form of a capillary with an enlargement. The presence of the capillary ensured equalization of the pressures inside and outside the ampoule without allowing oxygen access to the system. The solutions were exposed to the action of γ-radiation from a ^{60}Co source with a radiation intensity of $1.5 \cdot 10^{19}$ eV/l • sec ([3]).

Fig. 1. Dependence of the yield of oxidation of Fe^{2+} on the concentration of UO_2^{2+} and the pH of the medium. Solid curves are calculated from equation (1) at $k_4/k_6 = 0.84$.

Curve No.	1	2	3	4
$[UO_2^{2+}]$, g-eqv. $\cdot 10^{-3}$	4.26	14.91	20.02	42.60

Curve No.	1	2	3	4
$[Fe^{2+}]$, g-eqv. $\cdot 10^{-3}$	50.05	50.05	26.0	50.05

Curve No.	5	6	7	8
UO_2^{2+}, g-eqv. $\cdot 10^{-3}$	77.63	129.4	258.8	517.5
$[Fe^{2+}]$, g-eqv. $\cdot 10^{-3}$	50.05	50.05	50.05	50.05

The influence of the concentration of UO_2^{2+} on the oxidation of Fe^{2+} was studied at different acidities of the solution. The measurement results, shown in Fig. 1, indicate a considerable decrease in the yield of oxidation of Fe^{2+} with increasing concentration of UO_2^{2+} and decreasing concentration of H^+ ions. Figure 2 presents curves of the dependence of $G_{Fe^{3+}}$ on the concentration of the uranyl ion at various pH values, obtained from the data of Fig. 1.

Discussion. In the literature the following reactions are usually assumed for the radiolytic oxidation of aqueous Fe^{2+} solutions in the absence of O_2 (see, for example, papers ([4–9])):

$$(n+2k)\,H_2O \equiv (m+2l)\,H_2O = nH + mOH + kH_2 + lH_2O_2; \qquad \text{(I)}$$

$$Fe^{2+} + OH \to Fe^{3+} + OH^-; \qquad \text{(II)}$$

$$Fe^{2+} + H_2O_2 \to Fe^{3+} + OH + OH^-; \qquad \text{(III)}$$

$$H + H^+ \to {H_2}^+; \qquad \text{(IV)}$$

$$Fe^{2+} + {H_2}^+ \to Fe^{3+} + H_2. \qquad \text{(V)}$$

The inhibiting action of UO_2^{2+} on the process of oxidation of Fe^{2+} is apparently effected by the reactions:

$$UO_2^{2+} + H \to UO_2^+ + H^+; \qquad \text{(VI)}$$

Fig. 2. Effect of the concentration of UO_2^{2+} on $G_{Fe^{3+}}$ at different pH values

Figure 2: Fig. 2. Effect of the concentration of UO_2^{2+} on $G_{Fe^{3+}}$ at different pH values

Fig. 3. Dependence of $[H^+]/[UO_2^{2+}]$ on $F(G) = \frac{{}^1/_2 G - k}{n + k - {}^1/_2 G}$

Figure 3: Fig. 3. Dependence of $[H^+]/[UO_2^{2+}]$ on $F(G) = \frac{{}^1/_2 G - k}{n + k - {}^1/_2 G}$

$$UO_2^+ + OH \rightarrow UO_2^{2+} + OH^-, \qquad \text{(VII)}$$

which were proposed in work ([1]) for uranyl-ion concentrations above $0.05\,M$. The presence of pentavalent uranium in an irradiated solution of uranyl-ion salts was subsequently shown by N. B. Miller, V. I. Veselovskii, and V. A. Vorotyntsev*.

The assumption of the possibility of competition between UO_2^{2+} and Fe^{2+} for the oxidizing components of radiolysis, similar to that made in work ([1]) for solutions of tetravalent uranium, leads to the conclusion that the yield of oxidation of Fe^{2+} is independent of the acidity of the medium. Since this conclusion contradicts the data of the present work, such an inhibition mechanism was not taken into account here. The inhibiting action of Fe^{3+} is not considered, since only the initial oxidation yields were determined.

Fig. 2. Effect of the concentration of UO_2^{2+} on $G_{Fe^{3+}}$ at different pH values

Fig. 3. Dependence of $[H^+]/[UO_2^{2+}]$ on

$$F(G) = \frac{{}^1/_2 G - k}{n + k - {}^1/_2 G}$$

Using the steady-state method and assuming $G_{H_2^+} = 0$, we find that, when reactions (I)–(VII) are taken into account, G is a function of the concentration of only two components of the solution, namely H^+ and UO_2^{2+}:

$$\frac{k_4}{k_6} \frac{[H^+]}{[UO_2^{2+}]} = \frac{{}^1/_2 G - k}{n + k - {}^1/_2 G} = F(G). \qquad (1)$$

On the basis of equation (1), the curve of the dependence of G on $\lg[H^+]$ or $\lg[UO_2^{2+}]$, at a constant value of the concentration of the other component, can be obtained by the method ([10]) applied in work ([11]), namely, by plotting the curve of the dependence of the quantity G on $\lg F$. Such a curve, for all values, for example, of the concentrations of UO_2^{2+}, will have the form of the experimental curve of the dependence of G on $\lg[H^+]$ and will differ from the latter only in its position along the abscissa axis. By superposing such a theoretical curve on the experimental one, one can calculate the ratio of the constants k_4/k_6. Agreement of the theoretical curve constructed in this way with all the experimental curves measured at different values of the concentration of UO_2^{2+} is indeed observed, as is seen from Fig. 1. The curves of Fig. 1 are calculated from equation (1), with the values used in work ([1]) adopted for n and k. The degree of agreement of equation (1) with experiment is more clearly seen from Fig. 3,

* Presented at the Second All-Union Conference on Radiation Chemistry in 1960.

where the dependence of $F(G)$ on the ratio $[H^+]/[UO_2^{2+}]$ is plotted. The points obtained lie on a straight line passing through the origin, whose slope is $k_4/k_6 = 0.84 \pm 0.04$.

Attention should be paid to the dashed curve in Fig. 1: it also agrees well with the theoretical curve, although it was obtained with a twofold decrease in the concentration of Fe^{2+}. This shows that G does not depend on the concentration of Fe^{2+}, as is also reflected in equation (1). The good quantitative agreement of theory with experiment when the concentrations of UO_2^{2+} and H^+ are varied over a range of more than two orders of magnitude indicates the fruitfulness of the radiolysis model proposed by Allen.

It may be assumed that the adopted mechanism of inhibition of the oxidative process by the uranyl ion will also be valid for other systems. The mechanism adopted for low concentrations of UO_2^{2+} in work (1) is possibly due to the lower rate of the reaction $U^{4+} + OH$ than that of the reaction $Fe^{2+} + OH$.

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Note: Figure translations are in progress. See original paper for figures.