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ON THE SLOW STAGE IN OXIDATION REACTIONS BY HYDROGEN ATOMS ACCORDING TO THE WEISS MECHANISM

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The mechanism proposed by Weiss for the radiolytic oxidation of FeII solutions by hydrogen atoms (^{1}), according to reactions (4) and (5), has recently been quantitatively confirmed by a study of the kinetics of oxidation of FeII and FeII $+UO_2^{2+}$ solutions. It was found that the rate of oxidation of FeII by H atoms is determined by the competition of reaction (4) and the reaction $H + H \rightarrow H_2$ for the H atom (^{2}). In the presence of UO_2^{2+}, the rate of oxidation of FeII is determined by the competition of H^+ and UO_2^{2+} ions for the H atom (^{3}). In both cases reaction (4) proved to be the slow stage of oxidation; this followed from the fact that FeII ions did not participate in the competition for H atoms and that the oxidation yield did not depend on the FeII concentration, but did depend on pH and on the concentration of UO_2^{2+}.

The Weiss mechanism with reaction (4) as the slow stage has a curious feature. Since the oxidation kinetics here is determined only by the competition for the H atom between the H^+ ion and an acceptor of the H atom, it is easy to see (see equation (1)) that, for all H acceptors, the curves of the dependence of the FeII oxidation yield on pH at constant acceptor concentration must, at any FeII concentration, have the same form and differ from one another only in their position along the pH axis, this position being uniquely determined by the concentration of the acceptor. Such a phenomenon was indeed observed in the oxidation of FeII when the H acceptor was the uranyl ion: with increasing concentration of UO_2^{2+}, the curves of the dependence of $G_{-(\mathrm{FeII})}$ on pH, without changing their form, shifted along the pH axis (^{3}). Obviously, under the Weiss mechanism these curves must retain the same form also with an acceptor different from UO_2^{2+}. It was of interest to test this conclusion experimentally. As an H acceptor different from UO_2^{2+}, we chose UIV, which is not oxidized by H atoms, but at high concentrations is reduced by them (^{4}).

Figure 1 gives the oxidation yields of deoxygenated sulfuric-acid solutions of FeII + UIV as a function of pH and of the UIV concentration in a Co^{60} source at an absorbed-radiation intensity of $1.60 \cdot 10^{19}$ eV/l$\cdot$sec. The FeII concentration was varied from 2.0 to 106.6 mN. The value $G_{-(\mathrm{FeII+UIV})}$ (i.e., the sum of the oxidized equivalents of iron and uranium per 100 eV) decreases with pH and with increasing UIV concentration, but does not depend on the FeII concentration, as it should if the slow stage of the Weiss mechanism is reaction (4).

The equation for $G_{-(\mathrm{FeII+UIV})}$ under the Weiss mechanism with slow stage (4) is easily derived by taking into account that radiolysis in a FeII solution without UIV proceeds according to reactions (1)–(5), with $G_{-(\mathrm{FeII})} = m + 2l + n$. Obviously, oxidative reactions of UIV or UIII, similar to reactions (2), (3), and (5), should not have affected G, and, if only reactions of uranium oxidation occurred, then the observed-

would give the equality $G_{-(\mathrm{FeII+UIV})} = G_{-\mathrm{FeII}}$. Since $G_{\mathrm{FeII+UIV}} < G_{\mathrm{FeII}} = m + 2l + n$,

$$(n + 2k)\mathrm{H_2O} \equiv (m + 2l)\mathrm{H_2O} \rightarrow n\mathrm{H} + m\mathrm{OH} + k\mathrm{H_2} + l\mathrm{H_2O_2}, \tag{1}$$

$$\mathrm{FeII} + \mathrm{OH} \rightarrow \mathrm{FeIII} + \mathrm{OH^-}, \tag{2}$$

$$\mathrm{FeII} + \mathrm{H_2O_2} \rightarrow \mathrm{FeIII} + \mathrm{OH} + \mathrm{OH^-}, \tag{3}$$

$$\mathrm{H} + \mathrm{H^+} \rightarrow \mathrm{H_2^+}, \tag{4}$$

$$\mathrm{FeII} + \mathrm{H_2^+} \rightarrow \mathrm{FeIII} + \mathrm{H_2}, \tag{5}$$

$$\mathrm{UIV} + \mathrm{H} \rightarrow \mathrm{UIII} + \mathrm{H^+}, \tag{6}$$

then part of the products of reaction (1) must be consumed in the reduction of uranium, probably by reaction (6) or a similar one. Each act of the latter lowers G by 2 equivalents (in such an act one H atom is consumed in reduction and, in addition, one atom of UIII appears, detected in the analysis of the solution as a loss of one oxidizing equivalent), and, consequently,

$$G_{-(\mathrm{FeII+UIV})} = m + 2l + n - 2n\frac{k_6[\mathrm{UIV}][\mathrm{H}]}{k_4[\mathrm{H}][\mathrm{H^+}] + k_6[\mathrm{UIV}][\mathrm{H}]},$$

where k_4 and k_6 are the rate constants of reactions (4) and (6), and n, m, k, l are the initial yields of H, OH, H_2, H_2O_2 per 100 eV. After transformation we obtain equation (I), showing that for a radiolysis mechanism according to reactions (1) –(6) with slow stage (4),

$$\frac{k_4[\mathrm{H^+}]}{k_6[\mathrm{UIV}]} = \frac{\frac{1}{2}G - k}{n + k - \frac{1}{2}G}. \tag{I}$$

Fig. 1. Dependence of the yield of Fe II oxidation on the concentration of UIV (m N) and on the pH of the medium. The solid curves were calculated from equation (I) at

$$\frac{k_4}{k_6} = 1.25.$$

1—4.87—5.01; 2—9.73; 3—19.73—20.02; 4—50.05; 5—98.9—103.37

G is determined only by the competition of H^+ and UIV for the H atom. This equation is identical with the equation obtained in work (^{3}) for the uranyl ion; the form of the curves of the dependence of G on pH with such an equation does not depend on the value of the constant k_4/k_6. As is seen from Fig. 1, the experimental points over an interval of almost two orders of magnitude of H^+ and UIV concentrations fit well on the theoretical curves constructed from equation (I) with the value

$$\frac{k_4}{k_6} = 1.25 \pm 0.05.$$

Thus, the form of the curves presented in work (^{3}) for the acceptor UO_2^{2+}, and of the curves in Fig. 1 for UIV, is identical, which is in agreement with the theory.

Fig. 2. Total yield of oxidation of UIV and UIII ($[UIV] \sim 100$ m N, $[H^+] = 2.24$ N)

The Weiss oxidation mechanism with slow stage (4) has one more curious feature: it is easy to see that the magnitude of the total oxidation of the solution should not depend on the nature of the acceptors oxidized by the molecular ion H_2^+ or by other products of reaction (1). This magnitude is determined only by the nature of the acceptor competing with the H^+ ion for the H atom. Hence it follows that, for example, for a UIV solution containing

not FeII, but another active acceptor of the ion H_2^+, the same equation (I), with the same value of the constant k_4/k_6 that was found for FeII solutions, will be valid. It seemed interesting to test this consequence experimentally.

As an acceptor of the ion H_2^+, different from FeII, we chose UIII. The values of $G_{UIII+UIV}$ for UIII + UIV solutions under radiolysis are given in Fig. 2, from which it is evident that in a ~ 0.1 N UIV solution (without UIII), at $[H^+] \simeq 2$, the oxidation yield is $G = 4.9$. According to Ref. (1), this indicates that at the given UIV concentration the latter is not reduced and is not oxidized by H atoms. In the presence of $\sim 1\%$ UIII in such a solution, the value of G, as is seen from Fig. 2, reaches 8.0–8.2, i.e., coincides with the oxidation yield of the FeII solution. This value of G does not change with increasing UIII concentration.

The quantitative agreement of the values of G for FeII and UIV + UIII solutions indicates that UIII is a good acceptor of H_2^+ ions. However, G in the UIII + UIV solution decreases with increasing pH and UIV concentration, as should be observed for the Weiss mechanism with the slow step (4).

Table 1

Oxidation yields of the UIII + UIV solution at various pH values and UIV concentrations

[UIV]	$[H^+]$	G	$\frac{k_4}{k_6} = \frac{[UIV]}{[H^+]} \frac{\frac{1}{2}G - k}{n + k - \frac{1}{2}G}$
0.100	2.24	8.00	1.31
0.100	0.45	7.20	1.35
0.400	2.24	7.40	1.38
0.400	0.45	5.30	1.35

Table 1 gives the values of G for UIII + UIV solutions found at various concentrations of H^+ and UIV, and in the last column–the values of the constant k_4/k_6 calculated for these solutions from equation (I) using the data of Table 1. The experimental values of the constant k_4/k_6 obtained for the UIII + UIV solution agree well with the value of the same constant found for the FeII + UIV solution (1.25 and 1.35, respectively).

The quantitative agreement of equation (I) with the experimental data for the FeII + UIV solution over a wide concentration interval, the coincidence of the constant k_4/k_6 found from the oxidation kinetics of such different solutions as FeII + UIV and UIII + UIV, the independence of G from the concentration of FeII and UIII, and the dependence of G on pH and UIV concentration are convincing evidence for the occurrence, in FeII and UIII solutions, of the oxidative reaction of hydrogen atoms by the Weiss mechanism, with reaction (4) as the slow step. In conclusion, we note that in a solution of UIV alone the slow oxidation step according to the Weiss mechanism is apparently the reaction of uranium with the molecular ion H_2^+, as follows from Ref. (5).

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