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PHYSICAL CHEMISTRY

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Abstract

Full Text

PHYSICAL CHEMISTRY

V. N. SHUBIN and P. I. DOLIN

RADIATION TRANSFORMATIONS OF IRON IONS IN $HClO_4$ SOLUTIONS SATURATED WITH HYDROGEN AND OXYGEN UNDER PRESSURE

(Presented by Academician A. N. Frumkin, 18 IV 1961)

In previous works ([1], [2]) it was shown that reliable conclusions about the mechanism of radiolysis of aqueous solutions of iron ions in the absence of oxygen can be drawn from results obtained under conditions in which the products of water radiolysis are completely consumed in competing reactions, the rates of which can be controlled by changing the concentrations of the dissolved substances. The most convenient in this case proved to be a system containing Fe^{2+}, Fe^{3+}, H_2, and H^+, in which the direction of the radiolysis process and its rate are determined by the competition of Fe^{2+} and H_2 for OH radicals and the competition of Fe^{3+} and H^+ for H atoms.

Fig. 1. Dependence of the oxidation yield on the concentration of Fe^{2+}.
$\left[Fe^{3+}\right] \simeq 10^{-3}$ M;
$[HClO_4] \simeq 10^{-2}$ M;
$P_{O_2} = 10.2$ atm.; $\left[Fe^{2+}\right] / [H_2] \simeq$ const.

In the radiolysis of solutions of Fe^{2+} and Fe^{3+} containing oxygen, it may be expected that the process will be determined by the competition of Fe^{3+} and O_2 for H atoms and the competition of Fe^{2+} and Fe^{3+} for HO_2 radicals. The ratio of the rates of the last two competing reactions must be affected by the dissociation reaction of HO_2, which depends on the pH of the solution. In the presence of H_2, competition arises between H_2 and Fe^{2+} for OH radicals.

It is known that for a solution of Fe^{2+} in the presence of O_2 the following mechanism of radiation oxidation was postulated ([3]):

$$H + O_2 \rightarrow HO_2; \tag{1}$$

$$HO_2 + Fe^{2+} \rightarrow Fe^{3+} + HO_2^-; \tag{2}$$

$$HO_2^- + H^+ \rightarrow H_2O_2; \tag{3}$$

$$H_2O_2 + Fe^{2+} \rightarrow +Fe^{3+}OH^- + OH; \tag{4}$$

$$OH + Fe^{2+} \rightarrow Fe^{3+} + OH^-. \tag{5}$$

In the presence of Fe^{3+}, in (4) the following reactions are also assumed:

$$H + Fe^{3+} \rightarrow Fe^{2+} + H^+; \tag{6}$$

$$HO_2 \rightleftarrows H^+ + O_2^-; \tag{7}$$

$$O_2^- + Fe^{3+} \rightarrow Fe^{2+} + O_2. \tag{8}$$

Similar systems were studied by Allen and Rothschild ([5], [6]). It was shown that under these conditions there is competition between Fe^{2+} and O_2 for the H atom (or H_2^+), and that the magnitude of the ratio of the rate constants of these reactions does not depend on pH. Using the mechanism given above, the authors determined from the experimental data the values of the ratios k_6/k_1 and $k_2/k_{Fe^{3+},HO_2}$.

However, in order to confirm the adopted mechanism, a possibly more complete experimental verification is necessary of the dependence, following from this mechanism, of the rate of the overall process on the ratio of the rates of competing reactions.

of competing reactions, which can be specified by varying the concentrations of the reacting substances. Such data are absent from the literature.

On the other hand, suggestions have been made ([7]) that reactions (2) and (3) should be replaced by the reaction:

$$2HO_2 \rightarrow H_2O_2 + O_2. \tag{9}$$

Then, obviously, the dependence of the overall process on the concentrations of the dissolved substances will be different.

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Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

If H_2 is present in the above-mentioned system, the possibility arises for a chain reaction to occur (^{8}). The chain will include reactions (1)–(4) or (1), (9), and (4), as well as:

$$OH + H_2 \rightarrow H_2O + H. \tag{10}$$

Chain termination will take place by reactions (5)–(8).

In the present work we report the results of studies of the action of γ-rays from Co^{60} on solutions of Fe^{2+} and Fe^{3+} ions saturated with H_2 and O_2 under pressure, while varying the concentrations of the indicated substances, as well as of H^+ ions.

Fig. 2. Graphical solution of equation (I) from the data of Table 1. a–$HClO_4$ concentration $\sim 0.12M$; 1–dependence on $[O_2]$; 2–dependence on $[Fe^{3+}]$; b–$HClO_4$ concentration $\sim 5 \cdot 10^{-3}M$; 3–dependence on $[O_2]$; 4–dependence on $[Fe^{3+}]$.

Experimental Part

The cell and apparatus for work under pressure have been described previously (^{8}). A solution saturated with air was placed in a steel bomb, into which H_2 and O_2 were then introduced successively up to the required pressure. Oxygen from the cylinder was purified by passing it through a trap immersed in liquid nitrogen.

The experiments were carried out with solutions of $Fe(ClO_4)_2$ and $Fe(ClO_4)_3$, which were prepared by dissolving spectrally pure iron in twice-distilled $HClO_4$. All working solutions were prepared with twice-distilled water. The dose rate was $\sim 1.75 \cdot 10^{15}$ eV/cm^3 • sec. The concentration of Fe^{2+} was determined with *o*-phenanthroline.

Fig. 3. Graphical solution of equation (I) from the data of Table 3. 1–dependence on $[Fe^{3+}]$; 2–dependence on $[Fe^{2+}]$; 3–dependence on $\frac{[Fe^{3+}]}{[H^+]}$.

Discussion of Results

It is easy to see that if radiolysis includes reaction (9), then the oxidation yield should not depend on $[Fe^{2+}]$, when the concentrations of all the remaining substances and the value $[Fe^{2+}]/[H_2]$ remain constant. As can be seen from Fig. 1, where the results of experiments of this kind are presented, the oxidation yield depends strongly on $[Fe^{2+}]$. This proves that radiolysis proceeds with the participation of reactions (2) and (3), and not reaction (9).

Then, assuming that the radiolysis yield is determined by reactions (1)–(8) and (10), we obtain* the following expression relating the radiation yields to the rates of the competing reactions:

[[unclear: equation continues on next page]]

* In deriving equation (I), the method described in detail previously (8) was used.

$$\left(1+\frac{k_6[\mathrm{Fe}^{3+}]}{k_1[\mathrm{O}_2]}\right)\left(1+\frac{k_8}{k_2}K_{\mathrm{HO}_2}\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}][\mathrm{H}^+]}\right)=$$

$$=\frac{\left[G(\mathrm{Fe}^{3+})-G_{\mathrm{H}}-G_{\mathrm{OH}}-2G_{\mathrm{H_2O_2}}\right]/(1+k_5[\mathrm{Fe}^{2+}]/k_{10}[\mathrm{H}_2])}{G(\mathrm{Fe}^{3+})-G_{\mathrm{H}}-G_{\mathrm{HO}}-2G_{\mathrm{H_2O_2}}+2\left[G_{\mathrm{H}}+(G_{\mathrm{OH}}+G_{\mathrm{H_2O_2}})/(1+k_5[\mathrm{Fe}^{2+}]/k_{10}[\mathrm{H}_2])\right]}$$

$$+\frac{4\left[G_{\mathrm{H}}+(G_{\mathrm{OH}}+G_{\mathrm{H_2O_2}})/(1+k_5[\mathrm{Fe}^{2+}]/k_{10}[\mathrm{H}_2])\right]}{G(\mathrm{Fe}^{3+})-G_{\mathrm{H}}-G_{\mathrm{OH}}-2G_{\mathrm{H_2O_2}}+2\left[G_{\mathrm{H}}+(G_{\mathrm{OH}}+G_{\mathrm{H_2O_2}})/(1+k_5[\mathrm{Fe}^{2+}]/k_{10}[\mathrm{H}_2])\right]}\equiv F(G). \tag{I}$$

Consideration of equation (I) shows that if in one of the parentheses on the left-hand side the concentration ratio remains constant, while in the other it changes, then the expression on the right-hand side must be a linear function of the latter quantity.

Table 1

Dependence of $G(Fe^{3+})$ on the concentrations of O_2 and Fe^{3+}.
$P_{H2} = 50$ atm; $[Fe^{3+}]/[Fe^{2+}] \simeq 13$

Acceptor:	O_2	O_2	O_2	O_2	O_2	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}
Concentration, mM	0.28	0.98	1.68	4.48	14.3	190	100	39	20	11	9.2

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Acceptor:	O_2	O_2	O_2	O_2	O_2	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{3+}
$G(Fe^{3+})$, mol/100 eV, $[H^+] \sim 0.12\,M$	3.4	11.9	13.5	18.5	21.5	5	6.7	12.2	–	18.5	–
$G(Fe^{3+})$, mol/100 eV, $[H^+] \sim 5 \cdot 10^{-3}\,M$	–	–	–	6.6	7	–	–	–	6.7	–	6.6

The dependence of the yield on the concentration of O_2 is given in Table 1. The graphical solution of equation (I) using the data of Table 1 is presented in Fig. 2. From the slope of the straight line we calculate the value $k_6/k_1 = 2.45 \cdot 10^{-2}$. The intercept cut off by the straight line on the ordinate axis is equal to

$$1 + \frac{k_8}{k_2} K_{HO_2} \frac{[Fe^{3+}]}{[Fe^{2+}][H^+]},$$

whence we find

$$\frac{k_8}{k_2} K_{H_2O} \simeq 3.1 \cdot 10^{-3} \text{ M/l}.$$

It is evident that if the Fe^{2+} ion can compete with O_2 for H atoms in the reaction:

$$Fe^{2+} + H \rightleftarrows FeH^{2+} \xrightarrow{+H^+} Fe^{3+} + H_2, \qquad (11)$$

then the first parenthesis in equation (I) will have the following form:

$$1 + (k_6[Fe^{3+}] + k_{11}[Fe^{2+}])/k_1[O_2].$$

In this case the yield should depend on $[Fe^{2+}]$ provided $[Fe^{3+}]/[O_2]$, $[Fe^{2+}]/[H_2]$, and $[Fe^{3+}]/[Fe^{2+}] \times [H^+]$ are kept constant. Table 2 presents the results of experiments in which the ratio $[Fe^{2+}]/[O_2]$ was varied while the indicated conditions were observed. As is seen, the oxidation yield practically does not change when the value of $[Fe^{2+}]/[O_2]$ is varied by two orders of magnitude. This convincingly confirms that a reaction of type (11) under the given conditions may be neglected.*

Fig. 4. Dependence of the oxidation yield on the pressure of O_2 above the solution. $[HClO_4] \simeq 0.1\,M$, $[Fe^{3+}] \simeq 8\cdot10^{-3}\,M$; $[Fe^{2+}] \simeq 1.2\cdot10^{-3}\,M$; $P_{H2} = 50$ atm.

From equation (I) it is seen that its graphical solution using the data for the dependence of the yield on $[O_2]$ and on $[Fe^{3+}]$ must be represented by a single straight line. Table 1 gives the dependence of the yield on the concentration of Fe^{3+}. The graphical solution of equation (I) using these data is presented in Fig. 2. The results obtained are in good agreement with the data on the dependence of $G(Fe^{3+})$ on $[O_2]$.

For the value k_6/k_1 in $0.8\,N$ H_2SO_4 solutions, Allen and Rothschild obtained $0.007\pm50\%$. If one takes into account (2) that in sulfuric acid, owing to complex formation, $[Fe^{3+}]_{\text{eff}} \simeq 0.27[Fe^{3+}]_{\text{total}}$, then k_6/k_1 will be equal to $2.6\cdot10^{-2}\pm50\%$, which agrees well with the value obtained by us.

* It follows from this that the competition between Fe^{2+} and O_2 for the radical particle observed in the work of Allen and Rothschild occurs via the ion-radical H_2^+.

To show that the radiolysis mechanism includes reactions (2), (7), and (8), the dependences of the yield of Fe^{3+} on the concentrations of H^+, Fe^{2+}, and Fe^{3+} were studied at

$$[Fe^{3+}]/[O_2] = \text{const.}$$

Table 2

Effect of the concentration of Fe^{2+} on $G(Fe^{3+})$

$[Fe^{3+}] \sim 9\cdot10^{-3}\,M$; $P_{O2} = 3.2$ atm; $[Fe^{2+}]/[H_2] \sim 0.8$; $[Fe^{2+}]\times[H^+] \sim 4.5\cdot10^{-4}$

Concentr. Fe^{2+}, mol/l	$9\cdot10^{-4}$	$9.7\cdot10^{-3}$	$9.2\cdot10^{-2}$
$G(Fe^{3+})$, mol/100 eV	14.2*	15.5	14.5

* With a correction introduced for the effect of the direct action of radiation on $HClO_4$.

Table 3

Dependence of the yield on the concentrations of Fe^{3+}, Fe^{2+}, and H^+.

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$$[\mathrm{Fe}^{3+}]/[\mathrm{O}_2] \simeq \text{const.}$$

Acceptor	Fe^{3+}	Fe^{3+}	Fe^{3+}	Fe^{2+}	Fe^{2+}	Fe^{2+}	H^+	H^+	H^+
Concentration, mM	63	8.4	0.15	0.14	0.81	8.3	5.1	45	450
$G(\mathrm{Fe}^{3+})$, mol/100 eV	3.7	25	43.5	−1	17.5	19.5	7.5	17	22

The results of these experiments are given in Table 3. A graphical solution of equation (I) from these results is presented in Fig. 3. From the slope of the straight line we calculate

$$k_8 K_{\mathrm{HO2}}/k_2 = 3.6 \cdot 10^{-3}\ \mathrm{M/l}.$$

For the value $k_{\mathrm{Fe}^{3+},\mathrm{HO}_2}/k_2$, Allen and Rothschild obtained the following values: $0.11 \pm 15\%$ and $0.3 \pm 50\%$ at pH 2.1 and 2.7, respectively. If it is taken into account that the reduction of Fe^{3+} by HO_2 radicals proceeds according to reactions (7) and (8), and that $[\mathrm{Fe}^{3+}]_{\mathrm{eff}} \simeq 0.27[\mathrm{Fe}^{3+}]_{\mathrm{total}}$, then for $k_8 K_{\mathrm{HO2}}/k_2$ we obtain, respectively: $3.75 \cdot 10^{-3}\ \mathrm{M/l} \pm 15\%$ and $2.4 \cdot 10^{-3}\ \mathrm{M/l} \pm 50\%$, which is in good agreement with the value obtained in our experiments.

These results show that oxygen is a very active acceptor of H atoms. It therefore seemed promising to use it to elucidate the role of excited water molecules in the radiolysis of Fe^{2+} and Fe^{3+} solutions by the coupled-acceptor method ([7]). It is easy to see that if, under these conditions, excited water molecules can take part in the reaction, then expression (I) will turn into the inequality:

$$\left(1 + \frac{k_6[\mathrm{Fe}^{3+}]}{k_1[\mathrm{O}_2]}\right)\left(1 + \frac{k_8}{k_2} K_{\mathrm{H2O}} \frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{3+}][\mathrm{H}^+]}\right) > F(G). \tag{II}$$

To verify this, yields were determined as a function of the oxygen pressure above the solution. The results obtained are presented in Fig. 4. In the region of low concentrations the yield increases with increasing O_2 pressure owing to suppression of reaction (6) by reaction (1). With a further increase in pressure the yield reaches a constant value, which remains unchanged up to O_2 concentrations of $\sim 0.1\ M$ (150 atm). Calculation from the data of Fig. 4 shows that, for the horizontal portion of the curve, condition (I), and not (II), is fulfilled. Thus, at $[\mathrm{O}_2] \ll 0.1M$, excited water molecules are not involved in the oxidation reaction of Fe^{2+}.

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The totality of the results obtained in this work shows that the mechanism of the radiolysis of Fe^{2+}, Fe^{3+} solutions in the presence of O_2 and H_2, including reactions (1)–(8) and (10), quantitatively describes the experimentally observed dependences of the overall process on the concentrations of the substances participating in the competing reactions.

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