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# Physical Chemistry

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**Abstract**

**Full Text**

## **Physical Chemistry**

**A. K. Pikaev, P. Ya. Glazunov, Academician Vikt. I. Spitsyn**

### **Mechanism of the Radiolytic Oxidation of Divalent Iron in Aqueous Sulfuric-Acid Solutions Containing Oxygen at High Absorbed-Dose Rates**

Earlier (<sup>1-3</sup>) we found a decrease in the value of  $G(\text{Fe}^{3+})$  for a Mohr' s-salt solution in 0.4 M  $\text{H}_2\text{SO}_4$ , saturated with air, at absorbed-dose rates exceeding  $10^{22}$  eV/ml·sec. A similar phenomenon was also observed by other authors (<sup>4-8</sup>). The decrease in  $G(\text{Fe}^{3+})$  is explained by the increased role, under these conditions, of competition between radical-radical reactions and radical-dissolved-substance reactions (<sup>2,6</sup>). Therefore it seemed possible, by varying the concentrations of  $\text{Fe}^{2+}$  ions and oxygen, to consider in greater detail the mechanism of the radiolytic oxidation of divalent iron, and also to investigate the reactivity of  $\text{Fe}^{2+}$  and  $\text{O}_2$  toward the products of water radiolysis.

The source of ionizing radiation was a direct-acceleration electron tube (<sup>9</sup>). High dose rates were produced by means of single electron pulses. Their duration was  $5 \cdot 10^{-6}$  sec. The electron energy was 0.8–1.0 MeV. The procedure for generating and measuring the pulses, as well as the experimental procedure, were described in our previous communication (<sup>2</sup>). The solutions were irradiated in glass cells with a glass membrane (50–70  $\mu$  thick) and a sealed-in platinum probe. The volume of the cells was 7–9 ml, and the thickness of the liquid layer in the cell was 4.0–4.5 mm. The solutions were prepared with twice-distilled water. The following reagents were used: Mohr' s salt ( "chemically pure" grade), sulfuric acid ( "special purity for semiconductor purposes" grade), and sodium chloride ( "chemically pure" grade). Oxygen-saturated solutions were prepared by bubbling purified oxygen through them for 25–40 min. Trivalent iron was determined spectrophotometrically at a wavelength of 340 m $\mu$ . The value of the molar extinction coefficient of  $\text{Fe}^{3+}$  in 0.4 M sulfuric acid at 24°C was taken as 2170 (<sup>10</sup>). In the calculations, the change in the extinction coefficient with temperature was taken into account (0.7% per degree).

Special attention was paid to adjustment of the beam. Before each series of experiments, the position of the beam was regulated by the luminescence of a quartz disk mounted in a special device. A defocusing device was used in the work, thanks to which the most favorable distribution of radiation intensity over the irradiated surface was achieved. The outlines of the beam were found from the coloration that arises upon irradiation in a block of polymethyl methacrylate

Figure 1

Figure 1: Figure 1

having the same shape as the cell. The average dose rate in the irradiated volume was estimated taking into account the range of electrons with energies of 0.8–1.0 MeV in water. The dose rate estimated in this way proved to be 1.5–1.8 times greater than the dose rate averaged over the entire volume of the solution. The dose per pulse, averaged over the entire volume of the cell, did not exceed  $5.5 \cdot 10^{17}$  eV/ml. The maximum dose referred to the irradiated volume was approximately  $9.5 \cdot 10^{17}$  eV/ml. This dose is substantially lower than the dose corresponding to complete consumption of oxygen even in a solution saturated with air. Depending on the dose rate, the solutions were irradiated with 1–10 pulses. Each value of  $G(\text{Fe}^{3+})$  is the average of 5–10 measurements.

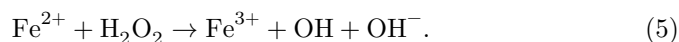
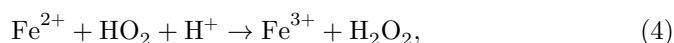
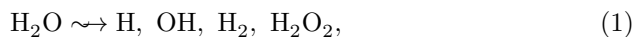
The absolute accuracy of the measurements of  $G(\text{Fe}^{3+})$  was  $\pm 10\%$ . The main source of error was connected with the difficulties of adjusting the geometry of the electron beam in different series of experiments. Within a single series of experiments, i.e., for a given beam geometry, the accuracy of the measurements was  $\pm 3\%$ .

Figure 1 gives the values of  $G(\text{Fe}^{3+})$  obtained by us for  $3 \cdot 10^{-3}$  and  $10^{-2}$  *M* solutions of Mohr's salt in 0.4 and 0.07 *M*  $\text{H}_2\text{SO}_4$ , saturated with air or oxygen and containing no sodium chloride, at different dose rates. In this figure, along with the new data, there are also shown results obtained by us earlier <sup>(2)</sup> using solutions containing  $10^{-3}$  *M* NaCl, recalculated using the values of the mean dose rate in the irradiated volume. As is seen from this figure,  $G(\text{Fe}^{3+})$  for solutions saturated with oxygen is higher than for solutions saturated with air.\* At the same time, the yield of  $\text{Fe}^{3+}$  in the case of a  $10^{-2}$  *M* ferrous sulfate solution in 0.4 *M*  $\text{H}_2\text{SO}_4$ , saturated with oxygen, is close to the standard value 15.5–15.6 ions/100 eV.

Fig. 1. Dependence of  $G(\text{Fe}^{3+})$  on dose rate for sulfuric-acid solutions of Mohr's salt containing oxygen: 1 – data of work <sup>(2)</sup>, recalculated using the values of the mean dose rate in the irradiated solution; 2 –  $3 \cdot 10^{-3}$  *M* solution of Mohr's salt in 0.4 *M*  $\text{H}_2\text{SO}_4$ , saturated with air; 3 – the same in 0.07 *M*  $\text{H}_2\text{SO}_4$ ; 4 –  $10^{-2}$  *M* solution of Mohr's salt in 0.4 *M*  $\text{H}_2\text{SO}_4$ , saturated with air; 5 –  $3 \cdot 10^{-3}$  *M* solution of Mohr's salt in 0.4 *M*  $\text{H}_2\text{SO}_4$ , saturated with oxygen; 6 –  $10^{-2}$  *M* solution of Mohr's salt in 0.4 *M*  $\text{H}_2\text{SO}_4$ , saturated with oxygen.

The literature data on the magnitude of  $G(\text{Fe}^{3+})$  at high dose rates are contradictory. According to <sup>(8)</sup>,  $G(\text{Fe}^{3+})$  under pulsed-irradiation conditions decreases when NaCl is added to the ferrous sulfate solution. The results of the present communication confirm the conclusion of that work. Thus, according to our data, addition of  $10^{-3}$  *M* NaCl to a  $3 \cdot 10^{-3}$  *M* solution of Mohr's salt leads to a decrease in  $G(\text{Fe}^{3+})$  by approximately 15% at a dose rate of  $10^{23}$  eV/ml · sec.

As is known (<sup>11</sup>), at low dose rates the radiolytic oxidation of  $\text{Fe}^{2+}$  ions in sulfuric-acid solutions saturated with air is determined by the occurrence of the following reactions\*\*:



OH radicals can interact with sulfuric acid:



However,  $\text{HSO}_4$  radicals, like OH radicals, oxidize  $\text{Fe}^{2+}$ :



\* An increase in  $G(\text{Fe}^{3+})$  for solutions saturated with oxygen was also observed in works (<sup>6, 8</sup>).

\*\* Under the action of radiation on water, a hydrated electron  $e_{\text{aq}}^-$  is also formed. However, in strongly acidic solutions it evidently interacts with  $\text{H}^+$  ions, being converted into H atoms.

Thus,

$$G(\text{Fe}^{3+}) = 3G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2}. \quad (8)$$

At high absorbed-dose rates, alongside reactions (2)–(7), reactions (9)–(11) may also occur:





Obviously, this will lead to a decrease in  $G(\text{Fe}^{3+})^*$ .

As can be seen from the data presented in Fig. 1, under conditions of pulsed irradiation  $G(\text{Fe}^{3+})$  depends substantially both on the concentration of  $\text{Fe}^{2+}$  ions and on the oxygen concentration. This indicates that at high absorbed-dose rates reaction (10) must be taken into account. The yield of  $\text{Fe}^{3+}$  does not depend on the concentration of sulfuric acid when the latter is decreased by almost an order of magnitude (see Fig. 1). Hence it may be concluded that reactions of type (6) play a small role in the radiolysis of the ferrosulfate system, if the concentration of  $\text{Fe}^{2+}$  ions is sufficiently high. Reactions (9) and (11) also need not be taken into account, since, according to the data of Ref. (6), the yields of hydrogen and hydrogen peroxide formed by reactions (1) and (4) practically do not change at high dose rates\*\*.

If, in accordance with the calculations carried out in Refs. (13, 14), one assumes that the initial yields of the products of water radiolysis do not depend on dose rate in the range we have studied, and that the radiolytic oxidation of  $\text{Fe}^{2+}$  ions is determined by a mechanism including reactions (1)–(5) and (10), then, using the steady-state concentration method and the material-balance equation for water radiolysis, the following equation can be obtained:

$$\frac{[1/2G(\text{Fe}^{3+}) + G_{\text{H}_2} - G_{\text{H}_2\text{O}_2}][G(\text{Fe}^{3+}) - 2G_{\text{H}_2}]}{3G_{\text{H}} + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} - G(\text{Fe}^{3+})} = \frac{K_2K_3}{K_{10}}(\text{Fe}^{2+})(\text{O}_2) \left( \frac{100N}{I} \right), \quad (12)$$

where  $G_{\text{H}}$ ,  $G_{\text{OH}}$ ,  $G_{\text{H}_2}$ , and  $G_{\text{H}_2\text{O}_2}$  are the initial yields of the corresponding products of water radiolysis;  $K_2$ ,  $K_3$ , and  $K_{10}$  are the rate constants of reactions (2), (3), and (10);  $(\text{Fe}^{2+})$  and  $(\text{O}_2)$  are the molar concentrations of  $\text{Fe}^{2+}$  and  $\text{O}_2$ ;  $N$  is Avogadro's number; and  $I$  is the dose rate in  $\text{eV/l} \cdot \text{sec}$ . The value calculated on the basis of our experimental data,

$$\frac{K_2K_3}{K_{10}},$$

is equal to  $(3.2 \pm 1.2) \cdot 10^7 \text{ l/mol} \cdot \text{sec}^{***}$ . In the calculations, values of  $G(\text{Fe}^{3+})$  were used for solutions not containing NaCl.

In Ref. (6) a method of treatment was described by means of which it is possible to determine the relative constants  $K_2/K_{10}$  and  $K_3/K_{10}$ . In this method it is assumed that the radicals H and OH are distributed uniformly in the volume of the solution, and their concentrations are exponential functions of time. The corresponding equation has the following form:

$$C_{\text{H}_2\text{O}} = \frac{(\text{H})_0(\text{OH})_0}{\frac{K_2}{K_{10}}(\text{Fe}^{2+}) + \frac{K_3}{K_{10}}(\text{O}_2) + (\text{H})_0 + (\text{OH})_0}, \quad (13)$$

where  $C_{\text{H}_2\text{O}}$  is the molar concentration of water formed by reaction (7), and  $(\text{H})_0$  and  $(\text{OH})_0$  are the average molar concentrations of the radicals H and OH existing—

\* The decrease in  $G(\text{Fe}^{3+})$  in the presence of  $\text{Cl}^-$  ions is apparently explained by competition between reaction (3) and the reaction involving chlorine atoms:  $\text{Cl} + \text{H} \rightarrow \text{H}^+ + \text{Cl}^-$ , which arise as a result of the interaction of OH radicals with  $\text{Cl}^-$  ions.

\*\* In Ref. (12) it was suggested that the decrease in  $G(\text{Fe}^{3+})$  observed by us (2) is due mainly to competition between reactions (3) and (9). However, the dependence of  $G(\text{Fe}^{3+})$  on the concentration of  $\text{Fe}^{2+}$  and oxygen, as well as the constancy of  $G_{\text{H}_2}$ , argue in favor of competition between reactions (2), (3), and (10).

\*\*\* The following values of the initial yields of the products of water radiolysis were used:  $G_{\text{H}} = 3.65$ ,  $G_{\text{OH}} = 2.95$ ,  $G_{\text{H}_2} = 0.45$ , and  $G_{\text{H}_2\text{O}_2} = 0.8$  (15).

present at the end of the pulse,  $(\text{Fe}^{2+})$  and  $(\text{O}_2)$  are the molar concentrations of  $\text{Fe}^{2+}$  and  $\text{O}_2$ , and  $K_2$ ,  $K_3$ , and  $K_{10}$  are the rate constants of the corresponding reactions.

In this case  $C_{\text{H}_2\text{O}} = 0.25\Delta G(\text{Fe}^{3+}) \cdot \frac{\bar{D}}{6.02 \cdot 10^{22}}$ , where  $\Delta G(\text{Fe}^{3+})$  is the difference between the standard value  $G(\text{Fe}^{3+}) = 15.6$  ions/100 eV and  $G(\text{Fe}^{3+})$  at the given dose rate,  $\bar{D}$  is the average dose in the irradiated volume per pulse in eV/ml;  $(\text{H})_0 = G_{\text{H}} \cdot \frac{\bar{D}}{6.02 \cdot 10^{22}}$  and  $(\text{OH})_0 = G_{\text{OH}} \cdot \frac{\bar{D}}{6.02 \cdot 10^{22}}$ .

**Table 1**

Calculation of the values of  $C_{\text{H}_2\text{O}}$ \*

Average dose rate, eV/ml · s	$\bar{D}$ , eV/ml	$(\text{Fe}^{2+})$ , $M \cdot 10^3$	$(\text{O}_2)$ , $M \cdot 10^4$	$(\text{H})_0$ , $M \cdot 10^5$	$(\text{OH})_0$ , $M \cdot 10^5$	Experimental	Calculated
						value of $C_{\text{H}_2\text{O}}$ , $M \cdot 10^5$	value of $C_{\text{H}_2\text{O}}$ , $M \cdot 10^5$
$1.1 \cdot 10^{23}$	$5.5 \cdot 10^{17}$	3.0	2.7	3.35	2.71	$0.83 \pm 0.07$	0.82
$1.0 \cdot 10^{23}$	$5 \cdot 10^{17}$	3.0	2.7	3.03	2.45	$0.83 \pm 0.12$	0.71

Average dose rate, eV/ml · s	$\bar{D}$ , eV/ml	(Fe <sup>2+</sup> ), M · 10 <sup>3</sup>	(O <sub>2</sub> ), M · 10 <sup>4</sup>	(H) <sub>0</sub> , M · 10 <sup>5</sup>	(OH) <sub>0</sub> , M · 10 <sup>5</sup>	Experimental value of C <sub>H<sub>2</sub>O</sub> , M · 10 <sup>5</sup>	Calculated value of C <sub>H<sub>2</sub>O</sub> , M · 10 <sup>5</sup>
1.0 · 10 <sup>23</sup>	5 · 10 <sup>17</sup>	3.0	2.7	3.03	2.45	0.73 ± 0.06	0.71
1.1 · 10 <sup>23</sup>	5.5 · 10 <sup>17</sup>	10.0	2.7	3.35	2.71	0.60 ± 0.10	0.59
1.5 · 10 <sup>23</sup>	7.5 · 10 <sup>17</sup>	3.0	12.0	4.56	3.69	0.72 ± 0.14	0.68
1.5 · 10 <sup>23</sup>	7.5 · 10 <sup>17</sup>	10.0	12.0	4.56	3.69	0.31 ± 0.20	0.59
5.0 · 10 <sup>22</sup>	2.5 · 10 <sup>17</sup>	3.0	2.7	1.52	1.23	0.22 ± 0.05	0.24
1.5 · 10 <sup>22</sup>	7.5 · 10 <sup>16</sup>	3.0	2.7	0.456	0.369	0.022 ± 0.015	0.029
3.0 · 10 <sup>21</sup>	1.5 · 10 <sup>16</sup>	3.0	2.7	0.091	0.074	0.0019 ± 0.0015	0.0013

\* In the calculations, the average value of  $G(\text{Fe}^{3+})$  in each series of experiments was used.

The best agreement of our experimental data with those calculated from equation (13) was obtained with the following values of the relative constants:

$$K_2/K_{10} = 6 \cdot 10^{-3} \quad \text{and} \quad K_3/K_{10} = 1.2 \cdot 10^{-1}$$

(see Table 1)\*.

Thus, the method described in <sup>(6)</sup> makes it possible to estimate the ratios of two constants. On the other hand, from an equation of type (12) it is possible to calculate the ratio of three constants. Obviously, this thereby opens up the possibility of estimating the absolute magnitudes of the rate constants of radiation reactions. By comparing these ratios, the following values of the constants were obtained:  $K_2 = 2.7 \cdot 10^8$ ,  $K_3 = 5.3 \cdot 10^9$ , and  $K_{10} = 4.5 \cdot 10^{10}$  l/mol · s. According to <sup>(17)</sup>,  $K_2 = 2.6 \cdot 10^8$  l/mol · s. According to <sup>(17)</sup>,  $K_3 \sim 10^9$  l/mol · s. An estimate of the constant  $K_{10}$  was made in <sup>(18)</sup>:  $K_{10} \approx 10^{10}$  l/mol · s.

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\* According to the data of <sup>(6)</sup>,  $K_2/K_{10} = 6.2 \cdot 10^{-3}$  and  $K_3/K_{10} = 2.2 \cdot 10^{-1}$ .

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

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