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Figure 1

Figure 1: Figure 1

## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# POST-EFFECTS IN SULFURIC-ACID SOLUTIONS OF FERROUS SULFATE SATURATED WITH AIR AND CONTAINING ETHYL ALCOHOL, UNDER THE ACTION OF PULSED ELECTRON RADIATION

*(Presented by Academician V. I. Spitsyn, July 17, 1961)*

It is known (1–8) that organic impurities increase $G(\mathrm{Fe}^{3+})$ in a ferrous-sulfate dosimetric solution. Duchek (2,3) showed that the addition of sodium chloride suppresses the influence of organic substances on the value of the final yield $G(\mathrm{Fe}^{3+})$, and also advanced certain suggestions concerning the causes of the increase in the yield of $\mathrm{Fe}^{3+}$ in the presence of alcohols. Until now, the time course of the process of radiolytic oxidation of $\mathrm{Fe}^{2+}$ in the presence of organic compounds in the solution has not been investigated in detail. Only Vermel (5) observed insignificant post-radiation oxidation of $\mathrm{Fe}^{2+}$ in an air-saturated solution containing hydrocarbons, as a result of the action of x-rays. Evidently, the kinetics of such a post-radiation process can be investigated most accurately only when pulsed electron radiation is used. In this case it becomes possible to deliver relatively high doses to the system in a very short interval of time.

**Fig. 1.** Dependence of $G(\mathrm{Fe}^{3+})$ on time after delivery of a pulse to a $0.4\,M$ sulfuric-acid solution saturated with air:
1—$2.5 \cdot 10^{-4}\,M$ $\mathrm{Fe}^{2+}$;
2—$2.5 \cdot 10^{-4}\,M$ $\mathrm{Fe}^{2+}$, $10^{-4}\,M$ $C_2H_5OH$;
3—$2.5 \cdot 10^{-4}\,M$ $\mathrm{Fe}^{2+}$, $4 \cdot 10^{-4}\,M$ $C_2H_5OH$;
4—$2.5 \cdot 10^{-4}\,M$ $\mathrm{Fe}^{2+}$, $10^{-3}\,M$ $C_2H_5OH$;
5—$2.5 \cdot 10^{-4}\,M$ $\mathrm{Fe}^{2+}$, $10^{-2}\,M$ $C_2H_5OH$;
6—$2.5 \cdot 10^{-4}\,M$ $\mathrm{Fe}^{2+}$, $10^{-1}\,M$ $C_2H_5OH$.

For the purpose of investigating post-effects in irradiated $0.4\,M$ sulfuric-acid solutions of ferrous sulfate saturated with air and containing ethyl alcohol, in the present work an electron tube of direct acceleration was used as the source of ionizing radiation, with a special device permitting the generation of powerful single electron pulses of duration $5 \cdot 10^{-6}$ sec. The method of obtaining and measuring these pulses was described in a previous communication by one of the authors of the present article (9). The electron energy was 0.8 MeV; the dose absorbed in one pulse was $1—2 \cdot 10^{18}$ eV (in the entire volume of the solution), which corresponded to a dose rate of approximately $2.5—5 \cdot 10^{22}$ eV/ml • sec.

The solutions were prepared with twice-distilled water; all reagents used were of sufficient purity. Irradiation of solutions containing $Fe^{2+}$ ions was carried out in a cell (volume 8 ml) with a glass membrane. This cell, by means of a special adapter, was connected to a spectrophotometric cuvette, which made it possible to carry out the measurements more rapidly and accurately. The concentration of $Fe^{3+}$ was determined by the usual spectrophotometric method.

The results obtained are presented in Figs. 1-4. Figure 1 shows the dependence of $G(Fe^{3+})$ on time after a single electron pulse was delivered to the solution, at a constant concentration of $Fe^{2+}$ ($2.5 \cdot 10^{-4}$ $M$) and at various concentrations of ethyl alcohol. Figure 2 illustrates the analogous dependence at various concentrations of $Fe^{2+}$ and a constant concentration of ethyl alcohol ($10^{-2}$ $M$). The curve in Fig. 3 represents the dependence of the final yield of $Fe^{3+}$ on the initial concentration of $Fe^{2+}$ in the solution; Fig. 4, the final yield of $Fe^{3+}$ on the initial concentration of ethyl alcohol in the solution.

**Table 1**

Dependence of $G(Fe^{3+})$ on time for solutions obtained by mixing an irradiated solution containing no $Fe^{2+}$ with a solution of ferrous sulfate

| Time, min | a | b | c | d | e | Time, min | a | b | c | d | e |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.0 | 2.4 | – | 5.6 | 5.1 | 4.9 | 10.0 | – | 12.9 | – | – | 14.6 |
| 1.5 | 2.7 | 5.2 | 7.1 | 6.3 | 6.8 | 11.0 | – | 13.3 | – | – | – |
| 2.0 | 2.9 | 6.4 | 8.2 | 7.2 | 8.1 | 12.0 | – | 13.6 | – | – | – |
| 2.5 | 3.0 | 7.1 | 9.3 | 8.0 | 8.9 | 13.0 | – | 13.9 | 16.9 | – | – |
| 3 | 3.0 | 7.7 | 10.3 | 8.9 | 9.7 | 14.0 | – | – | – | 14.0 | – |
| 3.5 | 3.1 | 8.4 | 11.0 | 9.8 | 10.5 | 15.0 | – | – | – | – | 15.6 |
| 4.0 | – | 9.0 | 11.6 | 10.5 | 11.3 | 18.0 | – | 14.8 | 17.1 | – | – |
| 4.5 | 3.1 | 9.6 | – | – | 12.0 | 19.0 | – | – | – | 14.5 | – |
| 5.0 | – | 10.0 | 12.8 | 11.4 | 12.4 | 20.0 | – | – | – | – | 15.9 |
| 5.5 | 3.1 | 10.5 | – | – | – | 23.0 | – | 15.3 | – | – | – |
| 6.0 | – | 10.9 | 13.8 | 11.9 | 13.2 | 28.0 | – | – | 17.1 | – | – |
| 7.0 | – | 11.5 | 14.8 | 12.4 | 13.7 | 30.0 | – | 15.7 | – | 14.7 | 16.1 |
| 8.0 | – | 12.1 | 15.5 | 13.0 | 14.0 | 40.0 | – | 15.8 | – | 14.9 | 16.3 |
| 9.0 | – | 12.6 | – | 13.3 | 14.3 | $\infty$ | 3.1 | 15.9 | 17.1 | 15.1 | 16.4 |

**Note.**

Fig. 2

Figure 2: Fig. 2

| | a | b | c | d | e |
|---|---|---|---|---|---|
| Composition of the irradiated solution | $H_2O$ | $H_2O$ | $0.4M\ H_2SO_4$ | $0.4M\ H_2SO_4 + +0.15M\ C_2H_5OH$ | |
| Composition of the solution after mixing | $2.5 \cdot 10^{-4}M\ Fe^{2+} + +0.1M\ C_2H_5OH$ $0.4M\ H_2SO_4$ | the same | the same as b | the same as b | the same as b |
| Time from delivery of the pulse to mixing of the solutions, min | 2 | 2 | 2 | 1 | 20 |

**Fig. 2.** Dependence of $G(Fe^{3+})$ on time after pulse delivery for 0.4 $M$ sulfuric-acid solutions saturated with air:
1—$2.5 \cdot 10^{-4}$ $M$ $Fe^{2+}$, $10^{-2}$ $M$ $C_2H_5OH$;
2—$5 \cdot 10^{-4}$ $M$ $Fe^{2+}$, $10^{-2}$ $M$ $C_2H_5OH$;
3—$10^{-3}$ $M$ $Fe^{2+}$, $10^{-2}$ $M$ $C_2H_5OH$;
4—$2.5 \cdot 10^{-3}$ $M$ $Fe^{2+}$, $10^{-2}$ $M$ $C_2H_5OH$.

Table 1 summarizes the results obtained in the study of solutions that did not contain $Fe^{2+}$ ions during irradiation. In this case the solutions were irradiated in a cell (volume 6.5 ml) with a glass membrane. Then 3.5 ml of a solution containing $Fe^{2+}$ and the other substances in the amount necessary for comparison was added to the irradiated solution. After mixing, a sample of the resulting solution was transferred to a spectrophotometric cuvette. The composition of the final solution is given without taking into account concentration changes caused by irradiation. The measurement error was determined by the accuracy of determination of the absorbed dose ($\pm10\%$). The relative error for different points on a single curve is associated with the accuracy of rapid measurements on the spectrophotometer. During the first 5 min it does not exceed $\pm2\%$, and subsequently $\pm1\%$.

From Figs. 1 and 2 it is evident that, in irradiated sulfuric-acid solutions of ferrous iron containing ethyl alcohol and saturated with air, considerable post-radiation oxidation of $Fe^{2+}$ is observed. Oxygen plays an essential role in this

Fig. 3. Dependence of the final yield of Fe3+ (for t = infinity) on the initial concentration of Fe2+ in 0.4 M sulfuric acid solutions containing 10^-2 M C2H5OH and saturated with air.

Figure 3: Fig. 3. Dependence of the final yield of Fe3+ (for t = infinity) on the initial concentration of Fe2+ in 0.4 M sulfuric acid solutions containing 10^-2 M C2H5OH and saturated with air.

Fig. 4. Dependence of the final yield of Fe3+ (for t = infinity) on the initial concentration of ethyl alcohol in 0.4 M sulfuric acid solutions containing 2.5 • 10^-4 M Fe2+ and saturated with air. 1—initial concentration of C2H5OH in M • 10^3; 2—initial concentration of C2H5OH in M • 10^1.

Figure 4: Fig. 4. Dependence of the final yield of Fe3+ (for t = infinity) on the initial concentration of ethyl alcohol in 0.4 M sulfuric acid solutions containing 2.5 • 10^-4 M Fe2+ and saturated with air. 1—initial concentration of C2H5OH in M • 10^3; 2—initial concentration of C2H5OH in M • 10^1.

process. When a solution of the following composition was irradiated: $2.5 \cdot 10^{-4}$ $M$ $Fe^{2+}$, 0.4 $M$ $H_2SO_4$, and $10^{-1}$ $M$ $C_2H_5OH$, from which the air was⋯

was removed by passing argon*, a value of $G(Fe^{3+})$ equal to approximately 5 ions/100 eV was obtained. No post-effect was detected.

The study established that the process of post-radiation oxidation of ferrous iron, depending on the concentration of $Fe^{2+}$ and $C_2H_5OH$, lasts from several minutes to 1 hour. The increase in $G(Fe^{3+})$ due to the post-effect is the greater, the lower the concentration of $Fe^{2+}$ ions. In the case of low concentrations of ethyl alcohol (up to $10^{-3}$ $M$), this increase is almost proportional to the concentration of $C_2H_5OH$. At high concentrations of $C_2H_5OH$ (more than $10^{-2}$ $M$), a further increase in the ethanol concentration does not lead to an increase in

**Fig. 3.** Dependence of the final yield of $Fe^{3+}$ (for $t = \infty$) on the initial concentration of $Fe^{2+}$ in 0.4 $M$ sulfuric acid solutions containing $10^{-2}$ $M$ $C_2H_5OH$ and saturated with air.

**Fig. 4.** Dependence of the final yield of $Fe^{3+}$ (for $t = \infty$) on the initial concentration of ethyl alcohol in 0.4 $M$ sulfuric acid solutions containing $2.5 \cdot 10^{-4}$ $M$ $Fe^{2+}$ and saturated with air. 1—initial concentration of $C_2H_5OH$ in $M \cdot 10^3$; 2—initial concentration of $C_2H_5OH$ in $M \cdot 10^1$.

$G(Fe^{3+})$. In solutions containing more than $10^{-3}$ $M$ $C_2H_5OH$ and less than $5 \cdot 10^{-4}$ $M$ $Fe^{2+}$, $G(Fe^{3+})$ is more than twice as high as in solutions not containing alcohol. The time-dependent process of $Fe^{2+}$ oxidation in the presence of $C_2H_5OH$ can be initiated by hydrogen peroxide.

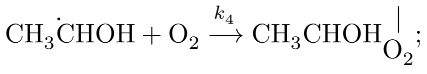
Evidently, the radiolytic oxidation of $Fe^{2+}$ in the presence of ethanol and oxygen, as well as the analogous process initiated by hydrogen peroxide, is a chain process. Apparently, this process is described by the mechanism proposed by Dykherst ($^3$):

$$H_2O \longrightarrow H, OH, H_2, H_2O_2; \tag{0}$$

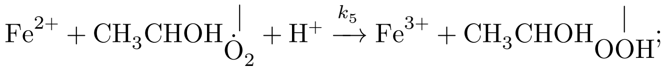
$$H + O_2 \xrightarrow{k_1} HO_2; \tag{1}$$

$$Fe^{2+} + OH \xrightarrow{k_2} Fe^{3+} + OH^-; \tag{2}$$

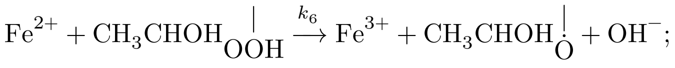
$$CH_3CH_2OH + OH \xrightarrow{k_3} CH_3\dot{C}HOH + H_2O; \tag{3}$$



$$CH_3\dot{C}HOH + O_2 \xrightarrow{k_4} CH_3CHOH\underset{O_2}{|}; \tag{4}$$



$$Fe^{2+} + CH_3CHOH\underset{\dot{O}_2}{|} + H^+ \xrightarrow{k_5} Fe^{3+} + CH_3CHOH\underset{OOH}{|}; \tag{5}$$



$$Fe^{2+} + CH_3CHOH\underset{OOH}{|} \xrightarrow{k_6} Fe^{3+} + CH_3CHOH\underset{\dot{O}}{|} + OH^-; \tag{6}$$

* Argon was purified by passing it through a sodium-potassium alloy.

$$Fe^{2+} + CH_3CHOH + H^+ \xrightarrow{k_7} Fe^{3+} + CH_3CHO + H_2O; \tag{7}$$

$$\dot{O}$$

$$CH_3CH_2OH + CH_3CHOH \xrightarrow{k_8} CH_3CHO + CH_3\dot{C}HOH + H_2O; \tag{8}$$

$$\dot{O}$$

$$Fe^{2+} + HO_2 + H^+ \xrightarrow{k_9} Fe^{3+} + H_2O_2; \tag{9}$$

$$Fe^{2+} + H_2O_2 \xrightarrow{k_{10}} Fe^{3+} + OH + OH^-. \tag{10}$$

The mechanism of the process initiated by hydrogen peroxide includes reactions (10), (2)–(8).

When the solution contains more than $10^{-3}$ $M$ $C_2H_5OH$ and less than $5 \cdot 10^{-4}$ $M$ $Fe^{2+}$, the chain includes reactions (4)–(6) and (8), and its length exceeds unity. The dependence of $G(Fe^{3+})$ on the concentrations of $Fe^{2+}$ and $C_2H_5OH$ is connected with the values of the relative rate constants of reactions $k_2/k_3$ and $k_7/k_8$. The absence of a dependence of $G(Fe^{3+})$ on the ethanol concentration at high concentrations of the latter is apparently due to the occurrence under these conditions of certain other reactions. As an example here one may cite the recombination reaction of peroxide radicals ($^{10}$):

$$2CH_3CHOH \longrightarrow CH_3CHOH + CH_3CHO + O_2. \qquad (10)$$

$$\dot{O}_2 \qquad OOH$$

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