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Abstract

Full Text

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RADIOLYSIS OF AQUEOUS FERROUS SULFATE SOLUTIONS UNDER THE ACTION OF DECIMICROSECOND ELECTRON PULSES

(Presented by Academician V. I. Spitsyn, 19 VII 1963)

Earlier (^{1,2}) we showed that $G(\mathrm{Fe}^{3+})$, under the action of microsecond electron pulses on an aqueous ferrous sulfate solution in $0.4\,M$ H_2SO_4 saturated with air, decreases as the absorbed-dose rate increases. The use of two independent methods of kinetic treatment of the experimental data obtained (one of them based on the assumption that, under these conditions, the method of stationary concentrations is applicable, and the other on the assumption that reactions of radicals with dissolved substances occur only after the pulse has passed through the solution) enabled us to calculate approximately the absolute values of the rate constants of certain radiation reactions (^{2}).

In order to estimate the degree of approximation in such a calculation of the constants, we developed a method for generating decimicrosecond electron pulses and carried out an investigation of the radiolysis of aqueous ferrous sulfate solutions under the action of this type of radiation*.

As before (^{1,3}), the pulses were generated in a direct-acceleration electron tube powered by a Cockcroft–Walton voltage multiplier. The rectangular pulse injected into the accelerating field of the tube was shaped by two four-wire lines connected in series. The line was calculated for a pulse duration of $5 \cdot 10^{-7}$ sec. Figure 1 shows an oscillogram of the pulse. The same figure also shows the time “mark” (one division corresponds to 10^{-7} sec). As follows from the figure, the pulse duration is $6 \cdot 10^{-7}$ sec. The maximum current in the pulse was 0.8 A. The electron energy was 0.9—1.0 MeV.

Fig. 2

Figure 2: Fig. 2

Fig. 1. Oscillogram of an electron pulse (below, the time "mark")

For complete elimination of the "dark" current, a mechanical shutter was used, installed at the exit window of the accelerator and synchronized with the delivery of the controlling light pulse to the photomultiplier of the trigger circuit for discharge of the forming line. In addition, during the pauses between pulses a positive potential was applied to the cathode of the injector. Thanks to these devices, the action of the "dark" current was practically negligible in comparison with the effect of the pulse itself.

The solutions were irradiated in glass membrane cells with a sealed-in platinum probe. Twice-distilled water and reagents of sufficient purity were used for preparing the solutions. The volume of solution in the cell was 7-9 ml, and the thickness of the liquid layer was 4.0-4.5 mm. The irradiation and dose-measurement procedure has been described in our previous communications (1,2). In the calculations, the values of the dose rate were used, averaged over the irradiated volume. In all cases $3 \cdot 10^{-3}$ M solutions of Mohr' s salt in 0.4 M H_2SO_4, saturated with air or oxygen and containing no NaCl, were used.

Ferric iron was determined spectrophotometrically. The value of the molar extinction coefficient of Fe^{3+} in 0.4 M H_2SO_4 at a wavelength of 304 mμ was taken to be 2170 (at $24°C$) (4). The consumption of oxygen as a result of irradiation was measured by the method described in (5). This method is based on oxidation of Fe^{2+} ions by the oxygen present in the solution in an alkaline medium, and on spectrophotometric measurement of the amount of Fe^{3+} ions formed after sulfuric acid has been added to the solution. The analyses were carried out in a special chamber through which argon, containing no oxygen, was continuously passed. The alkali and acid solutions used for the analyses (their concentration was 5 M) were saturated with argon. Sulfuric acid was added in such an amount that its concentration in the final solution was 0.4—1.0 M. In preliminary independent experiments the optical absorption due to Fe^{3+} ions formed as a result of irradiation at the same dose was determined. This absorption (after correction for dilution) was subtracted from the total optical density of the final solution. The accuracy of determining $G(-O_2)$ was $\pm 7\%$.

Fig. 2. Dependence of the concentration of the Fe^{3+} ions formed on dose ($3 \cdot 10^{-3}$ M solution of Mohr' s salt in 0.4 M H_2SO_4, saturated with air; dose rate $5 \cdot 10^{23}$ eV/ml · sec)

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* It should be noted that during the passage of such a pulse, radiation reactions in the bulk of the solution practically do not occur.

Fig. 3

Figure 3: Fig. 3

Figure 2 gives the dependence of the concentration of the ferric iron formed on dose at a dose rate of $5 \cdot 10^{23}$ eV/ml • sec. Similar curves were also obtained for other dose rates. From their slopes the values of $G(Fe^{3+})$ were calculated. Figure 3 shows the dependence of $G(Fe^{3+})$ on dose rate. Each yield value is the mean value measured in a separate independent series of 3-5 experiments. For comparison, the data obtained by us earlier (^{2}) using pulses of duration $5 \cdot 10^{-6}$ sec are also given there.

Fig. 3. Dependence of $G(Fe^{3+})$ on dose rate: 1, 2—data of (^{2}); 3—$3 \cdot 10^{-3}$ M solution of Mohr's salt in 0.4 M H_2SO_4, saturated with air; 4—the same solution, but saturated with oxygen

Figure 4 illustrates the dependence of the concentration of oxygen remaining in the solution on dose at a dose rate of $5 \cdot 10^{23}$ eV/ml • sec. The values

for $G(-\mathrm{O}_2)$, calculated from the slope of the curve in this figure, is 2.5 ± 0.15 molecules/100 eV.

The data obtained by us are satisfactorily described by the mechanism proposed in works (^{6,2}) and including the reactions:

$$\mathrm{H_2O} \rightsquigarrow \mathrm{H},\ \mathrm{OH},\ e^-_{aq},\ \mathrm{H_2},\ \mathrm{H_2O_2}; \tag{1}$$

$$e^-_{aq} + \mathrm{H}^+ \to \mathrm{H}; \tag{2}$$

$$\mathrm{Fe}^{2+} + \mathrm{OH} \to \mathrm{Fe}^{3+} + \mathrm{OH}^-; \tag{3}$$

$$\mathrm{H} + \mathrm{O_2} \to \mathrm{HO_2}; \tag{4}$$

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} \to \mathrm{Fe}^{3+} + \mathrm{OH} + \mathrm{OH}^-; \tag{5}$$

$$\mathrm{H}^+ + \mathrm{Fe}^{2+} + \mathrm{HO_2} \to \mathrm{Fe}^{3+} + \mathrm{H_2O_2}; \tag{6}$$

$$\mathrm{H} + \mathrm{OH} \to \mathrm{H_2O}. \tag{7}$$

On the basis of this mechanism, the following relation must be fulfilled:

Fig. 4. Dependence of the concentration of oxygen remaining in solution on dose (solution saturated with air; dose rate $5 \cdot 10^{23}$ eV/ml • s)

Figure 4: Fig. 4. Dependence of the concentration of oxygen remaining in solution on dose (solution saturated with air; dose rate $5 \cdot 10^{23}$ eV/ml • s)

$$\Delta G(\mathrm{Fe}^{3+}) = 4\Delta G(-\mathrm{O}_2), \tag{8}$$

where $\Delta G(\mathrm{Fe}^{3+})$ is the difference between the standard value $G(\mathrm{Fe}^{3+})$ (15.5—15.6 ions/100 eV) and the value of $G(\mathrm{Fe}^{3+})$ at the given high dose rate, and $\Delta G(-\mathrm{O}_2)$ is the difference between the yields of consumption of O_2 at low (3.65 molecules/100 eV) and high dose rate.

Fig. 4. Dependence of the concentration of oxygen remaining in solution on dose (solution saturated with air; dose rate $5 \cdot 10^{23}$ eV/ml • s)

According to our data, for a dose rate of $\sim 5 \cdot 10^{23}$ eV/ml•s, $\Delta G(\mathrm{Fe}^{3+}) = 4.5 \pm 0.4$ ions/100 eV, and $\Delta G(-\mathrm{O}_2) = 1.15 \pm 0.15$ molecules/100 eV, i.e., within the limits of experimental error equality (8) is fulfilled in this case.

Table 1

Calculation of the values of K_3K_4/K_7

No.	Dose rate, eV/ml • s	(O_2), $M \cdot 10^4$	$G(\mathrm{Fe}^{3+})$, ions/100 eV	K_3K_4/K_7, l/mol • s • 10^{-7}
1	$2.0 \cdot 10^{22}$	2.7	14.5	3.5
2	$5.4 \cdot 10^{22}$	2.7	13.3	3.8
3	$1.5 \cdot 10^{23}$	2.7	12.9	8.4
4	$1.7 \cdot 10^{23}$	2.7	12.6	8.1
5	$4.6 \cdot 10^{23}$	2.7	10.8	10.0
6	$4.7 \cdot 10^{23}$	2.7	11.2	12.0
7	$4.8 \cdot 10^{23}$	2.7	11.4	13.0
8	$5.0 \cdot 10^{23}$	2.7	10.6	10.0
9	$5.0 \cdot 10^{23}$	2.7	10.9	11.0
10	$5.0 \cdot 10^{23}$	12.0	12.9	6.3

Calculation of the relative constant K_3K_4/K_7 from equation (12), given in our communication (2), shows that its values coincide with those found earlier (2) ($3.2 \cdot 10^7$ l/mol • s) only at dose rates up to 10^{23} eV/ml • s. In the case of higher dose rates the values of K_3K_4/K_7 increase (see Table 1).

Obviously, at dose rates exceeding 10^{23} eV/ml • s, the method of stationary concentrations cannot be used for calculating relative constants.

Equation (13) (see (^{2})) was derived in work (^{6}) under the assumption that radiation reactions in the volume of the solution do not occur during the action of an electron pulse of duration $1.3 \cdot 10^{-6}$ s, and that the concentrations of the radicals H and OH are exponential functions of time. In this work it was calculated that $K_3/K_7 = 6.2 \cdot 10^{-3}$ and $K_4/K_7 = 2.2 \cdot 10^{-1}$. Later, the method of treatment under consideration was also used by us (^{2}) in studying the radiolysis of ferrous sulfate solutions under the action of electron pulses of duration $5 \cdot 10^{-6}$ s. According to the data of (^{2}), $K_3/K_7 = 6 \cdot 10^{-3}$ and $K_4/K_7 = 1.2 \cdot 10^{-1}$. Obviously, in the case of pulses of duration $6 \cdot 10^{-7}$ s, the first of the two assumptions indicated above is more correct than for pulses of duration $1.3 \cdot 10^{-6}$ or $5 \cdot 10^{-6}$ s.

Determination, by the method of fitting, of the constants K_3/K_7 and K_4/K_7 from equation (13) (^{2}), using the results of the present work, gave the following values of these constants: $K_3/K_7 = 3 \cdot 10^{-3}$ and $K_4/K_7 = 3 \cdot 10^{-2}$.

Table 2

Calculation of the values of (H_2O)

Dose rate, eV/ml • sec	(O_2), $M \cdot 10^4$	$G(Fe^{3+})$, ions/100 eV	$(H_2O)_{calc}$, $M \cdot 10^5$	$(H_2O)_{expt}$, $M \cdot 10^5$
$5.0 \cdot 10^{23}$	2.7	10.9	0.54	0.58 ± 0.08
$5.0 \cdot 10^{23}$	2.7	10.6	0.54	0.63 ± 0.08
$5.0 \cdot 10^{23}$	12.0	12.9	0.35	0.34 ± 0.09
$4.8 \cdot 10^{23}$	2.7	11.4	0.51	0.50 ± 0.08
$4.7 \cdot 10^{23}$	2.7	11.2	0.50	0.52 ± 0.09
$4.6 \cdot 10^{23}$	2.7	10.8	0.48	0.55 ± 0.08
$1.7 \cdot 10^{23}$	2.7	12.6	0.11	0.13 ± 0.04
$1.5 \cdot 10^{23}$	2.7	12.9	0.09	0.10 ± 0.03
$5.4 \cdot 10^{22}$	2.7	13.3	0.015	0.03 ± 0.013
$2.0 \cdot 10^{22}$	2.7	14.5	0.0023	0.0055 ± 0.005

In Table 2, the concentrations of water formed as a result of reaction (7), calculated from equation (13) using these values of the constants, are compared with the concentrations found from the experimental values of $G(Fe^{3+})$. The agreement, as can be seen, is satisfactory.

The constants K_3/K_7 and K_4/K_7 agree, within one order of magnitude, with those given in works (^{6}, ^{2}). Evidently, the constants K_3, K_4, and K_7 (^{2}), as well as the rate constants of reactions involving the hydrated electron (^{7}), have been calculated with the same degree of accuracy.

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