INVESTIGATION OF THE RADIOLYTIC OXIDATION OF FERROUS IRON AT HIGH IRRADIATION DOSE RATES

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

P. Ya. GLAZUNOV and A. K. PIKAEV

INVESTIGATION OF THE RADIOLYTIC OXIDATION OF FERROUS IRON AT HIGH IRRADIATION DOSE RATES

(Presented by Academician V. I. Spitsyn, September 28, 1959)

There are almost no data in the literature concerning the influence of high dose rates, over a wide range, on radiolytic transformations in aqueous solutions, although this question is of considerable scientific interest. Even the radiolytic oxidation of ferrous iron in dilute aqueous sulfuric-acid solution, which is one of the most widely used dosimetric systems, has been studied relatively little in this respect. It is known only (^{1}) that at high dose rates (beginning with 10^{21} eV/ml $\cdot$ sec) there occurs a noticeable decrease in the ratio $G(\mathrm{Fe}^{3+})/G(\mathrm{Ce}^{3+})$ (in the case of dilute aqueous solutions of Fe^{2+} and Ce^{4+} salts). In addition, there is a study (^{2}) determining the value of $G(\mathrm{Fe}^{3+})$ at a dose rate of $\sim 5 \cdot 10^{23}$ eV/ml $\cdot$ sec. In that work it was found that $G(\mathrm{Fe}^{3+})$ at such a dose rate differs hardly at all from the value of $G(\mathrm{Fe}^{3+})$ in the case of the dose rates usually used in radiation chemistry.

In the cited works, the high dose rates were produced by pulsed electron radiation. For this purpose, linear electron accelerators were used that had a high repetition frequency of pulse delivery (50 pulses per second and higher). In work (^{2}), individual pulses were selected by a mechanical selector, which, however, could not completely exclude the effects of the "dark" current. In another work (^{1}), it is not stated at all what devices were used to eliminate the influence of the "dark" current.

Earlier (^{3}), we determined the value of $G(\mathrm{Fe}^{3+})$ at a dose rate of 10^{21} eV/ml $\cdot$ sec. Solutions of ferrous sulfate in sulfuric acid were irradiated with single monoenergetic electron pulses generated in a high-voltage direct-acceleration electron tube powered by a cascade valve-capacitor voltage multiplier at 1.0–1.2 MV. The use of a special device made it possible to reduce the action of the "dark" current to 3–5% of the total effect of the pulse. The value of $G(\mathrm{Fe}^{3+})$ found by us was 15.0–15.1 ions/100 eV. It was of undoubted interest to determine the value of $G(\mathrm{Fe}^{3+})$ at higher dose rates. First, such an investigation is of considerable importance for the chemical dosimetry of ionizing radiation. Second, it will provide some information on the behavior of the products of water radiolysis under conditions in which the tracks of ionizing particles overlap.

Fig. 1. Circuit of the pulse modulator

Figure 1: Fig. 1. Circuit of the pulse modulator

For this purpose, we improved the methods for generating electron pulses in a direct-acceleration tube. As a result, we succeeded in studying the radiolytic oxidation of ferrous iron in sulfuric-acid aqueous solutions at dose rates up to 10^{23} eV/ml • sec. As before (4), pulsed electron radiation was obtained by modulating a rectangular pulse of the accelerating voltage of the electron-gun injector tube. In order to reduce the pulse duration (to 1–5 μsec) and eliminate from the modulator circuit the pulsed step-up transformer (inevit–

of the source (distortion of the pulse fronts), a pulse modulator with two artificial forming lines in the discharge circuit was used, making it possible to obtain at the load a voltage equal to the charging voltage. The charging voltage of the forming line was 16 kV.

As the discharger in the modulator, a high-voltage thyratron was used. The discharger was controlled by a trigger-pulse generator assembled according to the circuit of a blocked blocking oscillator, with an FEU-19 photoelectric device for remote starting of the modulator. The photoelectric device was controlled by means of a time relay by a light pulse produced by an IS-50 flash lamp. A rectangular pulse of negative voltage (16 kV) is applied to the cathode of the electron gun, which injects an electron-current pulse into the accelerating field of the tube. An increase in the emission of the tungsten cathode was achieved by activating it with thorium dioxide.

Fig. 1. Circuit of the pulse modulator

However, increasing the dose power per pulse to 10^{22} eV/ml $\cdot$ sec led to a considerable increase in the magnitude of the "dark" current (up to 15–25% of the total pulse effect), which, naturally, could distort the results of determining $G(\mathrm{Fe}^{3+})$. For this reason, a special device was used that completely eliminated the influence of the "dark" current. The circuit of this device included the application of a blocking positive potential to the gun cathode through the matching resistance of the artificial line and the decoupling element DGTs-27 (see Fig. 1).

Previously(3), the energy of pulsed electron radiation absorbed by the irradiated system was measured by us using a ballistic galvanometer. However, when working with a ballistic galvanometer there is a considerable objective error, and calculation of the measurement results takes much time. In this connection, we developed an integrator that records the absorbed energy for each pulse and sums it over the entire series of pulses. The integrator operates according to a circuit that converts the quantity of electricity in the current pulse into a signal whose duration is a function of the current amplitude.

The principle of operation of the integrator is as follows. The pulse of accelerated electrons absorbed in the reaction cell is led, by means of a platinum probe, to

Fig. 2. Diagram of experiments for determining $G(\text{Fe}^{3+})$.

Figure 2: Fig. 2. Diagram of experiments for determining $G(\text{Fe}^{3+})$.

a capacitance C, discharged through a resistance R. The sig-

the discharge signal is amplified and phase-inverted by a phase-inverter amplifier and is fed to the next relay—a Schmitt trigger. The Schmitt trigger produces a rectangular signal whose duration is a function of the amplitude of the pulse charging the capacitance C. This signal is fed to a gate circuit, which passes signals from the fixed-frequency generator for a time interval equal to the duration of the rectangular signal coming from the Schmitt trigger. The pulses of the fixed-frequency generator that have passed through the gate circuit are recorded by a PS-10000 counting device. In addition, the circuit provides for a counter of the number of current pulses arriving at the integrator. The pulse parameters were: shape—rectangular, duration—5 μsec, current per pulse—100-120 mA, dose rate—up to 10^{23} eV/ml · sec (at an energy of 0.9 MeV). Variation of the dose rate of the pulsed radiation was achieved by varying the cathode heating.

In determining the value $G(\text{Fe}^{3+})$, twice-distilled water was used; the reagents were of sufficient purity. A $3 \cdot 10^{-3}$ M solution of Mohr' s salt in 0.8 N H_2SO_4, without addition and with the addition of 10^{-3} M NaCl, was irradiated. Trivalent iron was determined spectrophotometrically. The value of the molar extinction coefficient of Fe^{3+} in 0.8 N H_2SO_4 at 304 mμ was taken to be 2170 (at 24°) (5). In the calculations, the change of the extinction coefficient with temperature (0.7% per degree) was taken into account. The solutions were irradiated in a glass cell with a glass membrane (membrane thickness about 100 μ).

Fig. 2. Diagram of experiments for determining $G(\text{Fe}^{3+})$.
1—glass cell with membrane, 2—beryllium exit window of the accelerator tube, 3—cathode-filament circuit and contacts for starting the pulse circuit, 4—phase-inverter amplifier, 5—Schmitt trigger, 6—gate circuit, 7—fixed-frequency generator, 8—counting circuit, 9—mechanical pulse counter, 10—PS-10000 counting unit.

The scheme of the experiments for measuring $G(\text{Fe}^{3+})$ at various dose rates is shown in Fig. 2. The amount of energy absorbed by the ferrous sulfate solution was determined by measuring the electron current in the solution by means of a platinum probe soldered into the cell, and by the integrator and counting device described above. An accurate estimate of the energy losses during passage of the electron beam through the cell membrane was carried out by the method described by us earlier (3). The magnitude and shape of the pulses were also monitored by the oscillographic method.

Table 1

Dose rate, eV/ml • sec	$G(\mathrm{Fe}^{3+})$, ions/100 eV	Dose rate, eV/ml • sec	$G(\mathrm{Fe}^{3+})$, ions/100 eV
10^{21}	15.0—15.1 ± 1.6*	$4.7 \cdot 10^{22}$	10.8 ± 0.9
$8 \cdot 10^{21}$	14.2 ± 1.5	$7.6 \cdot 10^{22}$	10.3 ± 0.5
$1.1 \cdot 10^{22}$	13.4 ± 0.6	$1.5 \cdot 10^{23}$	10.1 ± 0.5
$2.7 \cdot 10^{22}$	11.7 ± 1.0		

* $G(\mathrm{Fe}^{3+})$ at this dose rate was determined by us earlier (3).

Table 1 gives the values of $G(\mathrm{Fe}^{3+})$ determined by us at high dose rates. Each value of $G(\mathrm{Fe}^{3+})$ is the mean of 8-20 measurements. Depending on the dose rate, the solutions were irradiated with 1–10 electron pulses (with an energy of 0.9 MeV).

As the data of Table 1 show, the value of $G(\mathrm{Fe}^{3+})$ decreases markedly with increasing dose rate, beginning with dose rates of $\sim 10^{22}$ eV/ml • sec. The value reported in (2), $G(\mathrm{Fe}^{3+}) = 14.3$ ions/100 eV at

dose rate of $\sim 5 \cdot 10^{23}$ eV/ml • sec is apparently somewhat overestimated (perhaps, as noted above, owing to large "dark" currents). Therefore, when carrying out chemical dosimetry with the aid of the ferrous-sulfate dosimetric system, it is necessary to take into account the appreciable decrease in the value of $G(\mathrm{Fe}^{3+})$ in the case of very high dose rates.

At present it is generally accepted (⁶) that, because of the extremely low concentration of ferrous iron in the dosimetric system and the high radiation-chemical stability of sulfuric acid, the direct action of radiation on the dissolved substance is negligibly small, and therefore the oxidation of Fe^{2+} occurs at the expense of the products of water radiolysis. These products interact with ferrous iron and molecular oxygen present in the solution in the following manner:

$$\mathrm{Fe}^{2+} + \mathrm{OH} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH}^-, \tag{1}$$

$$\mathrm{H} + \mathrm{O}_2 \rightarrow \mathrm{HO}_2, \tag{2}$$

$$\mathrm{H}_2\mathrm{O}_2 + \mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{OH} + \mathrm{OH}^-, \tag{3}$$

$$\mathrm{H}^+ + \mathrm{Fe}^{2+} + \mathrm{HO}_2 \rightarrow \mathrm{Fe}^{3+} + \mathrm{H}_2\mathrm{O}_2. \tag{4}$$

Hence $G(\mathrm{Fe}^{3+}) = 3G_{\mathrm{H}} + G_{\mathrm{OH}} + 2G_{\mathrm{H_2O_2}}$, where G_{H}, G_{OH}, and $G_{\mathrm{H_2O_2}}$ are the yields of the corresponding products of water radiolysis.

With increasing dose rate, the probability of recombination of the radicals H and OH formed as a result of water radiolysis increases, owing to overlap of the tracks of ionizing particles: $H + H \rightarrow H_2$; $H + OH \rightarrow H_2O$; $OH + OH \rightarrow H_2O_2$. This should lead to an increase in G_{H_2} and $G_{H_2O_2}$ and a decrease in G_H and G_{OH}, i.e., to a decrease in the value of $G(Fe^{3+})$.

As the results of the present work show, $G(Fe^{3+})$ decreases beginning at a dose rate of $\sim 10^{22}$ eV/ml · sec. In this connection it may be supposed that, in aqueous solutions at such dose rates, effects associated with overlap of the tracks of ionizing particles become appreciable.

The possibility is not excluded that high dose rates influence reaction (2). However, to resolve this question, as well as for a quantitative estimate of the magnitude of the decrease in G_H and G_{OH} at high dose rates, further investigations are necessary.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
25 IX 1959

CITED LITERATURE

1. H. C. Sutton, J. Rotblat, *Nature*, **180**, 1332 (1957).
2. J. P. Keene, *Radiation Res.*, **6**, 424 (1957).
3. A. K. Pikaev, P. Ya. Glazunov, *Izv. AN SSSR, OKhN*, in press.
4. P. Ya. Glazunov, M. G. Kuz' min, in: *Proc. All-Union Conference on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 324.
5. R. H. Schuler, A. O. Allen, *J. Chem. Phys.*, **24**, 56 (1956).
6. A. O. Allen, in: *Collection of Reports by Foreign Scientists at the Geneva Conference*, Moscow, 1956.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.