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Abstract

Full Text

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RADIOLYTIC REDUCTION OF TETRAVALENT CERIUM IN THE PRESENCE OF MONOVALENT THALLIUM AT HIGH RADIATION DOSE RATES

(Presented by Academician V. I. Spitsyn, June 21, 1960)

Earlier (^{1}-^{3}) we showed that at high dose rates of irradiation, beginning at $\sim 10^{21}$ eV/ml • sec, owing to overlap of the tracks of ionizing particles and the resulting change in the yields of radical and molecular products of the radiolysis of water, there occurs a noticeable decrease in the radiation yield of Fe^{3+} (upon irradiation of sulfuric-acid aqueous solutions of ferrous sulfate in the presence of air) and an increase in the radiation yield of Ce^{3+} (upon irradiation of sulfuric-acid aqueous solutions of ceric sulfate). In order to further study the influence of high dose rates on the course of radiolytic transformations in aqueous solutions, we investigated radiation-chemical processes in sulfuric-acid solutions of mixtures of the sulfates of Ce^{4+} and Tl^{+} at irradiation dose rates up to $\sim 10^{23}$ eV/ml • sec.

Fig. 1. Dependence of $G(\mathrm{Ce}^{3+})$ on dose rate for the system Ce^{4+}—Tl^{+} (concentration of Ce^{4+} $2 \cdot 10^{-4}$ M, concentration of Tl^{+} 10^{-2} M)

High dose rates were produced by means of single monoenergetic electron pulses (energy 0.8 MeV) generated on a straight-acceleration accelerator tube (^{2}, ^{3}). The experimental procedure and the method for measuring the dose rate were described in our preceding communications (^{2}, ^{3}). In all experiments, twice-distilled water was used.

The following reagents were used: ceric sulfate $\mathrm{Ce(SO_4)_2 \cdot 4H_2O}$ (“pure” grade), twice recrystallized from bidistilled water with the addition of a small amount of sulfuric acid; thallous sulfate (analytical grade), recrystallized from bidistilled water; and also cerous sulfate (analytical grade) and sulfuric acid (chemically pure grade), without preliminary purification. The solutions were irradiated in a glass cell with a glass membrane (membrane thickness about $60\,\mu$). The irradiated volumes were 7 ml; the thickness of the liquid layer was 5 mm.

The amount of Ce^{3+} formed upon irradiation was determined spectrophotometrically. The value of the molar extinction coefficient of Ce^{4+} in $0.8\,N$ $\mathrm{H_2SO_4}$ at 320 $\mathrm{m}\mu$ was taken as 5580 (^{4}). Tl^{3+} was determined by an indirect method. First, the content of Ce^{4+} in the irradiated solution was measured spectrophotometrically; then a $10^{-3}\,M$ solution of Mohr' s salt in $0.8\,N$ $\mathrm{H_2SO_4}$ was added to the solution. In this process Tl^{3+} and Ce^{4+} oxidize a certain amount of Fe^{2+}. Having measured spectrophotometrically the concentration of Fe^{3+}, and knowing the amount of Ce^{4+} in the solution, one can determine the content of Tl^{3+}. This method proved satisfactory at irradiation dose rates of approximately up to 10^{22} eV/ml • sec. At higher dose rates, because of the very low concentration of Tl^{3+}, the accuracy of the determination was insufficiently high.

In studying the influence of high dose rates on the value of $G(\mathrm{Ce}^{3+})$, in the case of solutions of the Ce^{4+}—Tl^{+} mixture, an air-saturated···

0.8 N sulfuric-acid aqueous solution containing $2 \cdot 10^{-4}\,M$ Ce^{4+} and $10^{-2}\,M$ Tl^{+}. According to (5), $G(Ce^{3+})$ under the action of Co^{60} γ-rays (dose rate $2.5 \cdot 10^{15}$ eV/ml • sec) is 7.9 ions/100 eV, and $G(Ce^{3+})$ does not depend on the concentration of Tl^{+} in the range 10^{-5}–$10^{-2}\,M$. In our experiments, upon irradiation of a solution of the Ce^{4+}–Tl^{+} mixture of the above concentration with a continuous stream of electrons of energy 0.9 MeV and at a dose rate of $9.4 \cdot 10^{15}$ eV/ml • sec, the value $G(Ce^{3+})$ was 7.6 ± 0.2 ions/100 eV. The small discrepancy with (5) is apparently due to the fact that in our experiments the dose rate was approximately 4 times higher.

Upon irradiation of Ce^{4+}–Tl^{+} solutions with electron pulses, a noticeable decrease in $G(Ce^{3+})$ occurs with increasing dose rate. The results obtained are shown in Fig. 1. Depending on the dose rate, the Ce^{4+}–Tl^{+} solutions were irradiated with from 1 to 50 electron pulses*. Each value of $G(Ce^{3+})$ is the average of 5–15 measurements.

Figure 2 shows the dependence of the formation of Ce^{3+} in 0.8 N sulfuric-acid solution, with $2 \cdot 10^{-4}\,M$ $Ce(SO_4)_2$ and $10^{-2}\,M$ Tl_2SO_4, on dose under pulsed irradiation conditions (dose rate $5 \cdot 10^{22}$ eV/ml • sec). At high dose rates, $G(Ce^{3+})$ in the presence of Tl^{+} depends somewhat on the initial concentration of Tl^{+} ions in the solution. As can be seen from Fig. 3, $G(Ce^{3+})$ increases with increasing Tl^{+} concentration (proportionally to the logarithm of the Tl_2SO_4 concentration). Addition of Ce^{3+} to a Ce^{4+} solution leads to a decrease in $G(Ce^{3+})$. Figure 4 shows the dependence of $G(Ce^{3+})$ on the concentration of $Ce_2(SO_4)_3$ salt introduced into the solution at a dose rate of $\sim 5 \cdot 10^{22}$ eV/ml • sec (the initial solution contained $2 \cdot 10^{-4}\,M$ Ce^{4+}); for comparison, data from (5) at a dose rate of $2.5 \cdot 10^{15}$ eV/ml • sec are also presented.

Fig. 2. Dependence of the reduction of Ce^{4+} in the presence of $10^{-2}\,M$ Tl^{+} on dose at a dose rate of $5 \cdot 10^{22}$ eV/ml • sec

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From the values of $G(Tl^{3+})$ determined by us at high dose rates ($G(Tl^{3+})$ is the average of 5—12 measurements), given below, it is seen that the value $G(Tl^{3+})$ decreases markedly with increasing dose rate.

Dose rate, eV/ml • sec	$\sim 10^{21}$	$5 \cdot 10^{22}$
$G(Tl^{3+})$, ions/100 eV	1.5 ± 0.15	0.4 ± 0.2

According to (5), the mechanism of radiolytic transformations of Ce^{4+} and Tl^{+} in 0.8 N sulfuric-acid aqueous solution containing sulfuric-acid salts of Ce^{4+} and Tl^{+}, at low dose rates, is expressed by the following reactions:

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

$$Ce^{4+} + H \to Ce^{3+} + H^{+}; \tag{1}$$

$$2Ce^{4+} + H_2O_2 \to 2Ce^{3+} + 2H^{+} + O_2; \tag{2}$$

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

$$Ce^{4+} + Tl^{2+} \to Ce^{3+} + Tl^{3+}. \tag{4}$$

Hence

$$G(Ce^{3+})_{Tl^{+}} = G_H + G_{OH} + 2G_{H_2O_2}, \tag{5}$$

whereas

$$G(Tl^{3+}) = G_{OH}, \tag{6}$$

* In our experiments there was some averaging of the dose rate over the volume of the solution. However, this averaging does not significantly affect the value of $G(Ce^{3+})$.

Figure 3: Dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of $\mathrm{Tl_2SO_4}$ at a dose rate of $4.5 \cdot 10^{22}$ eV/ml • sec (concentration of Ce^{4+}—$2 \cdot 10^{-4}\,M$).

Figure 3: Figure 3: Dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of $\mathrm{Tl_2SO_4}$ at a dose rate of $4.5 \cdot 10^{22}$ eV/ml • sec (concentration of Ce^{4+}—$2 \cdot 10^{-4}\,M$).

where G_H, G_{OH}, and $G_{\mathrm{H_2O_2}}$ are the G-yields of the corresponding products of the radiolysis of water.

In setting up the present study, we assumed that measurement of the yields of radiation reactions in three systems: Fe^{2+}, Ce^{4+}, and Ce^{4+}—Tl^{+}—would enable us to make a quantitative estimate of the change in the yields of radical and molecular products of water radiolysis caused by overlap of the tracks of ionizing particles. According to ([5,6]), at low dose rates

$$G(\mathrm{Fe}^{3+}) = 3G_H + G_{\mathrm{OH}} + 2G_{\mathrm{H_2O_2}} \tag{7}$$

(for a 0.8 N sulfuric-acid aqueous dilute solution of Fe^{2+} saturated with air) and

$$G(\mathrm{Ce}^{3+}) = G_H - G_{\mathrm{OH}} + 2G_{\mathrm{H_2O_2}} \tag{8}$$

(for a 0.8 N sulfuric-acid aqueous dilute solution of Ce^{4+}). From equations 5, 7, and 8 one can obtain the following expressions:

$$G(\mathrm{Ce}^{3+})_{\mathrm{Tl}^+} - G(\mathrm{Ce}^{3+}) = 2G_{\mathrm{OH}}, \tag{9}$$

$$3G(\mathrm{Ce}^{3+})_{\mathrm{Tl}^+} - G(\mathrm{Fe}^{3+}) = 4G_{\mathrm{H_2O_2}} + 2G_{\mathrm{OH}}. \tag{10}$$

Fig. 3. Dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of $\mathrm{Tl_2SO_4}$ at a dose rate of $4.5 \cdot 10^{22}$ eV/ml • sec (concentration of Ce^{4+}—$2 \cdot 10^{-4}\,M$).

However, substitution into these expressions of the experimentally found values $G(\mathrm{Fe}^{3+})$, $G(\mathrm{Ce}^{3+})$, and $G(\mathrm{Ce}^{3+})^{*}_{\mathrm{Tl}^+}$ at a dose rate $\sim 5 \cdot 10^{22}$ eV/ml • sec leads to a negative value of $G_{\mathrm{H_2O_2}}$ for all the Tl^{+} concentrations investigated.

On this basis, we assume that at high dose rates Tl^{2+}, formed by reaction 3, is able both to interact with Ce^{4+} according to reaction 4 and to enter into certain side reactions. Among the side processes, the principal one is apparently the reduction of Tl^{2+} by hydroperoxide radicals (or H atoms)**:

$$\mathrm{Tl}^{2+} + \mathrm{HO_2} \rightarrow \mathrm{Tl}^{+} + \mathrm{H}^{+} + \mathrm{O_2} \tag{11}$$

Figure 4: Dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of Ce^{3+} at dose rates: 1—5 · 10^{22} eV/ml • sec, 2—2.5 · 10^{15} eV/ml • sec ([5]).

Figure 4: Figure 4: Dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of Ce^{3+} at dose rates: 1—5 · 10^{22} eV/ml • sec, 2—2.5 · 10^{15} eV/ml • sec ([5]).

or, perhaps, by hydrogen peroxide:

$$\mathrm{Tl}^{2+} + \mathrm{H_2O_2} \rightarrow \mathrm{Tl}^{+} + \mathrm{H}^{+} + \mathrm{HO_2}. \tag{12}$$

Disproportionation of Tl^{2+} according to reaction (13),

$$2\mathrm{Tl}^{2+} \rightarrow \mathrm{Tl}^{+} + \mathrm{Tl}^{3+}, \tag{13}$$

probably plays an insignificant role, since within the experimental error

$$\frac{1}{2}\left[G(\mathrm{Ce}^{3+})_{\mathrm{Tl}^{+}} - G(\mathrm{Ce}^{3+})\right] = G(\mathrm{Tl}^{3+}).$$

Under conditions of high dose rates, the reverse reaction of Tl^{3+} with hydrogen peroxide is also highly probable:

$$\mathrm{Tl}^{3+} + \mathrm{H_2O_2} \rightarrow \mathrm{Tl}^{2+} + \mathrm{H}^{+} + \mathrm{HO_2} \tag{14}$$

Fig. 4. Dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of Ce^{3+} at dose rates: 1 —5 · 10^{22} eV/ml • sec, 2—2.5 · 10^{15} eV/ml • sec ([5]).

or

$$\mathrm{Tl}^{3+} + \mathrm{H_2O_2} \rightarrow \mathrm{Tl}^{+} + 2\mathrm{H}^{+} + \mathrm{O_2}. \tag{15}$$

This is confirmed by the deviation from the linear dependence of the reduction of Ce^{4+} in the presence of Tl^{+} on dose at high doses (see Fig. 2). In the case of low dose rates, the role of side reactions of Tl^{2+} ions in the radiolytic transformations of Ce^{4+} in the Ce^{4+}—Tl^{+} system is small, owing to the low concentration of Tl^{2+}.

The increase in the value of $G(\mathrm{Ce}^{3+})$ with increasing Tl^{+} concentration is apparently explained by competition of reaction (3) with reactions (16) and (17)*:

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* $G(\mathrm{Fe}^{3+})$ and $G(\mathrm{Ce}^{3+})$ were determined by us earlier ([2,3]).

** The occurrence of this reaction obviously leads to a decrease in the value of $G(\mathrm{Ce}^{3+})_{\mathrm{Tl}^{+}}$.

$$H + OH \rightarrow H_2O; \tag{16}$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O. \tag{17}$$

The decrease in $G(\mathrm{Ce}^{3+})$ with increasing Ce^{3+} concentration is, in all probability, caused, as in the case of low dose rates (^{5}), by competition of reaction (20) with reaction (19)

$$\mathrm{Ce}^{3+} + OH \rightarrow \mathrm{Ce}^{4+} + OH^-. \tag{20}$$

It should be noted that the dependence of $G(\mathrm{Ce}^{3+})$ on the concentration of Ce^{3+} is more sharply expressed in the case of high dose rates. At the same time, an intersection is observed of the curves expressing this dependence for dose rates of $\sim 5 \cdot 10^{22}$ and $2.5 \cdot 10^{15}$ eV/ml • sec, respectively. Beginning with a Ce^{3+} concentration of approximately $10^{-2}\,M$, the values of $G(\mathrm{Ce}^{3+})$ at a dose rate of $\sim 5 \cdot 10^{22}$ eV/ml • sec are smaller than the corresponding values at a dose rate of $2.5 \cdot 10^{15}$ eV/ml • sec. Consequently, to suppress the formation of an additional amount of H_2O_2 by reaction (19) (as a result of overlap of the tracks of ionizing particles), it is necessary to introduce into the solution containing Ce^{4+} about $10^{-2}\,M$ of a Ce^{3+} salt. At Ce^{3+} concentrations exceeding $10^{-2}\,M$, the change in $G(\mathrm{Ce}^{3+})$ in the case of high dose rates is apparently due mainly to a decrease in G_{H} (as a result of overlap of the tracks of ionizing particles).

Thus, at high dose rates, owing to the high concentration of radicals, the role of competition among interaction processes—radical-radical and radical-dissolved substance—as well as of side reactions of intermediate products in radiolytic transformations in dilute aqueous solutions, increases considerably.

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* At high dose rates, owing to overlap of the tracks of ionizing particles, the role of reactions (16) and (17), as well as of the reactions

$$H + H \rightarrow H_2; \qquad (18)$$

$$OH + OH \rightarrow H_2O_2 \qquad (19)$$

in radiolytic transformations in aqueous solutions increases appreciably.

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

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