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

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Abstract

Full Text

Physical Chemistry

A. K. Pikaev and P. Ya. Glazunov

RADIOLYTIC REDUCTION OF TETRAVALENT CERIU M 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 $G(\text{Ce}^{3+})$ on dose rate for the system $\text{Ce}^{4+}-\text{Tl}^{+}$ (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 $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ("pure" grade), twice recrystallized from bidistilled water with the addition of a small amount of sulfuric acid; thallos 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 $0.8\ N\ H_2SO_4$ at $320\ m\mu$ 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 $0.8\ N\ H_2SO_4$ 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 $10^{22}\ eV/ml \cdot sec$. 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 $G(Ce^{3+})$, 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 $2.5 \cdot 10^{15}\ eV/ml \cdot sec$) 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 $9.4 \cdot 10^{15}\ eV/ml \cdot sec$, 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 $5 \cdot 10^{22}\ eV/ml \cdot sec$). 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 $\sim 5 \cdot 10^{22}\ eV/ml \cdot sec$ (the initial solution contained $2 \cdot 10^{-4}\ M\ Ce^{4+}$); for comparison, data from (5) at a dose rate of $2.5 \cdot 10^{15}\ eV/ml \cdot sec$ 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 $5 \cdot 10^{22}\ eV/ml \cdot sec$

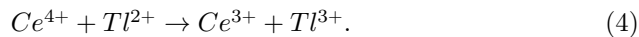
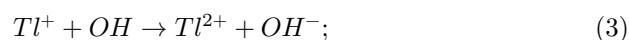
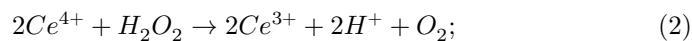
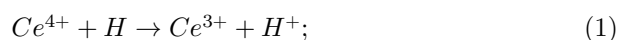
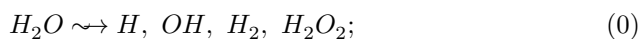
Fig. 2. Dependence of the reduction of Ce^{4+} in the presence of $10^{-2} M Tl^{+}$ on dose at a dose rate of $5 \cdot 10^{22}$ eV/ml · sec

Figure 2: 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

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:



Hence

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

whereas

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

* 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 $G(\text{Ce}^{3+})$ on the concentration of Tl_2SO_4 at a dose rate of $4.5 \cdot 10^{22}$ eV/ml · sec (concentration of $\text{Ce}^{4+} - 2 \cdot 10^{-4}$ M).

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

where G_H , G_{OH} , and $G_{\text{H}_2\text{O}_2}$ 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 $\text{Ce}^{4+} - \text{Tl}^+$ —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

$$G(\text{Fe}^{3+}) = 3G_H + G_{\text{OH}} + 2G_{\text{H}_2\text{O}_2} \quad (7)$$

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

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

(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:

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

$$3G(\text{Ce}^{3+})_{\text{Tl}^+} - G(\text{Fe}^{3+}) = 4G_{\text{H}_2\text{O}_2} + 2G_{\text{OH}}. \quad (10)$$

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

However, substitution into these expressions of the experimentally found values $G(\text{Fe}^{3+})$, $G(\text{Ce}^{3+})$, and $G(\text{Ce}^{3+})_{\text{Tl}^+}^*$ at a dose rate $\sim 5 \cdot 10^{22}$ eV/ml · sec leads to a negative value of $G_{\text{H}_2\text{O}_2}$ 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)**:

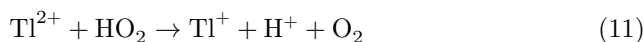
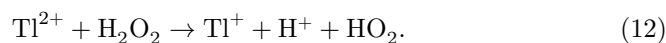


Figure 4: Dependence of $G(\text{Ce}^{3+})$ on the concentration of Ce^{3+} at dose rates: $1-5 \cdot 10^{22}$ eV/ml · sec, $2-2.5 \cdot 10^{15}$ eV/ml · sec ⁽⁵⁾.

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

or, perhaps, by hydrogen peroxide:



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



probably plays an insignificant role, since within the experimental error

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

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

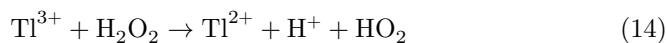
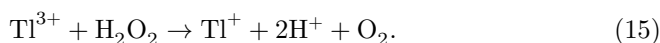


Fig. 4. Dependence of $G(\text{Ce}^{3+})$ on the concentration of Ce^{3+} at dose rates: $1-5 \cdot 10^{22}$ eV/ml · sec, $2-2.5 \cdot 10^{15}$ eV/ml · sec ⁽⁵⁾.

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

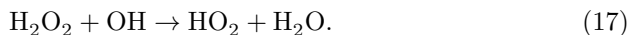
** The occurrence of this reaction obviously leads to a decrease in the value of $G(\text{Ce}^{3+})_{\text{Tl}^+}$.

or

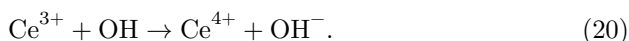


This is confirmed by the deviation from the linear dependence of the reduction of Ce^{4+} in the presence of Tl^+ on dose at high doses (see Fig. 2). In the case of low dose rates, the role of side reactions of Tl^{2+} ions in the radiolytic transformations of Ce^{4+} in the $\text{Ce}^{4+}-\text{Tl}^+$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

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



The decrease in $G(\text{Ce}^{3+})$ 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)



It should be noted that the dependence of $G(\text{Ce}^{3+})$ 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 $G(\text{Ce}^{3+})$ 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 $G(\text{Ce}^{3+})$ 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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CITED LITERATURE

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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



in radiolytic transformations in aqueous solutions increases appreciably.

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

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