

## $\gamma$ -Radiolysis of Aqueous Solutions of Tellurium

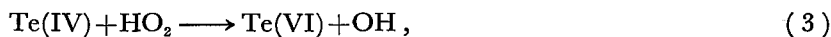
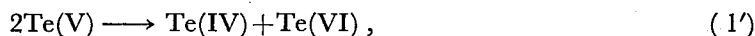
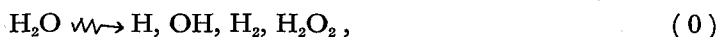
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Radiation induced reactions of Te(IV) and Te(VI) compounds labelled with  $^{132}\text{Te}$  and  $^{123m}\text{Te}$  respectively, in deaerated 0.4 M  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  solution, were investigated by the use of a  $^{60}\text{Co}$   $\gamma$ -ray source. The yield of radiation induced oxidation of Te(IV) and that of reduction of Te(VI) were very small and increased in proportion to their concentrations. Based on the reaction mechanism proposed by M. Haissinsky *et al.*, who had shown that almost all the OH and H radicals reacted with the stable radiolytic products ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ ) to yield water, the dependence of the yield of oxidation or deduction on the concentrations of tellurium compounds was elucidated quantitatively. The rate constant of the reaction  $\text{Te(VI)} + \text{H}$  was estimated to be about  $5 \times 10^6 \text{ M}^{-1} \text{ sec.}^{-1}$

### I. INTRODUCTION

$\gamma$ -Radiolysis of Te(IV) or Te(VI)\*\* in 0.4 M  $\text{H}_2\text{SO}_4$  solutions was investigated by M. Haissinsky *et al.*<sup>1)</sup> and the following mechanism was proposed:



Since several competing reactions can occur at the same time, the kinetics of the overall process is complex and depends on the chemical atmosphere. For example, in the absence of oxygen, the reduction of Te(VI) (reaction (2)) can compete effectively with the oxidation of Te(IV) (reaction (1)). Therefore, it is desirable to investigate in detail the overall kinetics with Te(IV) and Te(VI) labelled with respective tracers.

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\*\* Te(IV) is probably present as a mixture of  $\text{H}_2\text{TeO}_3$  and  $\text{HTeO}_2^+$  in acid solution and Te(VI) is as a mixture of  $\text{H}_6\text{TeO}_6$  and  $\text{H}_2\text{TeO}_4$ .<sup>3)</sup> For simplification we denote as Te(IV) and Te(VI).

In this paper, the radiation induced reactions of tellurium compounds in de-aerated 0.4 M  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  solutions are investigated and the results are explained by the mechanism proposed by M. Haissinsky *et al.*<sup>1)</sup>

## II. EXPERIMENTAL

$^{132}\text{Te}$  (half life: 78 h) was separated from fission products and  $^{123m}\text{Te}$  (half life: 117 d) was produced by irradiating natural tellurium at the Kyoto University Reactor.  $\text{Te(IV)}$  labelled with  $^{132}\text{Te}$  ( $\sim 1$  mCi/g) and  $\text{Te(VI)}$  labelled with  $^{123m}\text{Te}$  ( $\sim 1$  mCi/g) were prepared.<sup>2)</sup> The concentrations of  $\text{Te(IV)}$  and  $\text{Te(VI)}$  in 0.4 M  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  solutions are shown in table I. Sample solutions were de-aerated with nitrogen gas for about two hours, were sealed in quartz tubes and were then irradiated with  $\gamma$ -ray at the  $^{60}\text{Co}$   $\gamma$ -ray irradiation facility of the Institute for Chemical Research, Kyoto University. The dose rate was kept constant at  $6.5 \times 10^4$  rad/h.

After irradiation, the sample solution was transferred into 10 ml of 6 M HCl containing each 10 mg of  $\text{Te(IV)}$  and  $\text{Te(VI)}$  carriers. The solution was passed through an ion-exchange column (2 cm $\phi$   $\times$  5 cm) containing Dowex-1X8 (RCl, 100 $\sim$ 200 mesh) and the column was washed with several free volumes of HCl solution of the same concentration.  $\text{Te(VI)}$ , which passed through the column, was reduced to the metallic form by boiling the solution with hydrazine hydrochloride and  $\text{NaHSO}_3$ .  $\text{Te(IV)}$  absorbed in the column was eluted with 20 ml of 0.1 M HCl solution and was reduced to the metallic form by  $\text{NaHSO}_3$ . The chemical yields of  $\text{Te(IV)}$  and  $\text{Te(VI)}$  were found to be 80 $\sim$ 90 %.

The 159 KeV  $\gamma$ -ray associated with  $^{123m}\text{Te}$  and the 228 KeV  $\gamma$ -ray associated with  $^{132}\text{Te}$  were analysed with a 54 cm<sup>3</sup> Ge(Li) detector connected to 400 ch. PHA, and the amounts of oxidation of  $\text{Te(IV)}$  and those of reduction of  $\text{Te(VI)}$  were obtained.

## III. RESULTS AND DISCUSSION

Both the amounts of oxidation of  $\text{Te(IV)}$  and those of reduction of  $\text{Te(VI)}$  induced by radiation were proportional to the absorbed dose ( $1 \times 10^5 \sim 5 \times 10^5$  rad). Table I shows the yields of oxidation of  $\text{Te(IV)}$  and reduction of  $\text{Te(VI)}$  ( $G(\text{Te(VI)})$  and  $G(\text{Te(IV)})$ ). It was testified at the same time that there was no exchange reaction between  $\text{Te(IV)}$  and  $\text{Te(VI)}$  in the unirradiated samples.

From the table, we can draw two conclusions: (A) compared with the well known yields of OH radicals and H atoms in acid solution ( $g_{\text{OH}}=2.96$ ,  $g_{\text{H}}=3.68^{4)}$ , the observed yields of oxidation and reduction of tellurium compounds are very low, and (B) the yields increase in proportion to their own concentrations as shown in Figs. 1 and 2.

The predominant reactions in  $\text{H}_2\text{SO}_4$  solutions must be those with the stable radiolytic products ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ ) (reactions (4) to (8)), since  $\text{SO}_4^{2-}$  ion is not reactive. In  $\text{HNO}_3$  solutions, on the other hand, H atoms also react with  $\text{NO}_3^-$  ions following the reaction:



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It was shown in Fig. 2 that the yield of reduction in the  $\text{HNO}_3$  solution is much lower than that in the  $\text{H}_2\text{SO}_4$  solution.

Table I. The Yields of Oxidation and Reduction of Tellurium Compounds in 0.4 M  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  Solution

Sample	[Te (IV)]	[Te (VI)]	$G(\text{Te (VI)})$	$G(\text{Te (IV)})$
$\text{H}_2\text{SO}_4$ -1	2.1 ( $10^{-4}\text{M}$ )	4.5 ( $10^{-4}\text{M}$ )	0.070	0.066
2	2.3	2.3	0.066	0.036
3	2.1	1.2	0.059	0.017
4	2.3	0.5	0.056	0.007
5	1.3	4.3	0.045	0.064
6	0.5	4.7	0.030	0.063
7	0.2	4.8	0.008	0.061
$\text{HNO}_3$ -1	2.1	2.9	0.040	0.020
2	2.0	1.9	0.040	0.013
3	2.0	0.8	0.041	0.006
4	2.1	0.2	0.040	0.002
5	1.1	3.4	0.029	0.040
6	0.5	3.9	0.013	0.040
7	0.3	4.0	0.010	0.030

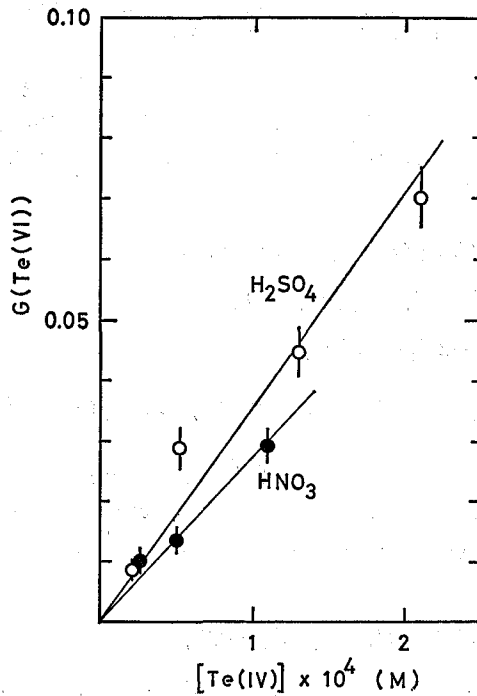


Fig. 1. The yield of oxidation  $G(\text{Te(VI)})$  vs.  $[\text{Te(IV)}]$ .  $[\text{Te(VI)}]$  is kept constant at  $\sim 4 \times 10^{-4}$  M and  $[\text{H}_2\text{SO}_4]$  or  $[\text{HNO}_3]$  is 0.4 M.

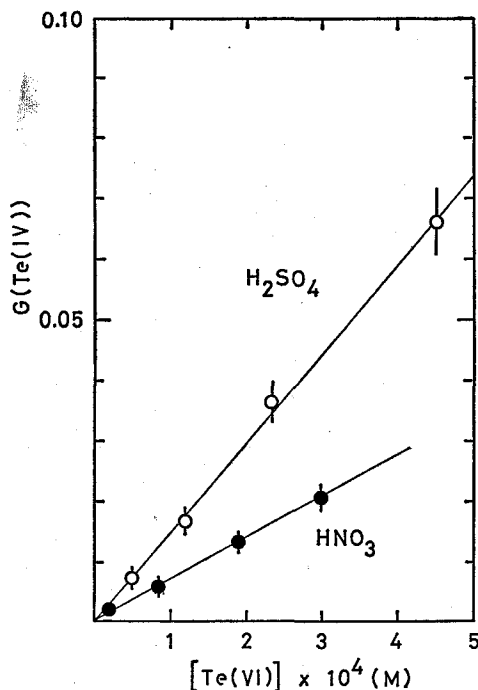


Fig. 2. The yield of reduction  $G(\text{Te(IV)})$  vs.  $[\text{Te(VI)}]$ .  $[\text{Te(IV)}]$  is kept constant at  $\sim 2 \times 10^{-4}$  M and  $[\text{H}_2\text{SO}_4]$  or  $[\text{HNO}_3]$  is 0.4 M.

Since the yields of reactions (1)~(3) are negligibly small, application of stationary state kinetics in  $\text{H}_2\text{SO}_4$  solution to OH, H, and  $\text{HO}_2$  radicals leads to the following equations:

$$G(\text{OH}) = 2.96 + G_6 - G_7 - G_8 = 0, \quad (\text{I})$$

$$G(\text{H}) = 3.68 - G_5 - G_6 + G_8 = 0, \quad (\text{II})$$

$$G(\text{HO}_2) = -2G_4 + G_5 + G_7 = 0, \quad (\text{III})$$

where the values 2.96 and 3.68 are the primary radiolytic yields of OH and H radicals, respectively.<sup>4)</sup>

$G(\text{H}_2\text{O}_2)$  was found to be about 0.3 in the sample  $\text{H}_2\text{SO}_4-1$ . This yield is nearly equal to that measured by M. Haissinsky *et al.* in a deaerated solution containing  $5 \times 10^{-4}$  M Te(IV) or  $5 \times 10^{-4}$  M Te(VI).<sup>1)</sup> We can get the following equation:

$$G(\text{H}_2\text{O}_2) = 0.81 + G_4 - G_6 - G_7 \approx 0.3, \quad (\text{IV})$$

where the value 0.81 is the primary radiolytic yield of  $\text{H}_2\text{O}_2$ <sup>4)</sup>. As the rate constant  $k_5$  is known to be large enough to permit stationary state kinetics on oxygen ( $k_5 = 1.2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ ),<sup>5)</sup> we can also get the following equation:

$$G(\text{O}_2) = G_4 - G_5 \approx 0. \quad (\text{V})$$

Combining equations (I) to (V), we obtain the following reaction yields:

$$\begin{aligned} G_4 &\approx G_5 \approx G_7 \approx 3.32, \\ G_6 &\approx 0.51, \quad G_8 \approx 0.15. \end{aligned} \quad (\text{VI})$$

It is of interest that one can estimate the rate constant  $k_2$  using the obtained reaction yields  $G_2$  and  $G_6$ . We can write:

$$\frac{G_2}{G_6} = \frac{2G(\text{Te(IV)})}{G_6} = \frac{k_2[\text{Te(VI)}]}{k_6[\text{H}_2\text{O}_2]}.$$

From the mean value of  $[\text{H}_2\text{O}_2]$  in the irradiation of about  $1 \times 10^{-4}$  M combined with the value of  $G(\text{Te(IV)})/[\text{Te(VI)}] = 1.5 \times 10^2$  obtained from Fig. 2, with  $G_6 \approx 0.51$  and with  $k_6 = 9 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$  <sup>6)</sup> we can get:

$$k_2 \approx 5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$$

Because the concentration of hydrogen peroxide could not be measured accurately and because several approximations were included in the deduction, the value of  $k_2$  thus obtained is tentative. However, this value is significantly lower than that of  $1.05 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$  found by M. Haissinsky *et al.*<sup>1)</sup> Their value  $G_2$  obtained indirectly from observing  $G_2 - G_{11}$ , might be overestimated compared with our value  $G_2$  which was measured directly.

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