γ-Radiolysis of Aqueous Solutions of Tellurium

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Received December 23, 1976

Radiation induced reactions of Te(IV) and Te(VI) compounds labelled with $^{132}$Te and $^{123m}$Te respectively, in deaerated 0.4 M H$_2$SO$_4$ or HNO$_3$ solution, were investigated by the use of a $^{60}$Co γ-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 (H$_2$O$_2$, H$_2$, 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 Te(VI)+H was estimated to be about $5 \times 10^6$ M$^{-1}$ sec.$^{-1}$

I. INTRODUCTION

γ-Radiolysis of Te(IV) or Te(VI)** in 0.4 M H$_2$SO$_4$ solutions was investigated by M. Haissinsky et al. and the following mechanism was proposed:

$$H_2O \rightarrow H, OH, H_2, H_2O_2 ,$$

$$Te(IV) + OH \rightarrow Te(V) ,$$

$$2Te(V) \rightarrow Te(IV) + Te(VI) ,$$

$$Te(VI) + H \rightarrow Te(V) ,$$

$$Te(IV) + HO_2 \rightarrow Te(VI) + OH ,$$

$$2HO_2 \rightarrow H_2O_2 + O_2 ,$$

$$H + O_2 \rightarrow HO_2 ,$$

$$H_2O_2 + H \rightarrow H_2O + OH ,$$

$$H_2O_2 + OH \rightarrow H_2O + HO_2 ,$$

$$H_2 + OH \rightarrow H_2O + H .$$

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 H$_2$TeO$_3$ and HTeO$_2^+$ in acid solution and Te(VI) is as a mixture of H$_6$TeO$_6$ and H$_2$TeO$_4$. 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 H₂SO₄ or HNO₃ solutions are investigated and the results are ex-
plained by the mechanism proposed by M. Haissinsky et al.13

II. EXPERIMENTAL

¹²³Te(half life: 78 h) was separated from fission products and ¹²³ᵐTe (half life:
117 d) was produced by irradiating natural tellurium at the Kyoto University Re-
actor. Te(IV) labelled with ¹²³Te (~1 mCi/g) and Te(VI) labelled with ¹²³ᵐTe
(~1 mCi/g) were prepared.39 The concentrations of Te(IV) and Te(VI) in 0.4
M H₂SO₄ or HNO₃ solutions are shown in table I. Sample solutions were deaerated
with nitrogen gas for about two hours, were sealed in quartz tubes and were then
irradiated with γ-ray at the ⁶⁰Co γ-ray irradiation facility of the Institute for Chemical
Research, Kyoto University. The dose rate was kept constant at 6.5 × 10⁴ rad/h.

After irradiation, the sample solution was transferred into 10 ml of 6 M HCl
containing each 10 mg of Te(IV) and Te(VI) carriers. The solution was passed
through an ion-exchange column (2 cm²×5 cm) containing Dowex-1X8 (RCl,
100~200 mesh) and the column was washed with several free volumes of HCl solu-
tion of the same concentration. Te(VI), which passed through the column, was
reduced to the metallic form by boiling the solution with hydrazine hydrochloride
and NaHSO₃. 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 NaHSO₃. The chemical yields
of Te(IV) and Te(VI) were found to be 80~90 %.

The 159 KeV γ-ray associated with ¹²³ᵐTe and the 228 KeV γ-ray associated
with ¹³²Te were analysed with a 54 cm² Ge(Li) detector connected to 400 ch. PHA,
and the amounts of oxidation of Te(IV) and those of reduction of Te(VI) were ob-
tained.

III. RESULTS AND DISCUSSION

Both the amounts of oxidation of Te(IV) and those of reduction of Te(VI) in-
duced by radiation were proportional to the absorbed dose (1×10⁵~5×10⁵ rad).
Table I shows the yields of oxidation of Te(IV) and reduction of Te(VI) (G(Te(VI))
and G(Te(IV))). It was testified at the same time that there was no exchange
reaction between Te(IV) and 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 (gOH=2.96, gH=3.68⁹),
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 H₂SO₄ solutions must be those with the stable
radiolytic products (H₂O₂, H₂, O₂) (reactions (4) to (8)), since SO₂⁻ ion is not re-
active. In HNO₃ solutions, on the other hand, H atoms also react with NO₃⁻ ions
following the reaction:

\[ \text{H} + \text{NO}_3^- \rightarrow \text{NO}_2 + \text{OH}^- \]  

(9)
It was shown in Fig. 2 that the yield of reduction in the HNO₃ solution is much lower than that in the H₂SO₄ solution.

Table I. The Yields of Oxidation and Reduction of Tellurium Compounds in 0.4 M H₂SO₄ or HNO₃ Solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Te (IV)]</th>
<th>[Te (VI)]</th>
<th>G(Te (VI))</th>
<th>G(Te (IV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄-1</td>
<td>2.1 (10⁻⁴M)</td>
<td>4.5 (10⁻⁴M)</td>
<td>0.070</td>
<td>0.066</td>
</tr>
<tr>
<td>2</td>
<td>2.3</td>
<td>2.3</td>
<td>0.066</td>
<td>0.036</td>
</tr>
<tr>
<td>3</td>
<td>2.1</td>
<td>1.2</td>
<td>0.059</td>
<td>0.017</td>
</tr>
<tr>
<td>4</td>
<td>2.3</td>
<td>0.5</td>
<td>0.056</td>
<td>0.007</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>4.3</td>
<td>0.045</td>
<td>0.064</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>4.7</td>
<td>0.030</td>
<td>0.063</td>
</tr>
<tr>
<td>7</td>
<td>0.2</td>
<td>4.8</td>
<td>0.008</td>
<td>0.061</td>
</tr>
<tr>
<td>HNO₃-1</td>
<td>2.1</td>
<td>2.9</td>
<td>0.040</td>
<td>0.020</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>1.9</td>
<td>0.040</td>
<td>0.013</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>0.8</td>
<td>0.041</td>
<td>0.006</td>
</tr>
<tr>
<td>4</td>
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<td>0.040</td>
<td>0.002</td>
</tr>
<tr>
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<td>3.4</td>
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<td>0.040</td>
</tr>
<tr>
<td>6</td>
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<td>3.9</td>
<td>0.013</td>
<td>0.040</td>
</tr>
<tr>
<td>7</td>
<td>0.3</td>
<td>4.0</td>
<td>0.010</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Fig. 1. The yield of oxidation G(Te(VI)) vs. [Te(IV)]. [Te(VI)] is kept constant at ~4×10⁻⁴ M and [H₂SO₄] or [HNO₃] 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) $\sim$ (3) are negligibly small, application of stationary state kinetics in H$_2$SO$_4$ solution to OH, H, and HO$_2$ radicals leads to the following equations:

\begin{align*}
G(\text{OH}) &= 2.96 + G_6 - G_7 - G_8 = 0, \\
G(\text{H}) &= 3.68 - G_5 - G_6 + G_8 = 0, \\
G(\text{HO}_2) &= -2G_4 + G_5 + G_7 = 0,
\end{align*}

where the values 2.96 and 3.68 are the primary radiolytic yields of OH and H radicals, respectively.

$G(\text{H}_2\text{O}_2)$ was found to be about 0.3 in the sample H$_2$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). We can get the following equation:

\begin{equation}
G(\text{H}_2\text{O}_2) = 0.81 + G_4 - G_6 - G_7 = 0.3, \tag{IV}
\end{equation}

where the value 0.81 is the primary radiolytic yield of H$_2$O$_2$. As the rate constant $k_5$ is known to be large enough to permit stationary state kinetics on oxygen ($k_5 = 1.2 \times 10^{10}$ M$^{-1}$ sec$^{-1}$), we can also get the following equation:
\[ G(O_2) = G_4 - G_5 = 0. \]  
\[ \text{Combining equations (I) to (V), we obtain the following reaction yields:} \]

\[ G_4 = G_5 = G_6 = 3.32, \]
\[ G_6 = 0.51, \quad G_6 = 0.15. \]

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:

\[ \frac{G_2}{G_6} = 2G(\text{Te}(IV)) = \frac{k_2[G(\text{Te}(VI))]}{k_6[H_2O_2]}. \]

From the mean value of \([H_2O_2]\) 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 \( G_6 = 0.51 \) and with \( k_6 = 9 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1} \), we can get:

\[ k_2 = 5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}. \]

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. Their value \( G_2 \) obtained indirectly from observing \( G_2 - G_1 \), might be overestimated compared with our value \( G_2 \) which was measured directly.

**ACKNOWLEDGMENT**

We would like to thank Mr. Rintaro Katano at the Institute for Chemical Research, Kyoto University for his aid in performing the irradiations.

**REFERENCES**