Tellurium(V). A Pulse Radiolysis Study

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Four different tellurium(V) oxoradicals, assumed to be H₂TeO₄⁻, TeO₃⁻, H₃TeO₄²⁻, and TeO₄³⁻, were detected by the pulse radiolysis technique. H₂TeO₄⁻ is the product of the reaction of OH with HTeO₃⁻, whereas HTeO₃²⁻ and TeO₃⁻ arise by reactions of OH and O²⁻ with the TeO₂⁻. TeO₃⁻ is a secondary product formed by dehydration of H₂TeO₃⁻, a process catalyzed by HTeO₃⁻. The same tellurium(V) species except H₂TeO₄⁻ are formed by reaction of the hydrated electron with H₃TeO₄⁻, H₂TeO₃⁻, and H₄TeO₄²⁻. The spectra, kinetics of the reactions of the tellurium(V) species, the acidity constant of H₃TeO₄²⁻ (~10⁻¹³), and the apparent acidity constant of TeO₃⁻ (10⁻¹⁰) have been measured. The standard Gibbs energies of formation ΔG°(TeO₃⁻) = -214 kJ/mol, ΔG°(HTeO₃⁻) = -394 kJ/mol, and ΔG°(TeO₃²⁻) = -319 kJ/mol were determined from the rate constants for the forward and reverse reactions TeO₃²⁻ + O²⁻ ⇌ TeO₃⁻ and TeO₃⁻ + OH⁻ ⇌ HTeO₃⁻, combined with the acidity constants of TeO₃⁻ and H₃TeO₄²⁻ and the standard Gibbs energy of formation of OH, O²⁻, and TeO₂⁻. TeO₃⁻ is a strong reducing agent (Eₒ(red) = -0.40 V), which appears to reduce O₂, as well as a strong oxidant (Eₒ(ox) = 1.74 V), oxidizing CO₃²⁻ to CO₃⁻.

Introduction

Oxoradicals of the group six elements sulfur, selenium, and tellurium in the oxidation state V may be formed in aqueous solution.⁶ The only S(V) radical observed is SO₃²⁻; selenium similarly forms SeO₃⁻ and, in strongly alkaline solution also, HSeO₃²⁻. Whereas the S(V) and Se(V) radicals have been characterized in detail, little is known about the properties of the corresponding oxoradicals of tellurium. However, it has been shown previously that Te(V), like S(V) and Se(V), is amenable to study in aqueous solution by the pulse radiolysis technique.⁷⁻⁹ Here Te(V) species may be formed by reduction of telluric acid (H₂TeO₄⁻) and the tellurates (H₃TeO₄⁻, H₂TeO₃⁻) with the hydrated electron, eₒ⁻, as well as by oxidation of hydrogen tellurite (HTeO₃⁻) and tellurite (TeO₃⁻) with OH or O²⁻. A transient absorbance detected in an O₂-containing tellurite solution after irradiation was assigned to TeO₂⁻, a species similar to SO₃⁻ and SeO₃⁻. This assignment was substantiated by the detection of TeO₂⁻ in tellurite crystals irradiated with X-rays.¹¹ TeO₃⁻ has in the solid matrix the same symmetry (C₃ᵥ) as TeO₃²⁻. Also reactions of eₒ⁻ with telluric acid and tellurate have been studied, but no transient absorbance was assigned to Te(V) species.⁷,⁸

Since not only SeO₃⁻ but also HSeO₃²⁻ are observed by pulse radiolysis of aqueous selenite and selenate solutions⁸ a more comprehensive pulse radiolysis study of aqueous tellurite and tellurate may be expected similarly to reveal the formation of tellurium(V) species other than TeO₃⁻. In the present study, we have measured the spectra and kinetics of the transient absorbances that arise in aqueous solution by the reaction of OH and O²⁻ with telluric acid, and of those that arise by the reaction of eₒ⁻ with telluric acid. On the basis of these measurements we assign the absorbances to four Te(V) species of definite composition, and their evolution in time to reactions among these species. We have determined rate constants for the reactions and constants for the observed equilibria involving Te(V) species, and estimated the standard free energy of formation of these species. Moreover, we have measured the kinetics of the reactions of the Te(V) species with molecular oxygen and with hydrogen carbonate and carbonate. The properties of Te(V) oxoradicals are compared to those of the corresponding S(V) and Se(V) oxoradicals.

Experimental Section

Pulse radiolysis was made at ambient temperature (±1 °C) with the HCR linac at Risø delivering 10 MeV in single square pulses. The pulse length was varied between 0.1 and 1 μs. The dose, ranging from 2.5 to 20 Gy, was measured with the ferrocyanide dosimeter¹² taking the extinction coefficient of ferricyanide at 420 nm equal to 1000 cm⁻¹ M⁻¹ and the G-value (molecules/100 eV) for formation of ferricyanide equal to 5.9. Yields of products were calculated from the measured dose using published G-values corrected for spur reactions.¹³ The experimental setup for irradiation and for kinetic spectroscopy measurements were as previously described.⁶ Chemicals were reagent grade or of higher purity. Solutions were prepared with triply distilled water. Nitrous oxide, N₄⁸ (purity 99.998%), was ALPHAGAZ. Argon, oxygen, and nitrogen, all N₄⁰ (purity 99.99%), were supplied by Dansk Ilt og Brint.

Solutions were purged of oxygen by bubbling-through with Ar or N₂O at 0.1 MPa. In studies of reactions of eₒ⁻, Ar was
used. N\textsubscript{2}O was used when interference from reactions of e\textsubscript{aq} was to be avoided. N\textsubscript{2}O converts e\textsubscript{aq} into O\textsuperscript{−} in a fast reaction,

\[
\text{N}_2\text{O} + e_{\text{aq}}^- \rightarrow \text{N}_2 + \text{O}^- \quad k_1 = 9.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1}
\]

pH was adjusted by addition of sodium hydroxide and perchloric acid and was, for pH < 12, measured with a pH-meter (Radiometer pH M 64). For pH > 12, pH was taken equal to 14 + \log[NaOH]. The pK\textsubscript{a}-values for the dissociations of tellurous and telluric acid were determined by pH-metric titration of 10\textsuperscript{−3} M sodium tellurite and telluric acid with perchloric acid and sodium hydroxide, respectively, using a Radiometer titrator TTT 60 fitted with a Radiometer autoburette ABU (volume 0.25 mL). For H\textsubscript{2}TeO\textsubscript{3} we found pK\textsubscript{1} = 6.3 and pK\textsubscript{2} = 9.6, and for H\textsubscript{2}TeO\textsubscript{6} pK\textsubscript{1} = 7.8 and pK\textsubscript{2} = 11.0, in agreement with recently recommended values.\textsuperscript{17}

Simulation of kinetic data was performed using the computer package “Gepasi” equipped with the optimization module Multistart (Levenberg−Marquardt) Version 1.00.\textsuperscript{18−20}

Results and Discussion

Reaction of H\textsubscript{2}TeO\textsubscript{3} and HTeO\textsubscript{3}− with OH, and Reactions of TeO\textsubscript{3}− with OH and O\textsuperscript{−}. The measurements were made with 10\textsuperscript{−4}−10\textsuperscript{−2} M solutions prepared from sodium tellurite at pH ranging from 6.6 to 13.5. Measurements at pH < 6 proved unreliable since such solutions became turbid on standing. Upon irradiation of N\textsubscript{2}O-saturated tellurous solutions, a transient absorbance was observed to grow-in at $\lambda < 430$ nm in a pseudo first-order reaction with a rate constant proportional to the concentration of tellurous acid. We ascribe the transient absorbance to formation of Te(V) species by reactions of OH and O\textsuperscript{−}. (Absorbance changes owing to removal of Te(IV) by the irradiation were neglected throughout.) The spectrum and the time evolution of the transient absorbance depend on pH. Figures 1, 2, and 3, illustrate the absorbance changes observed after irradiation of 2 × 10\textsuperscript{−4} M Te(IV) solutions with a dose of 19.8 Gy. Figure 1 shows the spectrum of the transient absorbance measured 2 $\mu$s and 50 $\mu$s after the irradiation at pH 8.15, 10.6, and pH 13.5. The three spectra are clearly distinct initially (at 2 $\mu$s), and they evolve differently in time. At pH 13.5, no time evolution is detected. At pH 10.6, the absorbance decreases only slightly with time while the spectrum is unchanged. In contrast, the spectrum recorded at pH 8.15 2 $\mu$s after the irradiation is very different from that recorded after 50 $\mu$s, the initial maximum at 355 nm giving way to a shoulder at ~340 nm. Figure 2, showing the absorbance change at 300 and 380 nm after irradiation (dose 19.8 Gy). The smooth curves are simulations calculated with the Gepasi package\textsuperscript{21−23} (see text).

Figure 3 shows the pH-dependence of the transient absorbance at 380 nm. The absorbance increases with increasing pH and...
Tellurium(V). A Pulse Radiolysis Study

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TABLE 1: Summary of Reactions and Constants

<table>
<thead>
<tr>
<th>reaction/equilibrium</th>
<th>rate constant/M⁻¹.s⁻¹; pK-values</th>
<th>ionic strength/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O + e⁻ → N₂ + O⁻</td>
<td>k₁ = 9.1 × 10⁹</td>
<td>&lt;10⁻⁵</td>
</tr>
<tr>
<td>H₂TeO₄⁻ + OH⁻ → H₃TeO₄⁻ + H⁺</td>
<td>k₂ = (6.1 ± 0.6) × 10⁶</td>
<td>&lt;10⁻³</td>
</tr>
<tr>
<td>TeO₂⁻ + O⁻ ↔ TeO₃⁻</td>
<td>k₃ = (4.8 ± 0.5)b × 10³</td>
<td>&lt;10⁻³, 10⁻²—0.3</td>
</tr>
<tr>
<td>TeO₂⁻ + OH⁻ → H₃TeO₄⁻</td>
<td>k₄ = (1.0 ± 0.10) × 10⁴</td>
<td>0.1; 10⁻²—0.3</td>
</tr>
<tr>
<td>H₂TeO₄⁻ → H₂TeO₄⁻ + H₂O</td>
<td>k₅ = 10⁴</td>
<td>5 × 10⁻³</td>
</tr>
<tr>
<td>H₂TeO₄⁻ + H₂O → H₂TeO₃⁻ + H₂O</td>
<td>k₆ = 10⁴</td>
<td>5 × 10⁻³</td>
</tr>
<tr>
<td>H₂₂TeO₄⁻ + H₂O → H₂₂TeO₅⁻ + H²O</td>
<td>k₇ = 10⁴</td>
<td>10⁻²—3 × 10⁻²</td>
</tr>
<tr>
<td>H₂TeO₄⁻ → H₂TeO₃⁻ + H⁺</td>
<td>k₈ = 10³</td>
<td>10⁻³—0.3</td>
</tr>
<tr>
<td>H₂TeO₄⁻ + H₂O → H₂TeO₃⁻ + H⁺</td>
<td>k₉ = 10³</td>
<td>10⁻²</td>
</tr>
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<td>H₂TeO₄⁻ + H₂O → H₂TeO₃⁻ + H₂O</td>
<td>k₁₀ = 10³</td>
<td>&lt;10⁻²</td>
</tr>
<tr>
<td>H₂TeO₄⁻ + H₂O → H₂TeO₅⁻ + H⁺</td>
<td>k₁₁ = 10³</td>
<td>&lt;10⁻²</td>
</tr>
<tr>
<td>H₂TeO₄⁻ + H₂O → H₂TeO₅⁻ + 2H₂O</td>
<td>k₁₂ = 10³</td>
<td>&lt;10⁻²</td>
</tr>
<tr>
<td>H₂TeO₄⁻ + H₂O → H₂TeO₅⁻ + 2H₂O</td>
<td>k₁₃ = 10³</td>
<td>&lt;10⁻²</td>
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<td>H₂TeO₄⁻ + H₂O → H₂TeO₅⁻ + H₂O</td>
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<td>&lt;10⁻²</td>
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<tr>
<td>H₂TeO₄⁻ + H₂O → H₂TeO₅⁻ + 2H₂O</td>
<td>k₁₅ = 10³</td>
<td>&lt;10⁻²</td>
</tr>
</tbody>
</table>

As shown in Figure 4, the transient absorption spectrum is similar to that obtained in N₂O-saturated tellurite solutions at the same pH. These observations suggest that HTeO₂⁻ and TeO₄⁻ may disappear by the reverse of reactions 4 and 5

H₄TeO₄⁻ → H₂TeO₄⁻ + OH⁻  k₄
TeO₂⁻ + O⁻ ↔ TeO₃⁻  k₅

as well as by the reactions 13 and 14. The reactions -4 and -5 parallel the thermal split-off of O⁻ or OH from the electron adducts of selenate,² periodate,²⁴ and peroxinate.²⁵

At pH < 11, the transient absorption spectrum is similar to that observed in tellurite solutions after the transient ascribed to H₂TeO₄⁻ has decayed. Moreover, the absorbance decays without change of spectrum in a second-order process that matches the decay of TeO₃⁻.

These observations indicate that TeO₃⁻ is formed directly by reaction of e⁻ with H₂TeO₆

H₂TeO₆ + e⁻ → TeO₃⁻ + 3H₂O  k₁₅

rather than via H₂TeO₄⁻ as is the case in the reaction of OH with HTEO₃⁻.

The reactions and equilibria discussed above are summarized in Table 1.

**Determination of the Spectra of TeO₃⁻, H₂TeO₄⁻, H₂TeO₅⁻, and TeO₄⁻**

The spectra of TeO₃⁻, H₂TeO₄⁻, H₂TeO₅⁻, and TeO₄⁻, represented by the extinction coefficients versus wavelength, ε₉TeO₃⁻(λ), ε₉H₂TeO₄⁻(λ), ε₉H₂TeO₅⁻(λ), and ε₉TeO₄⁻(λ), are shown in Figure 4, ε₉TeO₃⁻(λ), ε₉H₂TeO₄⁻(λ), and ε₉TeO₄⁻(λ), were obtained from transient absorbances measured in 2 × 10⁻³ M telluric acid 2 µs after the irradiation at pH 8, 11.4, and 13.48, respectively.

Figure 4. Spectra of TeO₃⁻, H₂TeO₄⁻, H₂TeO₅⁻, and TeO₄⁻ calculated from measurements (see text).

Owing its large base strength, TeO₄⁻ cannot be made the predominant Te(V) solute. εTeO₄⁻(λ) was obtained from eq 16

εTeO₄⁻(λ) = (ε(λ) - εH₂TeO₄⁻(λ)(1 - x₉TeO₄⁻))(λ)  (16)

where ε(λ) is the spectrum of the equilibrium mixture of TeO₃⁻ and H₂TeO₅⁻ in 0.3 M NaOH, and x₉TeO₄⁻ is the fraction of Te(V) present as TeO₄⁻, found to be 0.63 in 0.3 M NaOH (see eq 25 below).

The overlap of reactions 2 and 3 with reactions 6 and 6a precludes a direct determination of the spectrum of H₄TeO₆⁻. ε₉H₂TeO₄⁻(λ) shown in Figure 4 was calculated from absorbances measured 2 µs after the irradiation of a tellurite solution at pH 8 (where Te(V) species other than TeO₃⁻ and H₂TeO₄⁻ may be neglected) and the concentrations at that time of H₂TeO₄⁻ and TeO₃⁻. These concentrations were obtained as a function of time from a simulation of the absorbance at 350 nm during the first 5 µs after the irradiation. The simulation was based on the reactions 3, 6 and 6a, accounting for the formation of H₂TeO₄⁻ and its transformation into TeO₃⁻, respectively,
The value of $k_{6}$ to $k_{18}$ supplemented by the competing removal of OH by reactions 17 and 18

$$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$$  \hspace{1cm} (17)

$$\text{H} + \text{OH} \rightarrow \text{H}_2\text{O}$$  \hspace{1cm} (18)

The value of $e_{\text{TeO}_3^-}$ at 350 nm and the values of the rate constants $k_3$, $k_6$, and $k_{6a}$ used in the simulation were as determined (Table 1). The rate constants of reactions 17 and 18 and $k_{6a}$ were taken to be $5.5 \times 10^7$ M$^{-1}$ s$^{-1}$ and $7 \times 10^9$ M$^{-1}$ s$^{-1}$, respectively. Fitting the calculated absorbance to the measured by adjusting the value of $e_{\text{H}_2\text{TeO}_4^-}$ at 350 nm, we then obtained the concentrations of $\text{H}_2\text{TeO}_4^- \text{ and TeO}_3^-$ 2 $\mu$s after the irradiation. With these concentrations and $e_{\text{TeO}_3^-}$, we obtained $e_{\text{H}_2\text{TeO}_4^-}$ shown in Figure 4 from the measured absorbance.

**Determination of Rate Constants for Reactions of $\text{H}_2\text{TeO}_4^-$, $\text{TeO}_3^-$, $\text{H}_2\text{TeO}_4^2-$, and $\text{TeO}_3^2-$**. Rate constants determined below are shown in Table 1. Throughout the analysis we neglect possible reactions of hydrogen tellurite and tellurate with the hydrogen atom formed in the primary radiolytic process.

Recalling that the observed kinetics of absorbance change was independent of pH in the region from 6 to 8.5, we may assume that the rate constants $k_3$ and $k_6$ for the reactions of OH with $\text{H}_2\text{TeO}_3$ and $\text{HTeO}_3^-$ are similar. $k_4$ and the rate constants for the reactions of OH and $\text{O}^-$ with $\text{TeO}_3^2-$, $k_4$ and $k_5$, were determined from the rate of growing-in of the absorbance at 350 nm after irradiation of $10^{-2}$ M hydrogen tellurite and tellurate solutions with 2.5 Gy (Table 1). The values of $k_4$ and $k_5$ were determined from the rate observed in solutions at pH 8 and at pH 13.3, respectively. Then, $k_4$ was determined from the relation

$$k_{19} = k_4 \times x_{\text{OH}} + k_5 \times (1 - x_{\text{OH}})$$  \hspace{1cm} (19)

where $k_{19} = 4.4 \times 10^9$ M$^{-1}$ s$^{-1}$ is the rate constant for formation of tellurium(V) at pH 10.9 and $x_{\text{OH}}$ is given by $x_{\text{OH}} = (1 + K_{\text{OH}} \times 10^{\beta_{\text{OH}}})^{-1}$, under the assumption that the equilibrium between OH and $\text{O}^-$ is maintained during the reaction ($K_{\text{OH}} = 10^{-11.9}$).16

The rate constants $k_6$ and $k_{6a}$ for the uncatalyzed and the catalyzed dehydration of $\text{H}_2\text{TeO}_4^-$ were obtained from measurements of the rate constant $k_{6b}$ for the decrease of absorbance at 350 nm in solutions at pH 8 containing $\text{HTeO}_3^-$ in varying concentration. Figure 5 shows a plot of $k_{6b}$ against [HTeO$_3^-$]. $k_6$ and $k_{6a}$ shown in Table 1 were obtained from a fit of a linear function to the plot, $k_6$ as the constant term, and $k_{6a}$ as the coefficient to [HTeO$_3^-$]. We noted that the data do not allow an accurate determination of $k_6$. We find $k_6$ to be around $10^4$ s$^{-1}$, which is the same order of magnitude as found for the uncatalyzed dehydration of the As(IV) species As(OH)$_2$O$^{2-}$.

Reaction 7 between $\text{H}_2\text{TeO}_4^-$ and $\text{TeO}_3^2-$ was not observed directly. A value of $\sim 10^8$ M$^{-1}$ s$^{-1}$ was estimated for the rate constant, $k_7$.

The rate constants $k_{11}$, $k_{12}$, and $k_{13}$ for the reactions 11–13, by which $\text{TeO}_3^-$ and $\text{HTeO}_3^2-$ disappear, were determined from $k_{22}$, the second-order rate constant for the decay of the absorbance OD(t) at 350 nm measured at pH values between 8.15 and 11.76. Since in the actual experiments pH remains constant and equilibrium between $\text{TeO}_3^-$ and $\text{HTeO}_3^2-$ is maintained during the decay, the fraction $x_{\text{TeO}_3^-}$ of the total concentration c(t) of Te(V) that is present as $\text{TeO}_3^-$ remains constant. Consequently, the integrated rate equation for the simultaneous disappearance of $\text{TeO}_3^-$ and $\text{HTeO}_3^2-$ may be expressed by

$$c(t)^{-1} - c(t = 0)^{-1} = (2k_{11} \times x_{\text{HTeO}_3^-} + k_{12} \times x_{\text{TeO}_3^-} - (1 - x_{\text{TeO}_3^-}) + 2k_{13} \times (1 - x_{\text{TeO}_3^-}))^{-1} \times t$$  \hspace{1cm} (20)

where $x_{\text{TeO}_3^-} = (1 + K_{\text{S,9}} \times 10^{\beta_{\text{HTeO}_3^2-}})^{-1}$; ($K_{\text{S,9}} = 1.1 \times 10^{-10}$, see below).

The integrated rate equation for disappearance of the absorbance may be expressed by

$$\text{OD}(t)^{-1} - \text{OD}(t = 0)^{-1} = k_{22} \times t = (c(t)^{-1} - c(t = 0)^{-1}) / (l \times e_{\text{TeO}_3^-} \times x_{\text{TeO}_3^-} + l \times e_{\text{HTeO}_3^2-} \times (1 - x_{\text{TeO}_3^-}))$$  \hspace{1cm} (21)

where $l$ is the length of the optical cell (5.5 cm).

From eqs 20 and 21 we find

$$k_{22} = (2k_{11} \times x_{\text{HTeO}_3^-} + k_{12} \times x_{\text{TeO}_3^-} - (1 - x_{\text{TeO}_3^-}) + 2k_{13} \times (1 - x_{\text{TeO}_3^-})) / (l \times e_{\text{TeO}_3^-} \times x_{\text{TeO}_3^-} + l \times e_{\text{HTeO}_3^2-} \times (1 - x_{\text{TeO}_3^-}))$$  \hspace{1cm} (22)

Figure 6 shows a plot of $k_{22} \times (l \times e_{\text{TeO}_3^-} \times x_{\text{TeO}_3^-} + l \times e_{\text{HTeO}_3^2-} \times (1 - x_{\text{TeO}_3^-}))$ against $x_{\text{TeO}_3^-}$ together with the least-squares fit of a quadratic function to the experimental points. By equating coefficients to like powers of $x_{\text{TeO}_3^-}$ in eqs 20 and in the quadratic function, we find the values for $k_{11}$, $k_{12}$, and $k_{13}$, shown in Table 1.

The rate constants $k_{-4}$ and $k_{-5}$ were determined from the first-order rate constant, $k_{23}$, for the decay of absorbance at 325 nm, measured at pH varying between 12.19 and 13.48. $k_{23}$ may be expressed by

$$k_{23} = k_{-5} \times x_{\text{TeO}_3^-} + k_{-4} \times (1 - x_{\text{TeO}_3^-})$$  \hspace{1cm} (23)

where $x_{\text{TeO}_3^-} = K_{\text{I,0}} \times 10^{\beta_{\text{HTeO}_3^2-}} + K_{\text{I,0}} \times 10^{\beta_{\text{HTeO}_3^2-}}$ is the fraction of the total Te(V) concentration that is present as $\text{TeO}_3^-$ in equilibrium with $\text{HTeO}_3^2-$. Figure 7 shows a plot of $k_{23}$ against $x_{\text{TeO}_3^-}$. $k_{-4}$ and $k_{-5}$ were found by fitting a linear function to the experimental points (Table 1).

**Test of the Mechanism.** The rate constants of the mechanism proposed above were determined under the assumption that overlap among the individual reactions could be neglected. However, a test performed without this assumption by simulating the time evolution of the absorbance measured at 380 nm in N$_2$O-saturated 2 $\times$ $10^{-4}$ M tellurite solutions at pH 8.15,
9.27, 9.62, 9.92, and 10.6, showed that the mechanism is consistent with this set of data (Figure 3). At pH 8.15, where the species H$_2$TeO$_4^-$ and TeO$_3^{2-}$ dominate, the important reactions of the mechanism are 3, 6, 6a, 11, 17, and 18. Here the calculated absorbance was fitted to the measured absorbance by adjusting the dose, allowing it to vary within ±4% of the nominal value, whereas the rate constants had the values given in Table 1, and the extinction coefficients of H$_2$TeO$_4^-$ and TeO$_3^{2-}$ at 380 nm were those shown in Figure 4.

At pH 9.27, 9.62, 9.92, and 10.6, the additional reactions 4, 7, 12, 13, as well as

$$\text{TeO}_3^{2-} + \text{B}^- + \text{H}_2\text{O} \rightleftharpoons \text{HTeO}_4^{2-} + \text{HB}$$  \hspace{1cm} (24) \text{.}(-24)

where (B$^-$ = TeO$_3^{2-}$ and OH$^-$), involving the species HTeO$_4^{2-}$, become important. Here the test was performed by fitting calculated absorances to the measured absorances by adjusting three parameters: the dose, again only within ±4% of the nominal value, and the pseudo first-order rate constants $k_{22}$ and $k_{24}$ as measured at 350 nm, 400 nm, 425 nm, and 325 nm. Straight lines are linear least-squares fits to the experimental points.

where

$$pK = \text{pH} + \log(k_{24} [\text{HB}] / k_{24} [\text{B}^-]) = 9.94 \pm 0.13 \text{ \hspace{1cm} (25)}$$

in agreement with the value for $pK$ ($pK_{8.9} = 9.96 \pm 0.15$ determined by the equilibrium measurements described below and therefore indicating the consistency of the mechanism for these four solutions also.

Equilibrium Constants, Standard Gibbs Energy of Formation, and Standard Electrode Potentials of TeO$_3^-$, H$_2$TeO$_4^-$, HTeO$_4^-$, and TeO$_3^{2-}$. The values of $pK$ for the apparent acid dissociation of TeO$_3^-$, $pK_{8.9} = 9.96 \pm 0.15$, and for the acid dissociation of HTeO$_4^{2-}$, $pK_{10} = 13.2 \pm 0.1$, were found from plots against pH of the left side of the equations

$$\log(\epsilon - \epsilon_{\text{TeO}_3^-})/(\epsilon_{\text{HTeO}_4^{2-}} - \epsilon) = \text{pH} - pK_{8.9} \text{ \hspace{1cm} (26)}$$

and

$$\log(\epsilon - \epsilon_{\text{HTeO}_4^{2-}})/(\epsilon_{\text{TeO}_3^{2-}} - \epsilon) = \text{pH} - pK_{10} \text{ \hspace{1cm} (27)}$$

(Figure 8). $\epsilon$ is the extinction coefficient measured at varying pH. $\epsilon_{\text{TeO}_3^-}$ and $\epsilon_{\text{HTeO}_4^{2-}}$, and $\epsilon_{\text{TeO}_3^{2-}}$, stand for the extinction coefficients of TeO$_3^-$, HTeO$_4^{2-}$, and TeO$_3^{2-}$, respectively. $pK_{8.9}$ was determined from measurements of $\epsilon$ at the wavelengths 325, 350, 375, 400, and 425 nm, $pK_{10}$ from measurements of $\epsilon$ at 325 nm. Since the large base strength of TeO$_3^{2-}$ precludes a direct determination of $\epsilon_{\text{TeO}_3^{2-}}$, $pK_{10}$ was determined from eq 27 by adjusting $\epsilon_{\text{TeO}_3^-}$ to $\epsilon_{\text{TeO}_3^{2-}} = 6400 \text{ M}^{-1} \text{ cm}^{-1}$ by trial
and error until the required linear dependence on pH was obtained.

The determination of the rate constants for both pairs of forward and the reverse reactions 4, –4, and 5, –5 allows us to determine the standard Gibbs energy of formation of TeO₄³⁻, HTeO₄²⁻, and TeO₃⁻. These may be calculated from

$$\Delta G_{\text{f}}^{m}(\text{TeO}_4^{3-}) = RT \ln (k_x/k_2) + \Delta G_{\text{f}}^{m}(\text{TeO}_3^{2-}) + \Delta G_{\text{f}}^{m}(\text{O}^-)$$  

$$\Delta G_{\text{f}}^{m}(\text{HTeO}_4^{2-}) = RT \ln (k_x/k_2) + \Delta G_{\text{f}}^{m}(\text{TeO}_3^{2-}) + \Delta G_{\text{f}}^{m}(\text{OH}^-)$$  

and

$$\Delta G_{\text{f}}^{m}(\text{TeO}_3^-) = RT \ln K_{x9} + \Delta G_{\text{f}}^{m}(\text{HTeO}_4^{2-}) - \Delta G_{\text{f}}^{m}(\text{H}_2\text{O})$$

The standard Gibbs energy of formation of H₃TeO₄ may be calculated from

$$\Delta G_{\text{f}}^{m}(\text{H}_3\text{TeO}_4^-) = \Delta G_{\text{f}}^{m}(\text{HTeO}_4^{2-}) + RT \ln K_{\text{HTeO}_4^-}$$

Taking $\Delta G_{\text{f}}^{m}(\text{TeO}_2^-) = -383.4 \text{ kJ/mol}$, $\Delta G_{\text{f}}^{m}(\text{O}^-) = 95 \text{ kJ/mol}$, $\Delta G_{\text{f}}^{m}(\text{OH}^-) = 27 \text{ kJ/mol}$, and $\Delta G_{\text{f}}^{m}(\text{H}_2\text{O}) = -237.13 \text{ kJ/mol}$, and estimating $K_{\text{HTeO}_4^-} = 10^{-7.22}$, for the dissociation of H₂TeO₄⁻, we find $\Delta G_{\text{f}}^{m}(\text{TeO}_3^{3-}) = -219 \text{ kJ/mol}$, $\Delta G_{\text{f}}^{m}(\text{HTeO}_4^{2-}) = -394 \text{ kJ/mol}$, and $\Delta G_{\text{f}}^{m}(\text{H}_2\text{TeO}_4^-) = -434 \text{ kJ/mol}$.

These results lead to $\Delta G^o = 17 \text{ kJ/mol}$ for the hydration of TeO₃⁻ and, hence, to the estimate $K_s = 10^{-3}$ for the equilibrium 8, –8, a value in agreement with the fact that reaction 8 was not observed.

The standard electrode potentials shown in Table 2 are calculated from the values of $\Delta G_{\text{f}}^{m}$ for the four Te(V) species and from published values of $\Delta G_{\text{f}}^{m}$ for the (IV) and (VI) species.¹⁷

**Reactions of Te(V) with O₂ and HCO₃⁻.** Te(V) species were found to react with O₂ under formation of a product having an absorption that increases with decreasing wavelength without reaching a maximum in the range (>250 nm) accessible with our instrument. The observable part of this spectrum resembles that of O₂⁻²⁸ as well as those of SO₃⁻²⁹ and the O₂-adduct of SO₄⁻, and the O₂-adduct of As(V).²³ Hence, with the reasonable assumption that an O₂-adduct of TeO₅⁻ (= TeO₅⁻) would also have a spectrum similar to that of O₂⁻, the observed spectrum suggests that the product is either O₂⁻ or TeO₅⁻, the reduction of O₂ implied by both assignments being consistent with the high reduction power of the Te(V) species (Table 2). However, the reaction between Te(V) and O₂ is very fast, which we take to suggest that TeO₅⁻ rather than O₂⁻ is the product.

The reactions of the Te(V) species H₂TeO₄⁻, TeO₃⁻, HTeO₄²⁻, and TeO₄³⁻ with O₂ may be

$$\text{H}_2\text{TeO}_4^- + \text{O}_2 \rightarrow \text{TeO}_5^- + \text{H}_2\text{O}$$  (32)

$$\text{TeO}_3^- + \text{O}_2 \rightarrow \text{TeO}_5^-$$  (33)

$$\text{HTeO}_4^{2-} + \text{O}_2 \rightarrow \text{TeO}_5^- + \text{OH}^-$$  (34)

and

$$\text{TeO}_4^{3-} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{TeO}_5^- + 2\text{OH}^-$$  (35)

The rate constants $k_{32}$, $k_{34}$, and $k_{35}$, for reactions 33, 34, and 35, were determined from measurements of the first-order rate constants for disappearance of Te(V) in N₂O-saturated 5 × 10⁻⁴ M tellurite solutions containing oxygen in the concentrations 1.9 × 10⁻⁴ M, 2.5 × 10⁻⁴ M, and 3.8 × 10⁻⁴ M O₂. At pH 7.9 the first-order rate constant for disappearance of Te(V) was found to be (1.7 ± 0.2) × 10⁶ s⁻¹ at 2.5 × 10⁻⁴ M O₂. Since the rate constant for the dehydration of H₂TeO₄⁻ in 5 × 10⁻⁴ M tellurite is three times larger, we assume that the value measured pertains to the pseudo first-order constant of reaction 33. With this assumption we find $k_{33} = (6.8 ± 0.8) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{34} = (3.1 ± 0.17) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was determined from measurements in solutions containing 1.9 × 10⁻⁴ M, 2.5 × 10⁻⁴ M, and 3.8 × 10⁻⁴ M O₂ at pH 11.1, at which pH HTeO₄²⁻ is the predominant species. $k_{35} = (2.5 ± 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was determined from the value of $k_{34}$ and the rate constant $k = (2.8 ± 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for disappearance of Te(V) determined in a solution containing 2.5 × 10⁻⁴ M O₂ at pH 13.3, where HTeO₄²⁻ and TeO₄³⁻ are present in approximately equal concentrations.

Pseudo first-order rate constants for the disappearance of Te(V) in solutions containing CO₃²⁻ and HCO₃⁻ were measured in N₂O-saturated 10⁻² M tellurite solutions and in 10⁻² M O₂-free tellurate solutions. The product of the reaction was identified by its spectrum as CO₃⁻³⁰. The total concentration of carbonate, [CO₃²⁻] + [HCO₃⁻], was varied between 10⁻² M and 6 × 10⁻⁴ M. The fractions $\chi_{\text{HCO}_3^-} = [\text{HCO}_3^-]/([\text{CO}_3^{2-}] + [\text{HCO}_3^-])$ and $\chi_{\text{TeO}_3^-} = [\text{TeO}_3^-]/([\text{HTeO}_4^{2-}] + [\text{TeO}_3^-])$ were calculated from pH of the solutions and the pK values of HCO₃⁻ and TeO₃⁻, taken as the values pertaining to infinite dilute solution (10.34 for HCO₃⁻²⁷ and 9.97 for TeO₃⁻) corrected by means of Güntelberg’s formula for the activity coefficients of ions.³¹

In strongly alkaline solution (pH ≥ 13), where the dominant Te(V) species are H₃TeO₄²⁻ and TeO₃³⁻, no reaction was observed, indicating that CO₃²⁻ does not react at a measurable rate with H₃TeO₄²⁻ and TeO₃³⁻, in accordance with the fact that $\Delta G^r$ for these reactions are positive.

Measurements in less alkaline solutions show that TeO₃⁻ is the only Te(V) species that reacts at a measurable rate with HCO₃⁻ and CO₃²⁻. We find that the decay of the absorbance at 350 nm is of pseudo first order with a rate constant that for fixed $\chi_{\text{HCO}_3^-}$ (and $\chi_{\text{TeO}_3^-}$) is proportional to [CO₃²⁻] + [HCO₃⁻]. Further we find that the second-order constant, $k_{36}$, for the reaction of Te(V) with total carbonate (CO₃²⁻ + HCO₃⁻) divided by $\chi_{\text{TeO}_3^-}$ varies linearly with $\chi_{\text{HCO}_3^-}$, indicating that $k_{36}/\chi_{\text{TeO}_3^-}$ may be expressed by

$$k_{36}/\chi_{\text{TeO}_3^-} = k_{37} \chi_{\text{HCO}_3^-} + k_{38}(1 - \chi_{\text{HCO}_3^-})$$  (36)
Denoting the standard Gibbs energy changes for the total aqueous solution of its corresponding base, $\text{SeO}_4^{2-}$, low acid strength, which of course precludes the detection in where $k$ in the total concentration $10^{-10}$ M, and in which the total concentration of $\text{HCO}_3^-$ in Ar-saturated solutions containing $\text{H}_6\text{TeO}_6$, $\text{H}_5\text{TeO}_6$ and $\text{H}_2\text{TeO}_4^2-$ in the total concentration $10^{-2}$ M. The points $\square$ were measured in $\text{N}_2$-saturated solutions containing $\text{HTeO}_4^-$ and $\text{TeO}_2^-$ in the total concentration $10^{-2}$ M, and in which the total concentration of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ was varied between $5 \times 10^{-3}$ M and $6 \times 10^{-2}$ M. The points $\times$ were measured in Ar-saturated solutions containing $\text{H}_2\text{TeO}_4^-$, $\text{H}_2\text{TeO}_5^-$, and $\text{H}_3\text{TeO}_5^2-$ in the total concentration $10^{-2}$ M, and in which the total concentration of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ was varied between $10^{-3}$ M and $2 \times 10^{-2}$ M.

where $k_{39}$ and $k_{38}$ are the rate constants of

$$\text{HCO}_3^- + \text{TeO}_3^- \rightarrow \text{CO}_3^- + \text{HTeO}_4^-$$

$\Delta G^\circ = -11 \text{ kJ/mol}$ (37)

and

$$\text{CO}_3^{2-} + \text{TeO}_3^- = \text{CO}_3^- + \text{TeO}_3^{2-}$$

$\Delta G^\circ = -15 \text{ kJ/mol}$ (38)

respectively. $\Delta G^\circ$ for reactions are calculated taking the standard electrode potential of $\text{CO}_3^-$/CO$_3^{2-}$ equals 1.59 V.32

Figure 9 shows a plot of $k_{39}/x_{\text{HCO}_3^-}$ against $x_{\text{HCO}_3^-}$. From a linear least-squares fit to the experimental points we find $k_{37} = 1.6 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$ and $k_{38} = 1.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$. We note that $k_{38}$ is much larger than $k_{37}$, reflecting that reaction 37 takes place by hydrogen atom transfer, and reaction 38 by electron transfer.

Comparison of the Oxoradicals of S(V), Se(V), and Te(V). The only four-coordinated Se(V) oxoradical observed in aqueous solution is HSeO$_3^{2-}$. This species is detected only in strongly alkaline solution (pH > 13) indicating an extremely low acid strength, which of cause precludes the detection in aqueous solution of its corresponding base, SeO$_4^{3-}$. This species, however, has been observed in X-ray-irradiated crystals containing SeO$_2^{2-}$.

The low acid strength of HSeO$_3^{2-}$ as compared to that of HTeO$_4^{2-}$, and the fact that $\text{H}_2\text{TeO}_3^-$ is observed whereas $\text{H}_2\text{SeO}_3^-$ is not, may be rationalized by comparing the set of reactions $8$, $-8$, $9$, and $-9$ with the corresponding set

$$\text{SeO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SeO}_4^- \rightleftharpoons \text{HSeO}_4^{2-} + \text{H}^+$$

(39), (39), 39, 40, (39, 39, 40, 41)

Denoting the standard Gibbs energy changes for the total

<table>
<thead>
<tr>
<th>electrode process</th>
<th>$E$/Volt</th>
<th>ref</th>
</tr>
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<tbody>
<tr>
<td>$\text{SO}_3^- + e^- = \text{SO}_4^{2-}$</td>
<td>0.73 ± 0.01</td>
<td>1</td>
</tr>
<tr>
<td>$\text{SeO}_3^- + e^- = \text{SeO}_4^{2-}$</td>
<td>1.68 ± 0.01</td>
<td>6</td>
</tr>
<tr>
<td>$\text{TeO}_3^- + e^- = \text{TeO}_4^{2-}$</td>
<td>1.74 ± 0.02</td>
<td>this work</td>
</tr>
<tr>
<td>$\text{SO}_3^{2-} + 2\text{H}^+ + e^- = \text{SO}_4^{2-} + \text{H}_2\text{O}$</td>
<td>$-0.91 ± 0.01$</td>
<td>6</td>
</tr>
<tr>
<td>$\text{SeO}_3^{2-} + 2\text{H}^+ + e^- = \text{SeO}_4^{2-} + \text{H}_2\text{O}$</td>
<td>$-0.03 ± 0.01$</td>
<td>6</td>
</tr>
</tbody>
</table>

Taking the acid constants $K_{39}$ and $K_9$ of H$_2$SeO$_4^{-}$ and H$_2$TeO$_4^{-}$ to be equal and assuming, moreover, that the rate constant of the uncatalyzed hydration of SeO$_3^-$ is equal to that of TeO$_3^-$, i.e., $k_{39} = k_8$ we find

$$-RT \ln K_{39,40} + RT \ln K_{8,9} = \Delta G^\circ(39) - \Delta G^\circ(8) =$$

$$RT \ln k_{39,40}/k_{8,9} (42)$$

Table 3: Standard Electrode Potentials of SO$_3^-$, SeO$_3^-$, and TeO$_3^-$. Notes and References.
Tellurium(V). A Pulse Radiolysis Study
