Oxygen-17 Nuclear Magnetic Resonance and Oxygen Exchange in Aqueous Solutions of Telluric Acid

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Abstract: The ^{17}O signal of telluric acid, H_6TeO_6, in aqueous solutions was found to be shifted -120 ppm relative to the solvent water signal. The kinetics of oxygen exchange between tellurate and water was studied by following the increase in intensity of this signal as a function of time upon dissolving H_6TeO_6 in water enriched in ^{17}O. The pseudo-first-order rate constants for oxygen exchange of H_6TeO_6 and $H_5TeO_6^-$ are 0.14 and 350 min^{-1} at 27°, respectively. The rate of exchange is not affected by strong acids or chloride ions. Upon neutralization of the first hydrogen of telluric acid, the integrated intensity of its ^{17}O resonance decreases gradually. This effect is explained in terms of the formation of polytellurate ions.

Oxygen exchange between water and oxyanions of the second- and third-row elements has been studied extensively,[1,2] while relatively limited attention has been paid to the oxyanions of the heavier nonmetallic elements. In the former group of ions the oxygen exchange is acid catalyzed, and it was inferred that the reaction involves labile protonated species as intermediates. In contrast, oxygen exchange of periodic acid was found to be independent of strong acid concentrations, and it was suggested that the exchange rate is controlled by the dissociation of the I–O bond rather than by a nucleophilic substitution by water.[3] Because of the similarity in structure and chemical behavior of telluric and periodic acids, we thought it would be of interest to compare the oxygen-exchange reaction of these two compounds.

In solutions of oxyanions in water enriched in ^{17}O under conditions where oxygen exchange occurs, it is usually possible to see separate nmr peaks for the ^{17}O nuclei of the solvent water and of the oxyanions.[4,5] In some cases a signal due to the oxyanion is not observed because it is too broad or it coincides with the much stronger water signal. Obviously only a weak signal of the oxyanion, due to the natural abundance of ^{17}O, is observed when no appreciable oxygen exchange occurs. In solutions of telluric acid in water enriched in ^{17}O, the telluric acid line is observed 120 ppm downfield (at constant frequency) relative to the solvent water line, and its width at half-amplitude, $1/\pi T_2$, is 450 cps. This line is not observed immediately after dissolving H_6TeO_6 in water, but, rather, it increases in intensity to its equilibrium value within about 10 min. Hence it is possible to study conveniently the rate of exchange of oxygen between H_6TeO_6 and water by following the growth of the line as function of time. In the present paper we report results of such measurements in solutions containing variable amounts of strong base and acid.

Experimental Section

Nmr Spectrometer. The nmr spectrometer was the same as that described previously.[3]

Materials. Water enriched to 8 atom % ^{17}O was obtained from this Institute's plant and was distilled twice before use. Analar telluric acid (BDH) was used without further purification.

Rate Measurements. The oxygen-exchange rate between H_6TeO_6 and water was obtained by following the increase in intensity of the telluric acid ^{17}O signal upon dissolving it in water enriched in ^{17}O. Telluric acid was weighed into a 15-mm o.d. test tube which served as the nmr sample holder. Enriched water was added, and the telluric acid dissolved in it within about 0.75 min. The solvent water was kept in a constant temperature bath at 27° before and during the dissolution. The required amount of strong base (NaOH) or acid ($HClO_4$) was subsequently added and the sample placed into the nmr probe. The first recording of the spectrum was usually possible within about 1.5 to 2 min after dissolving the telluric acid. Readings of the signal were taken at intervals of 0.5 to 1 min. The telluric acid enriched in ^{17}O was recovered and used in other kinetic measurements. In these experiments the enriched telluric acid was dissolved in water of normal isotopic composition, and the rate of decay of its signal was followed.

The pseudo-first-order rate constant, k, for the exchange reaction was obtained graphically using the following equation[6]

$$-\ln\,[1 - F(t)] = k\frac{6[H_6TeO_6] + [H_2O]}{6[H_2O]}t \qquad (1)$$

where $F(t)$ is the fraction exchanged at time t and is calculated from the nmr peak intensity. The accuracy of the rate constants so obtained is estimated at ±15%.

Results and Discussion

Oxygen Exchange. The thermodynamic properties of telluric acid in aqueous solutions have been studied extensively.[7] It is a weak polybasic acid with $pK_1 = 7.7$ and $pK_2 = 10.95$ at 25°. It was thus possible to study separately the rate of oxygen exchange of the free acid and of its ionized forms. Preliminary experiments indicated that the rate of the oxygen exchange increases sharply upon addition of strong base, but that strong acids do not affect it. The oxygen exchange was measured in two series containing 1.12 m and 2.24 m H_6TeO_6 and various amounts of NaOH and $HClO_4$. The results of these measurements are summarized in Table I. The measurements could not be extended to NaOH concentrations above 1.6×10^{-2} m because the exchange rate became too fast to follow by this technique.

Upon addition of NaOH some of the telluric acid is converted into its monoanion. However, because of

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(1) H. Taube, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 17, 25 (1956).

(2) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, Chapter 8.

(3) I. Pecht and Z. Luz, *J. Am. Chem. Soc.*, 87, 4068 (1965).

(4) B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. Roy. Soc.* (London), **A269**, 469 (1962).

(5) J. A. Jackson and H. Taube, *J. Phys. Chem.*, 69, 1844 (1965).

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 193.

(7) H. R. Ellison, J. O. Edwards, and E. H. Healy, *J. Am. Chem. Soc.*, **84**, 1820 (1962).

Table I. Observed Pseudo-First-Order Rate Constant, k, for Oxygen Exchange in Solutions of Telluric Acid as a Function of NaOH and $HClO_4$ Added (27 ± 1°)

H_6TeO_6, m	NaOH, $m \times 10^3$	$HClO_4$, m	pH	$f \times 10^{3a}$	k, min^{-1}
1.12	0.00	...	3.20	0.6[b]	0.26
1.12	1.12	...	3.56	1.0	0.50
1.12	2.24	...	3.75	2.0	0.84
1.12	3.14	...	3.88	2.8	1.11
1.12	4.81	...	4.11	4.3	1.84
2.24	0.00	...	3.22	0.6[b]	0.35
2.24	5.60	...	3.40	2.5	0.87
2.24	11.60	...	3.58	5.2	1.84
2.24	16.30	...	3.70	7.3	2.55
1.12	...	0.14	0.61	0.0	0.18
2.50	...	0.14	0.43	0.0	0.17
1.40	...	0.96	0.00	0.0	0.18

[a] $f = [H_5TeO_6^-]/[H_6TeO_6]$ is the fraction of telluric acid neutralized. [b] Calculated assuming $[H_5TeO_6^-] = [H^+]$.

the fast proton exchange between the acid and the monoanion, only a single ^{17}O signal is observed and the rate constant, k, of oxygen exchange measured is the weighted average of that of telluric acid, k_T, and that of its monoanion, k_{T^-}; thus

$$\text{rate} = k\{[H_6TeO_6] + [H_5TeO_6^-]\} = k_T[H_6TeO_6] + k_{T^-}[H_5TeO_6^-] \quad (2)$$

Since in our experiments $[H_5TeO_6^-] << [H_6TeO_6]$, eq 2 reduces to

$$k = k_T + fk_{T^-} \quad (3)$$

where $f = [H_5TeO_6^-]/[H_6TeO_6]$ is the fraction of telluric acid neutralized. The value of f was calculated as the ratio of NaOH added to total H_6TeO_6 in the solution, except for the unneutralized solutions, where it was assumed that $[H_5TeO_6^-] = [H^+]$ and f was calculated from the measured pH. In the strongly acidic solutions f is obviously zero.

In Figure 1 the observed rate constant, k, for the two series studied is plotted against f. It is seen that within experimental accuracy the intercept and slope of both series is the same, giving: $k_T = 0.14$ min^{-1} and $k_{T^-} = 3.5 \times 10^2$ min^{-1}. Thus the pseudo-first-order rate constant for oxygen exchange of the tellurate monoanion is about three orders of magnitude bigger than that of the acid.

In principle another term, $k_{OH}[OH^-]$, should be included in eq 3. That this term cannot contribute appreciably to the observed rate of exchange may be seen from Table I; in the two series studied, the same rates are observed under conditions where the hydroxyl ion concentration varies by as much as a factor of 3.5 (as calculated from the pH). Still another term should be added to eq 3, *i.e.*, the contribution to the exchange due to the minute amount of doubly ionized tellurate ion. However, the exchange rate of this species is too low to contribute to the exchange in our experiments; the ^{17}O line width of water in a solution containing 0.1 *M* disodium tellurate was found to be 75 cps as compared to 67 cps in water containing just 0.1 *M* H_6TeO_6. If this broadening is due solely to exchange with the doubly charged tellurate ion, an upper limit of 300 sec^{-1} can be set for $k_{T^{2-}}$ which is far too small to contribute to the exchange rate under our experimental conditions. This broadening is, however, more likely due to the increase in viscosity of the solution.

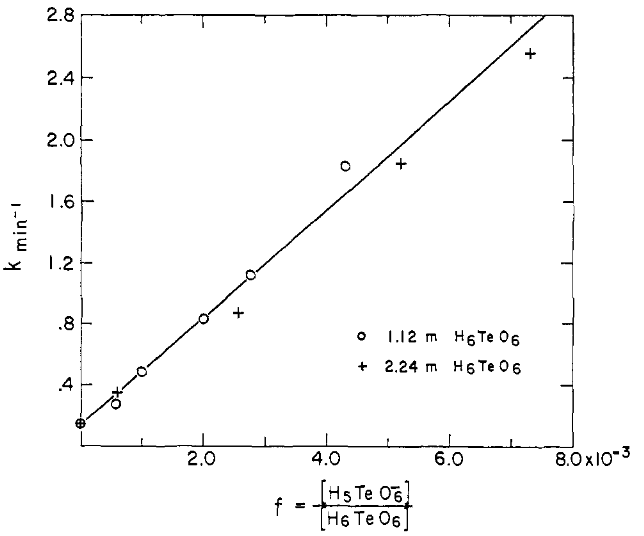

Figure 1. Observed rate constant, k, of oxygen exchange as a function of telluric acid neutralized, f (27 ± 1°).

As in the case of periodic acid[3] the oxygen exchange was not affected by $HClO_4$ (*cf.* Table I). Also when $HClO_4$ was substituted by HCl, the same rates were observed. Thus, following the discussion[3] of the oxygen-exchange kinetics of periodic acid, it is concluded that in this case the reaction also involves a dehydration–hydration equilibrium such as

$$H_6TeO_6 \rightleftarrows H_4TeO_5 + H_2O \quad (4)$$

and a similar reaction for tellurate monoanion.

It is interesting to compare the rate for oxygen exchange of the tellurate monoanion with the rates of its complex formation with glycols.[8] The rate law found for the latter reaction was: rate $= k[H_5TeO_6^-] \cdot [OH^-][\text{glycol}]$. To explain this rate law it was postulated that TeO_4^{2-} is formed prior to the rate-determining step by rapid dehydration of $H_4TeO_6^{2-}$ and serves as a reactive intermediate in the complexing reaction. Edwards noted[9] that such a mechanism requires that the oxygen-exchange rate of $H_5TeO_6^-$ be much faster than the rate of complex formation. A typical value for the specific rate, $(1/[H_5TeO_6^-])(d[H_5TeO_6^-]/dt)$, of complex formation, *e.g.*, with ethylene glycol at 25° and at pH 7.3, is 1.4×10^{-2} sec^{-1} in a solution containing 1 *M* glycol.[8] This value we compare with 3.5×10^2 min^{-1} = 58 sec^{-1} for the oxygen exchange of $H_5TeO_6^-$ in our solutions, which were much less basic, in agreement with the mechanism proposed for the complexation reaction. This, however, does not mean that oxygen exchange of $H_5TeO_6^-$ proceeds mainly *via* the same route as the complexation reaction, *i.e.*, the dehydration of $H_4TeO_6^{2-}$. It is more likely that the dominant mechanism is simply the dehydration of $H_5TeO_6^-$ similar to that described for H_6TeO_6 in eq 4.

^{17}O Spectra at High Concentration of Base. When enough NaOH was added to telluric acid solutions to neutralize several tenths of 1 equiv, the ^{17}O peak due to tellurate decreased in intensity without appreciable broadening. The integrated intensity of this line for two solutions of 0.53 and 1.94 *m* as a function of

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(8) H. R. Ellison, J. O. Edwards, and L. Nyberg, *J. Am. Chem. Soc.*, **84**, 1824 (1962).

(9) Reference 2, p 183.

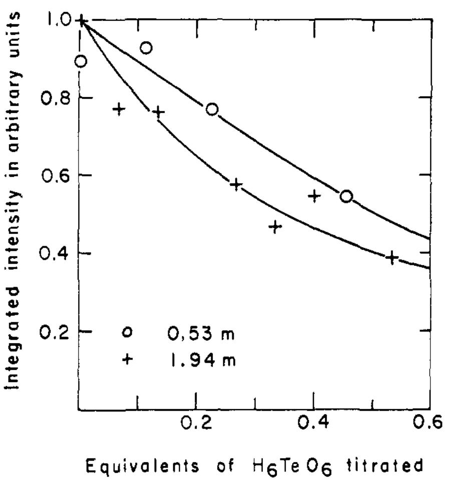

Figure 2. Integrated intensity of the ^{17}O signal of telluric acid as a function of equivalents neutralized.

equivalents of H_6TeO_6 neutralized is given in Figure 2. (The integrated intensity, in arbitrary units, was calculated as the product of the nmr peak height and the square of the peak-to-peak separation of the derivative of the absorption line.) Over the range of NaOH concentration given in Figure 2, the width of the tellurate line increased by a factor of 1.8, while the height of the line in the more concentrated solution decreased to one-eighth of its original value. When more NaOH was added to the solutions, the ^{17}O signal vanished completely. No significant broadening of the water line was observed over the whole range studied.

While this phenomenon is not completely clear, it seems to be due to the formation of new species upon neutralization of telluric acid. An attempt to detect their nmr signal was, however, unsuccessful. These new species are most probably polymeric forms of tellurate ions, the existence of which was suggested previously.[10,11] The ^{17}O nmr line width is mainly controlled by its quadrupolar relaxation and thus depends on the electric field gradient at the ^{17}O nucleus and on the tumbling time of the molecule.[12] If we assume that the electric field at the ^{17}O nucleus does not change appreciably upon polymerization of the telluric acid, the ^{17}O line width of the polytellurate ions will be greater than that of telluric acid because of their longer correlation time for tumbling.[12] This time increases as the cube of the molecular radius, and, since the height of the nmr derivative lines decreases as the square of the line width, a significant reduction in intensity is expected upon polymerization. The signal of the polytellurate ions would thus easily escape detection, especially if it is not shifted considerably from that of the water. In this discussion it is also assumed that the rate of the polymerization reaction is small compared to the line width ($\sim 10^3$ sec^{-1}) but sufficiently fast so that equilibrium is established before obtaining the first record.

(10) D. A. Everest and W. J. Popiel, *J. Inorg. Nucl. Chem.*, **6**, 153 (1958).

(11) J. E. Earley, D. Fortnum, A. Wojcicki, and J. O. Edwards, *J. Am. Chem. Soc.*, **81**, 1295 (1959).

(12) H. A. Christ and P. Diehl, *Proc. Colloq. AMPERE*, **11**, 224 (1963).