^{125}Te NMR Evidence for the Existence of Trinuclear Tellurate Ion in Aqueous Solution

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Deprotonation equilibria of telluric acid in aqueous solution were studied by the ^{125}Te NMR technique, and the presence of the tellurate ion that contains three Te nuclei was clearly shown by the coupling pattern of the NMR spectra of both natural and ^{125}Te-enriched telluric acids.

Chemical properties of telluric acid $Te(OH)_6$ are very different from those of sulfuric and selenic acids. Acid strength of telluric acid is very weak, and acid molecule and most tellurates of various stoichiometries contain TeO_6 octahedra. Although the specification of the telluric acid in aqueous solution has been studied with a great variety of methods among which are potentiometry, spectrometry, and isotope exchange, conclusions have disagreed in many cases.[1] Various schemes for the deprotonation equilibria of telluric acid have been proposed on the basis of the spectrophotometric measurement[2] and potentiometric titration.[3-5] The existence of polynuclear species such as trinuclear tellurate ion has been indicated by the telluric acid concentration dependence of K_{a1} value of $Te(OH)_6$,[3] while later studies proposed the equilibria including only mono- and dinuclear species.[4,5] These inconsistent results may be caused by the difficulty in distinguishing these equilibrium schemes by the potentiometric titration data. In the present study, ^{125}Te NMR technique has been employed to investigate the deprotonation equilibria of telluric acid, and distinct evidence for the presence of trinuclear tellurate ion has been obtained on the basis of the spin-spin coupling pattern of the ^{125}Te NMR spectra.

^{125}Te NMR spectra were recorded on Bruker AM-400 spectrometer working at 126.243 MHz. The probe temperature was 25 ± 1 °C throughout. The field-frequency stabilization was established by inserting a D_2O-filled capillary tube coaxially inside the 10 mm NMR tube. Spectra were obtained from the accumulation of 1000 - 20000 transients at acquisition time of 2 s. Chemical shift is referred to $Te(CH_3)_2$. In acidic aqueous solution (pH < 5) only one signal was observed at 707.0 ppm, which is attributed to $Te(OH)_6$. As the pH of the solution is raised, additional several resonance lines appear as shown in Figure 1a. Peak area of the signal observed at 682.9 ppm is almost twice that at 657.5 ppm irrespective of the pH or the concentration of telluric acid. Relative peak area of these two signals over the total peak area increases with an increase in the telluric acid concentration at constant pH. These facts suggest that these two resonance lines are from an identical deprotonated species that contains three Te atoms in the two types of chemical environments in the ratio 2:1. Since the probability that two or three ^{125}Te nuclei are simultaneously involved in the trinuclear species is low due to the low natural abundance of ^{125}Te of 6.99 %, it is difficult to observe the coupling between these two types of Te atoms. This coupling was observed by using the ^{125}Te-enriched telluric acid, which was synthesized from tellurium in which ^{125}Te was enriched to 92.8% (Techsnabexport, Moscow). Spectrum measured at pH 6.78 is shown in Figure 1b. Effect of isotope enrichment was seen only for the signals of the trinuclear species, which is composed of AB_2 and AB patterns with relatively strong coupling. These spectra were simulated with chemical shift values of each Te site and the coupling constant *J*. Coupling constant was calculated by using chemical shift values. Relative intensities of resonance lines accord with those calculated for AB_2 and AB patterns on the basis of the probability of the ^{125}Te distribution on three Te sites of the trinuclear species.[6] Simulated spectra are shown in Figure 1. Eight signals of AB_2 pattern and four signals of AB pattern are well explained by the common chemical shift values of each Te site and common coupling constant of 682.5 Hz between A and B sites.

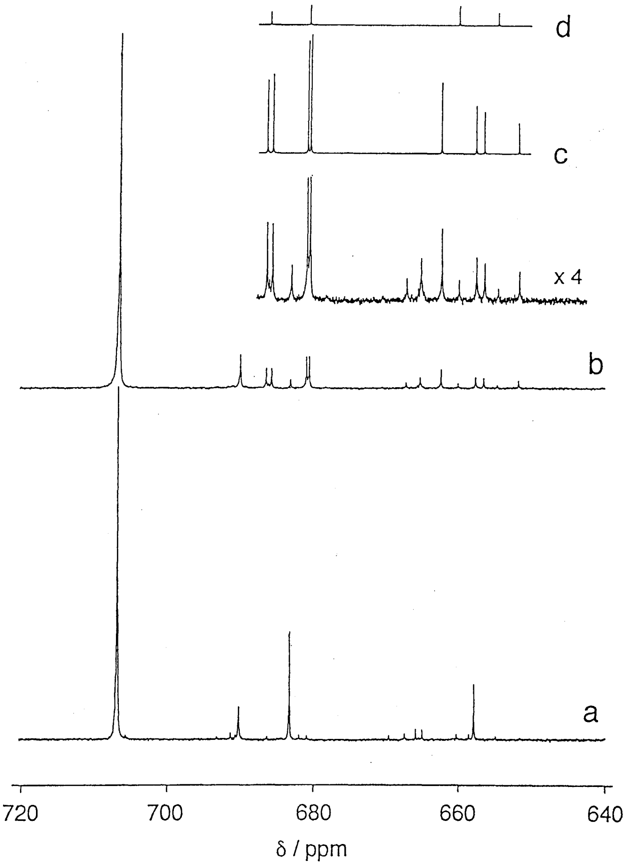
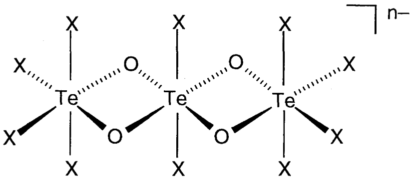


Figure 1. ^{125}Te NMR spectra of the aqueous solution of telluric acid observed for natural telluric acid (**a**) and ^{125}Te-enriched telluric acid (**b**) at pH 6.78 and C_{Te} = 0.20 mol kg^{-1}. Spectra **c** and **d** represent the simulated spectra for AB_2 and AB patterns, respectively. Signals owing to the species other than mono- and trinuclear species are not attributed yet.

Structures of molecule or salts of telluric acid studied by X-ray structure analysis contain TeO_6 octahedra in many cases.[7] Di-μ-oxo bridged structure was observed for the dinuclear tellurate ions such as $[Te_2O_6(OH)_4]^{4-}$ and $[Te_2O_8(OH)_2]^{6-}$.[7b,c] Although the composition of the trinuclear tellurate ion observed here is not known at the present stage, it is acceptable that this ion may contain the di-μ-oxo bridged linear chain structure:



X = OH^- or O^{2-}

Features of the NMR spectra shown in Figure 1 are well explained by this structure in which two terminal Te atoms are magnetically equivalent in the time scale of ^{125}Te NMR, although the circumstances of these sites may not be the same due to the difference in the degree of deprotonation of hydroxide groups bound to Te atoms.

Ratio of the peak area due to the trinuclear species was determined to be 22 ± 2% for the natural sample at $C_{Te} = 0.20$ mol kg^{-1} and pH = 6.78. Ratio of the trinuclear tellurate ion is calculated to be 5% by using the equilibrium constants reported.[3] However, this value may not correctly reflect the distribution of tellurate species in solution under the present conditions since only β_{11}, β_{21}, and β_{31} are available at the present stage.[8] Potentiometric titration is, of course, one of the best methods to study the deprotonation equilibria of telluric acid in solution, and thus it is desirable to analyze the emf data with taking into account the existence of the trinuclear tellurate ion observed in the present study.

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References and Notes

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8 β_{11}, β_{21}, and β_{31} are the equilibrium constants for the formation of monodeprotonated mono-, di-, and trinuclear species of telluric acid: $\beta_{11} = [TeO(OH)_5^-][H^+][Te(OH)_6]^{-1}$, $\beta_{21} = [Te_2O_3(OH)_7^-][H^+][Te(OH)_6]^{-2}$, and $\beta_{31} = [Te_3O_5(OH)_9^-][H^+][Te(OH)_6]^{-3}$.