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Hydrolysis of Titanium(III)[1, 2a]

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Received August 22, 1961

Stable solutions of titanium(III) have been prepared by an ion-exchange procedure using bromide and iodide media. The first hydrolysis constant for the aquo-titanium(III) ion has been measured by potentiometric titration. The value of log K_1, extrapolated to zero ionic strength, for the formation of the monohydroxo complex is 12.94 at 15°, 12.71 at 25°, and 12.26 at 35°.

Although stability constants for complex species of titanium(III) with chloride,[3] urea,[4] and oxalate[5] have been reported previously, the presence of hydrolyzed species in the equilibrium mixtures has been ignored. Furthermore, there is conflicting evidence for the effect of *p*H on the rate of oxidation of titanium(III) by iodine,[6] perchlorate,[3] and plutonium(VI).[7] The mechanisms proposed have involved both Ti^{+++} and $TiOH^{++}$ as the reacting ion, but thus far there has been no study of the hydrolysis constant of the aquo ion.

Some preliminary studies of absorption spectra have shown that the spectra of titanium(III) in perchlorate, bromide, and iodide solutions are identical. This has been taken as evidence of the absence of complexing by these ions. Perchloric acid solutions are stable only at 0° and therefore not suitable for this study. All the usual media, except bromide and iodide, were found either to complex or to oxidize titanium(III). By means of an ion-exchange procedure, we have prepared for the first time a stable solution of titanium(III) in a non-complexing aqueous solution.

At *p*H values above about 3.5 there is a rapid formation of polynuclear species which have not been identified. These species are far more sensitive to oxidation than either Ti^{+++} or $TiOH^{++}$.

Experimental

Preparation of Non-complexed Titanium(III) Solutions.—Titanium metal powder (Metal Hydrides, Inc., Beverly, Massachusetts) was allowed to react with 2 *N* sulfuric acid solution for 1–2 weeks. The long time was needed in order to obtain a high titanium(III) to hydrogen ion ratio. The solution was filtered and electrolytically reduced using a mercury cathode at a minimum current density of 0.25 amp. per cm.^{2}. The temperature of the solution was held at, or below, room temperature. Electrolysis was continued until the solution gave only a trace test for iron with thiocyanate (after oxidation by nitric acid). The electrolysis and all subsequent operations with titanium(III) were carried out under nitrogen or helium which first was purified by means of vanadous sulfate washing towers followed by contact with hot copper turnings. Carbon dioxide was removed with Ascarite. All solutions which came in contact with titanium(III) first were flushed with inert gas.

The titanium(III) sulfate solution was transferred to the top of a 50-mm. i.d. ion-exchange column containing 150 g.(dry) of 100–200 mesh Dowex AG 50-X12 cation-exchange resin. The column was loaded with titanium(III) by passing through a diluted solution until the effluent had the same faint blue color. The column was washed free from sulfate and the titanium(III) immediately was stripped from the column by a 2 *N* solution of the desired acid. The titanium(III) can be allowed to remain on the column for several weeks; however, it slowly reacts with the resin causing the formation of hydrogen sulfide and consequently increasing the amount of titanium(IV). The stock solution was stored in a pressurized storage buret under purified nitrogen.

Reagents and Equipment.—Varying amounts of potassium bromide were added to a solution of sodium hydroxide so that the neutralization procedure would not change the ionic strength.

The hydrobromic and hydriodic acids were reagent grade materials which were distilled from red phosphorus and stored in an inert atmosphere.

A Radiometer Model 4 *p*H meter was used to determine the hydrogen ion concentrations. Leeds and Northrup glass electrodes and a calomel reference electrode (pres-

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[1] Presented before the Inorganic Division at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961.

[2] (a) Based upon a dissertation submitted to the faculty of The University of California, Los Angeles, California, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; (b) On leave from the U. S. Naval Ordnance Test Station, China Lake, California.

[3] F. R. Duke and P. R. Quinncy, *J. Am. Chem. Soc.*, **76**, 3800 (1954).

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[5] V. V. Subbana, G. S. Rao, and A. K. Bhattacharya, *J. Sci. Ind. Research* (India), **18B**, 127 (1959); *Chem. Abstr.*, **53**, 18725g (1959).

[6] C. E. Johnson, Jr., and S. Winstein, *J. Am. Chem. Soc.*, **73**, 2061 (1951).

[7] S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **63**, 1502 (1959).

surized by a 2-ft. column of saturated sodium chloride) were calibrated by titrating the halide acid with base in a medium of the same ionic strength as the test solution. A syringe type semi-micro buret was used and readings were made to 0.0005 ml. for the buret and 0.001 unit on the *p*H meter.

Titanium(III) Stock Solution Standardizations.—Total titanium concentration was determined by oxidation with ammonium nitrate at *p*H 2–3 and precipitation of titanium dioxide by ammonium hydroxide. The titanium dioxide was dried and weighed. The titanium(III) concentration was determined by titration either under acidic conditions with dichromate, or at *p*H 5–7 using iodine after complexing the titanium with tartrate. The halide concentration was determined after oxidizing titanium(III) at *p*H 2–3 with nitrate by titration with silver(I).

Hydrolysis Procedure.—Generally, 2 ml. of stock solution was added to 48 ml. of the potassium halide solution and then titrated with standard base containing potassium halide to maintain constant ionic strength. The *p*H measurements usually were completed within 20–30 min. After the hydrolysis titration was completed, 10 ml. of a 2 *M* sodium tartrate solution was added and the titanium(III) concentration was checked by titration with iodine using either methylene blue or a potentiometric end-point. The radiometer setting was checked before and after the hydrolysis titration.

Results and Conclusions

The stability constant for the formation of Ti(OH)$^{+2}$ is indicated by equation 1.

$$K_1 = [\mathrm{Ti(OH)}^{+2}]/[\mathrm{Ti}^{+3}][\mathrm{OH}^-] \qquad (1)$$

Expressions in the equation represent concentrations in moles/liter. Unless otherwise indicated, *p*H is defined as the negative logarithm of the hydrogen ion concentration. For simplicity, molecules of water associated with the ionic species and ionic charges are not shown in the equations.

A parameter often used as a convenience in studying the formation of successive complexes is $\bar{n}$, which is defined as the total moles of the complexed ligand divided by the total moles of metal ion. For the present system

$$\bar{n} = \frac{[\mathrm{Ti(OH)}] + 2[\mathrm{Ti(OH)_2}] + 3[\mathrm{Ti(OH)_3}] + X[\text{polynuclear}]}{[\mathrm{Ti}] + [\mathrm{Ti(OH)}] + [\mathrm{Ti(OH)_2}] + [\mathrm{Ti(OH)_3}] + Y[\text{complex}] + Z[\text{polynuclear}]} \qquad (2)$$

$\bar{n}$ can be determined directly as shown in equation 3

$$\bar{n} = \frac{\text{eq. base added} - \text{initial eq. H}^+ + \text{vol.} \times [\mathrm{H}^+]}{\text{total moles titanium(III)}} \qquad (3)$$

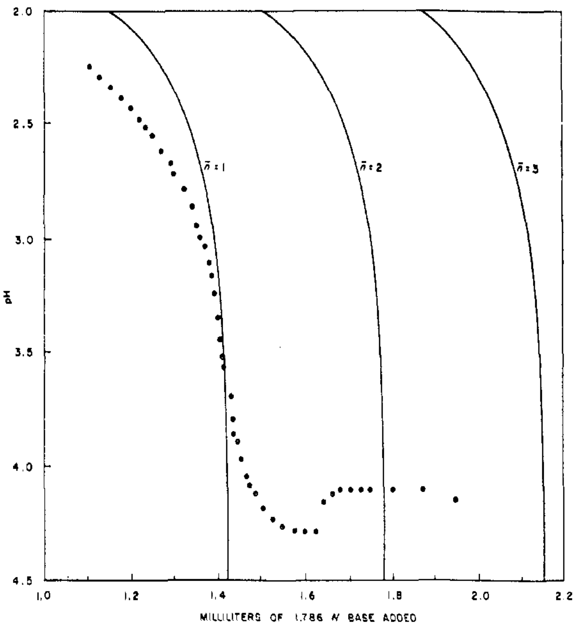

Fig. 1.—Typical hydrolysis titration curve of 12.7 m*M* titanium(III) in 0.75 *M* KBr solution over extended *p*H region.

Figure 1 shows a typical titration of a 12.7 m*M* titanium(III) solution. The solid $\bar{n}$ lines in Fig. 1 have been drawn by assuming that the formation constants of Ti(OH)$^{+2}$, Ti(OH)$_2$$^+$, and Ti(OH)$_3$ are infinitely large. They serve as guides to indicate the extent of hydrolysis at their intersection with the titration curve. These data indicate that insignificant amounts of hydrolysis products other than Ti(OH)$^{+2}$ formed at *p*H values less than 3. Consequently, calculations were performed on the basis that Ti^{+3} and Ti(OH)$^{+2}$ were the only species of titanium(III) present in this region. If the terms *X*, *Y*, and *Z* in equation 2 along with hydrolyzed species other than Ti(OH)$^{+2}$ are negligible, log K_1 therefore can be determined as follows

$$\log K_1 = \log \frac{\bar{n}}{1 - \bar{n}} + pK'_{\mathrm{w}} - p\mathrm{H} \qquad (4)$$

The value of log K_1 calculated from equation 4 will be higher than the true value if polynuclear species are present and lower if complex species are present. Since it is unlikely that the extraneous species will have the same equilibrium constants as for simple hydrolysis, significant changes in log K_1 should occur by varying the ligand or the titanium(III) concentration.

The First Hydrolysis Constant at Finite Ionic Strength.—Since stability constants for the hydrolysis were desired, the ionization constants of water, pK'_{W}, compiled by Harned and Owen[8] were used to determine the hydroxide concentrations from the known hydrogen ion concentrations

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(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Co., New York, N. Y., 1950, pp. 488, 578.

in bromide solutions. The calibrations of the electrode system with known concentrations of acid and base were used to determine pK'_W in 0.75 M KI solutions. A value of $pK'_W = 13.79$ with a standard deviation of 0.01 was obtained from four determinations. Log K_1 values were calculated using equation 4 at $\bar{n} = 0.5$, 0.6, and 0.7 for bromide solutions and 0.5 for iodide solutions. The data for a typical titration are shown in Table I and the variation of the values of log K_1 with changes in $\bar{n}$ are shown in Table II.

TABLE I
TYPICAL TITRATION DATA[a]

ml.	pH	$\bar{n}$	ml.	pH	$\bar{n}$
0.390	1.60	0.077	1.318	2.80	0.832
.699	1.80	.248	1.356	3.00	.890
.816	1.90	.311	1.382	3.20	.931
.916	2.00	.388	1.399	3.40	.962
1.002	2.10	.460	1.412	3.60	.980
1.070	2.20	.521	1.422	3.70	1.008
1.130	2.30	.581	1.433	3.80	1.036
1.181	2.40	.642	1.447	3.90	1.071
1.259	2.60	.741	1.474	4.00	1.144

[a] Original vol., 50.0 ml.; H^+, 1.896 mmoles; Ti(III), 1.944 mmoles; Ti(IV), 0.026 mmole; titrant, 1.7856 N NaOH; temp., 35°; ionic strength, 0.50 (KBr); pK'_w, 13.40.

TABLE II
LOG K_1 FOR VARYING $\bar{n}$ VALUES AT 25°, REPLICATE VALUES

Ionic strength	$\bar{n}$ 0.5	0.6	0.7
0.25	11.83	11.83	11.86
.25	11.83	11.83	11.86
.25	11.81	11.81	11.85
.25	11.78	11.79	11.81
.50	11.78	11.78	11.80
.50	11.82	11.82	11.84
.50	11.78	11.79	11.81
.50	11.78	11.77	11.79
.75	11.75	11.78	11.83
.75	11.70	11.71	11.75
.75	11.71	11.73	11.78
.75	11.72	11.74	11.79
1.5	12.02	11.96	12.00
1.5	12.03	11.98	11.99
1.5	11.96	11.98	11.95
1.5	12.04	12.00	12.01

The absence of extraneous species of titanium(III) is indicated by the following evidence. First, variation of the titanium(III) concentration gave no significant change in the value of log K_1 except when the concentration was almost double the maximum value for all of the other determinations when evaluated at the 95% confidence level for a two-tail Student's t test. However, even in this instance, log K_1 was not found to vary with the ligand concentration. Second, variation of halide concentration up to 4 M caused no change in the spectra of bromide or iodide titanium(III) solutions from those of perchlorate with an absorption maximum at 500 mμ. For a series of chloride solutions 1 M in hydrogen ion and 0.005 M in titanium(III), the absorption maximum varied from 505 mμ for 1 F chloride up to 555 mμ for 10 F. The spectrophotometric data consequently indicate that inner complex formation is absent. Third, if outer complex formation was very extensive, it might not show up by variation of $\bar{n}$ or the concentrations of titanium(III) for a given halide, as [Ti, X] could persist for even the lowest concentrations of titanium and halide. However, since $Ti(OH)^{+2}$ should form outer complexes to a much lesser degree than Ti^{+3}, it is improbable that log K_1 would remain as constant over as large a range of halide and OH^- concentrations as observed in Table II. Fourth, log K_1 was determined in iodide solution since outer complex formations should be lower with iodide than with bromide solutions. A smaller value for log K_1 was observed whereas a higher value would be expected if outer complexes are significant. Since ionic strength concepts are not strictly applicable at the concentration used, the values are not expected to be identical. Finally, and perhaps the most conclusive, log K_1 was found to have an average standard deviation of only 0.02 for all of the

TABLE III
LOG K_1 VALUES FOR THE FORMATION OF $TiOH^{++}$

$[Ti^{+3}]$, mM	Ionic strength	Temp., °C.	No. of detns.	Av. value	Est. std. dev.
14.0	0.25	15	12	12.07	0.03
14.0	.50	15	12	12.05	.04
14.0	.75	15	3	12.02	.02
14.0	1.50	15	9	12.23	.01
14.0	1.50	25	12	11.99	.03
14.0	0.25	25	12	11.82	.02
14.0	.50	25	12	11.80	.02
14.0	.75	25	12	11.75	.04
6.8[a]	.75	25	4	11.54	.01
3.6[a]	.75	25	1	11.54	...
0.8[a]	.75	25	1	11.48	...
12.7	.25	35	9	11.38	.02
12.7	.50	35	12	11.26	.02
25.4	.75	35	3	11.45	.01
12.7	.75	35	6	11.40	.02
6.3	.75	35	3	11.36	.01
3.2	.75	35	3	11.36	.09
12.7	1.50	35	9	11.55	.03

[a] In potassium iodide solution, others in potassium bromide.

determinations when the ligand concentration was changed corresponding to $n = 0.5$, 0.6, and 0.7. A significant change due to increased formation of polynuclear and more highly hydrolyzed species would be expected under these conditions.

The values obtained in 0.75 M iodide had to be corrected for the presence of titanium(IV), which was 11% of the total titanium. This was done by titrating titanium(IV) iodide solutions in the same manner as for the titanium(III). From these titrations, an $\bar{n}$ *vs.* *p*H curve was constructed for titanium(IV). The calculations for the titanium(III) solutions first were treated as if all of the titanium(IV) was completely hydrolyzed

$$Ti^{+4} + 2H_2O \longrightarrow TiO_2 + 4H^+ \qquad (5)$$

Making use of the known $\bar{n}$ *vs.* *p*H relationship for titanium(IV), the total equivalents of hydrogen ion was reduced in equation 3, corresponding to the incomplete hydrolysis of titanium(IV) for each titration point for titanium(III). This correction was not necessary for the bromide solutions in which only 4% of the titanium existed as titanium (IV). This was reduced further to about only 1% after hydrolysis in the *p*H region where $\bar{n} = 0.5$ and even less at larger $\bar{n}$ values.

Extrapolation to Zero Ionic Strength.—pK_w' values are not available for mixed titanium(III), potassium, and hydrogen ion systems, and it was not feasible to perform titrations below 0.25 M halide. However, in order to obtain an estimate of the activity equilibrium constant, an extrapolation from the higher ionic strengths was performed. The Guggenheim relationship recommended by Lee[9] for solutions of ionic strengths larger than can be handled by the Debye–Hückel limiting law was used

$$\log K\,(\text{conc.}) - [A(\Delta Z)^2 \sqrt{\mu}/(1 + \sqrt{\mu})] = \log K\,(\text{act.}) - b\mu \qquad (6)$$

where Z is the charge on the ion; $\Delta Z^2 = Z^2$ products$-Z^2$r eactants; b is constant; μ is the ionic strength; A is $1.825 \times 10^6\,(DT)^{-3/2}$; and D is the dielectric constant of the solvent. If y represents the left side of equation 5, the equations obtained for y at 15, 25, and 35° are

$$y_{15} = 12.94 + 0.64\mu \qquad (7)$$

$$y_{25} = 12.71 + 0.64\mu \qquad (8)$$

$$y_{35} = 12.26 + 0.68\mu \qquad (9)$$

Although all the values are not directly comparable because of the difference in ionic strength, Table IV shows a comparison of the present results along with other stability constants.[10] Although activity equilibrium constants have been estimated at different temperatures, it was not deemed wise to determine $\Delta H°$ and $\Delta S°$ from the $\Delta F°$ values thus obtained. The results of this type of calculation are noted for their large errors[11,12] and to perform them after the extrapolation from such high ionic strengths is not warranted.

TABLE IV

COMPARISON OF LOG K_1 VALUES FOR FORMATION OF FIRST HYDROXO COMPLEX OF METALS OF THE FIRST TRANSITION SERIES AT 25°

	log K_1	Ionic strength
Scandium(III)	9.4	0.01
Titanium(III)	11.8	.01
Vanadium(III)	11.2	Variable
Chromium(III)	10.0	.01
Iron(III)	11.6	.01

Polynuclear Species.—At *p*H values greater than 4, addition of base causes the typical increase in *p*H followed by a slow decrease back to a *p*H of about 4.1, as shown in Fig. 1. This type of behavior is typical of the formation of hydroxo or oxo-groups in polynuclear species[13]

$$2\,TiOH^{++} \rightarrow TiOTiOH^{+3} + H^+ \qquad (10)$$

The presence of oxo-groups also is indicated by the stability of the black color of these solutions upon the addition of sodium tartrate. When this complexing agent is added to titanium(III) solutions at initial *p*H values less than 4, a yellow-green color results. The yellow titanium(III) tartrate complex is stable at *p*H values as high as 8.

An 8 mM solution of titanium(III) in 0.75 M potassium iodide solution was studied spectrophotometrically at various *p*H values at 25° using the Cary Model 11 spectrophotometer. A portion of the solution was retained in the constant temperature bath so that the *p*H could be measured simultaneously with the measurement of the spectrum. A few of the initial spectra are shown in Fig. 2. The spectrum was found to be stable at *p*H values up to 2. At *p*H 2.7, the absorption had tripled at 800 mμ after 25 hr. even though the

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[9] T. S. Lee, "Treatise on Analytical Chemistry," edited by I. M. Kolthoff and P. J. Elving, Part I, Volume I, Interscience Encyclopedia, New York, N. Y., 1959, p. 253.

[10] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants," Part II, The Chemical Society, London, 1958.

[11] L. G. Sillén, *Quart. Revs.* (London), **13**, 146 (1949).

[12] J. Lewis and R. G. Wilkens, "Modern Coördination Chemistry, Principles and Methods," Interscience Publishers, New York, N. Y., 1960.

[13] J. C. Bailar, Jr., "The Chemistry of the Coordination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956, p. 453.

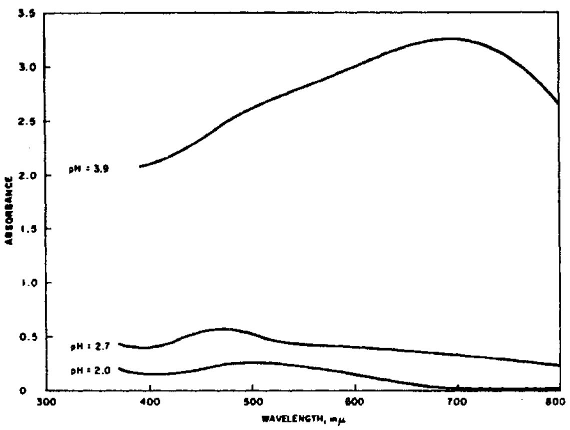

Fig. 2.—Variation of absorbance with *p*H for 8 m*M* titanium(III) in 0.75 *M* KI solution.

*p*H had remained constant. At *p*H 3.9, a 10% increase occurred at 800 mμ after only 15 min. From these results, it is concluded that polynuclear species with an absorption maximum near 700 mμ are slowly formed from $Ti(OH)^{+2}$, which has an absorption maximum at 480 mμ. The spectrophotometric evidence also indicates that negligible amounts of polynuclear species were present in the *p*H region where the log K_1 values were determined for the present work. Since the absorbance of this polynuclear species is so much larger than that of Ti^{+3}, spectrophotometric evidence of its existence is a much more sensitive measurement than the material balance which is reflected by the *p*H measurements. It also can be concluded from this and the titration shown in Fig. 1 that only negligible amounts of $Ti(OH)_2{}^+$ exist in these concentration ranges and that a simple $Ti(OH)_3$ is probably formed only by a very rapid addition of base to an acidic titanium(III) solution.

Whenever the *p*H was allowed to exceed 5, very rapid oxidation of the titanium(III) was found to occur. This presumably is due to the formation of hydrogen through reduction of water by titanium(III).[14]

Acknowledgment.—Special acknowledgment is due to the U. S. Naval Ordnance Test Station, China Lake, California, for granting a leave of absence and two fellowships to A. N. Fletcher.

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Compounds Exhibiting Coördination Number Eight. The Potassium Tetraoxalatometallates of Zirconium(IV), Hafnium(IV), Thorium(IV), and Uranium(IV)[1]

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Received September 27, 1961

The conditions have been studied for the preparation of the tetraoxalatometallates of zirconium(IV), hafnium(IV), thorium(IV), and uranium(IV), free of hydrolysis products. The zirconium and hafnium compounds are monoclinic with four molecules in the unit cell. The crystals belong to the space group $P2_1/a$, which permits the existence of mirror images in the solid state. Attempts to resolve the possible racemic pairs of these anions were unsuccessful. Oxalate exchange studies with C-14 containing oxalic acid showed that complete exchange occurred within a few minutes time of the experiment. It is shown that the anions lose oxalate by hydrolysis and/or aquation. The infrared spectra have frequencies for O–C–O vibrations about half way between those for the oxalate ion and a covalent oxalate molecule.

Introduction

For molecules or ions exhibiting coördination number eight, geometrical and optical isomers are possible, the number depending upon the kinds of groups involved and the geometry of the complex. The number of isomers for all classes of coördination number eight compounds has been calculated by Marchi.[3] For zirconium, hafnium, ura-

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[1] This article is based on a dissertation submitted by F. A. Johnson in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. Presented before the Division of Inorganic Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, September, 1958.

[2] National Science Foundation Predoctoral Fellow 1956–58.

[3] L. E. Marchi, W. C. Fernelius, and J. P. McReynolds, *J. Am. Chem. Soc.*, **65**, 329 (1943).