[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Complexes of Calcium Ion with Pyrophosphate and Triphosphate Ions[1]

BY JAMES I. WATTERS AND SHELDON M. LAMBERT

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The stabilities of the complexes of calcium ion with pyrophosphate and triphosphate ions have been calculated from the *p*H lowering due to complex formation during the titration of pyrophosphate ion and triphosphate ion with hydrogen ion. These various complexes and their corresponding complexity constants were obtained at 25° using tetramethylammonium chloride to adjust the ionic strength to unity: $CaP_2O_7^{2-}$, $\beta_{Ca(py)} = 10^{4.95}$; $Ca(HP_2O_7)^-$, $\beta_{Ca(Hpy)} = 10^{2.30}$; $CaP_3O_{10}^{3-}$, $\beta_{Ca(tp)} = 10^{5.44}$; $Ca(HP_3O_{10})^{2-}$; $\beta_{Ca(Htp)} = 10^{3.01}$.

Introduction

This is the fifth paper of a series on the acidity and complexes of polyphosphates.[2] The method used in these previous studies of complex formation were based on the *p*H lowering due to complex formation during an acidimetric titration in the presence of a relatively large excess of metal ion. The procedure was modified for the investigation of calcium complexes since addition of a stoichiometric excess of calcium ion resulted in the precipitation of both calcium pyrophosphate and calcium triphosphate. A known concentration of calcium ion which was small enough to avoid polyphosphate precipitation was maintained by equilibrating the solution containing a known initial concentration of sulfate ion as tetramethylammonium sulfate with solid $CaSO_4 \cdot 2H_2O$. The solubility product of $CaSO_4 \cdot 2H_2O$, used to calculate the calcium ion concentration, was experimentally determined in 1 *M* tetramethylammonium chloride at 25°. This modification should extend the application of this titration method to complexes of metals forming insoluble salts with basic ligands.

Quimby[3] mentions that the evaluation of complexity constants in systems containing calcium ion has been hampered by the limited range of solubility. He discussed experiments by Gray and Lemmerman[4] in which conductivity measurements were performed according to Job's method of continuous variations. This evidence indicated a (1:1) complex of calcium ion with triphosphate ion having a dissociation constant of the order of 3.1×10^{-7} at 30°. Martell and Schwarzenbach[5] studied the complexes of calcium and magnesium ions with triphosphate and adenosine triphosphate in the presence of alkali metal ions. Their results, based on an extrapolation of the titration curve into the region where precipitate forms indicate a (1:1) triphosphate complex having a complexity constant of $10^{4.95}$ in 0.1 *M* KCl at 20°. They also reported an acidic complex of calcium with $HP_3O_{10}^{4-}$ having a constant of $10^{3.1}$. Yatsimirskii and Vasil'ev[6] calculated a value of $10^{5.00}$ for the (1:1) calcium complex with pyrophosphate by colorimetric determination of *p*H. MacAvoy[7] studied the triphosphate complex by using ion exchange and transference methods to determine the free calcium ion content in solution. He reported a constant in the range $10^{5.72}$ to $10^{4.80}$. Prior to the present study, the effect of complexes with the alkali metals, reported in previous papers,[2b,c] have been neglected.

$$K'_{N-1} = \frac{[H^+][(HL) + (MHL)]}{(H_2L)} = K_{N-1}[1 + \beta_{MHL}(M)] \quad (1)$$

$$K'_N = \frac{[H^+][(L) + (ML)]}{(HL) + (MHL)} = \frac{K_N[1 + \beta_{ML}(M)]}{1 + \beta_{MHL}(M)} \quad (2)$$

The symbol L indicates the pyrophosphate or triphosphate ligand, K_{N-1} and K_N are the last two acidity constants of pyrophosphoric and triphosphoric acid, obtained in the absence of complex forming metal ions, K'_{N-1} and K'_N are the corresponding apparent acidity constants, observed in the presence of known concentrations of these metal ions while β_{ML} and β_{MHL} are the complexity constants for the complexes ML and M(ML).

Experimental

The preparation of the tetramethylammonium pyrophosphate and triphosphate solutions from the sodium salt by means of the ion-exchange resin, Dowex 50-X2, 100–200 mesh, has been discussed in previous papers.[2b,c] A stock solution of 0.5 *M* $CaCl_2$ was prepared from Mallinckrodt Analytical reagent and standardized by determining the chloride content volumetrically with silver nitrate. The tetramethylammonium sulfate was prepared from tetramethylammonium chloride by the use of the ion-exchange resin, Dowex 2-X7.5, 20–50 mesh, medium porosity, in the sulfate form. The general experimental procedure consisted of titrating the solutions containing various concentrations of calcium and polyphosphate ions and an excess of hydrogen ion added as hydrochloric acid with a solution of tetramethylammonium hydroxide containing the same concentrations of calcium and polyphosphate ions. All solutions were adjusted to an ionic strength of unity with tetramethylammonium chloride and the solutions were thermostatically kept at 25.0 ± 0.1° under an atmosphere of nitrogen. The *p*H measurements were made with the Beckman Model G *p*H meter equipped with a "general purpose" glass electrode. All solutions were carbonate-free and were titrated immediately after preparation to avoid hydrolysis and precipitate formation. Once the polyphosphate concentration and the shape of the curves had been determined, duplicate aliquots were titrated to various "*a*" values and then equilibrated with solid $CaSO_4 \cdot 2H_2O$ before measuring the *p*H.

The solid $CaSO_4 \cdot 2H_2O$ was prepared by the reaction of a

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[1] Abstracted in part from the Ph.D. thesis of Sheldon M. Lambert submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1957.

[2] (a) J. I. Watters, E. D. Loughran and S. M. Lambert, THIS JOURNAL, **78**, 4855 (1956); (b) J. I. Watters, S. M. Lambert and E. D. Loughran, *ibid.*, **79**, 3651 (1957); (c) S. M. Lambert and J. I. Watters, *ibid.*, **79**, 4262 (1957); **79**, 5606 (1957).

[3] O. Quimby, *J. Phys. Chem.*, **58**, 603 (1954).

[4] J. A. Gray and K. E. Lemmerman, unpublished experiments, Research Department, Chemical Division, Procter and Gamble Co., Miami Valley Laboratory, Cincinnati 31, Ohio.

[5] A. Martell and G. Schwarzenbach, *Helv. Chim. Acta*, **39**, 653 (1956).

[6] K. B. Yatsimirskii and V. P. Vasil'ev, *Zhur. fiz Khim*, **30**, 28 (1956).

[7] T. C. MacAvoy, Dissertation Abstracts, Vol. XVII, **10**, 2148 (1957).

TABLE I

THE SOLUBILITY PRODUCT OF $CaSO_4 \cdot 2H_2O$

Tetramethylammonium chloride added to adjust the ionic strength to unity. The initial sulfate ion concentration and the calcium ion concentration obtained spectrophotometrically are listed; 25°.

$((CH_3)_4N)_2SO_4$, M	$(Ca^{2+}) \times 10^3$	pK_{sp}
0.0550	10.8	3.23
.1100	6.32	3.16
.1375	5.01	3.16
.2000	4.18	3.08
	Av.	3.16 ± 0.08

TABLE II

DATA AND RESULTS FOR THE TITRATION OF SOLUTIONS CONTAINING VARIOUS CONCENTRATIONS OF CALCIUM AND PYROPHOSPHATE OR TRIPHOSPHATE ION

"a" is the number of equivalents of H^+ per mole of ligand, C_L is the total polyphosphate ion concentration and C_{Ca} is the total calcium ion concentration. Numerical values obtained for the logarithm of the stepwise formation constant follow the designated constant.

"a"	pH	$C_L \times 10^3$	$C_{Ca} \times 10^3$	log β	
A. Calcium and pyrophosphate ($\mu = 1.00$)					
0.50	8.93	2.5	0.00		
.50	6.70	5.955	2.76[a]	log $\beta_{Ca(py)}$	4.97
.50	6.58	5.955	2.35[a]		5.14
.50	6.89	5.955	2.00[a]		4.88
.50	7.03	5.955	1.78[a]		4.78
				Av.	4.95 ± 0.25
1.50	6.13	2.5	0.00		
1.50	5.89	2.568	4.17[a]	log $\beta_{Ca(Hpy)}$	2.25
1.50	5.79	2.568	5.01[a]		2.36
				Av.	2.30 ± 0.15
B. Calcium and triphosphate ($\mu = 1.00$)					
0.50	8.81	2.5	0.00		
.50	6.52	5.530	4.17[a]	log $\beta_{Ca(tp)}$	5.40
.50	6.49	5.530	8.32[a]		5.38
.50	6.41	3.000	4.47		5.52
.50	6.51	2.701	2.35[a]		5.46
.50	6.52	2.701	2.69[a]		5.44
				Av.	5.44 ± 0.25
1.50	5.83	2.5	0.00		
1.50	4.84	2.765	8.838	log $\beta_{Ca(Htp)}$	3.08
1.50	4.77	2.765	11.73		3.02
1.50	4.58	2.765	17.51		3.02
1.50	4.74	2.701	13.73		2.97
1.50	4.65	2.701	19.62		2.89
1.50	4.88	2.701	7.848		3.08
				Av.	3.01 ± 0.15
C. Calcium and pyrophosphate ($\mu = 2.00$)					
0.50	9.00	10.20	0.00		
.50	7.30	10.20	1.05	log $\beta_{Ca(py)}$	4.77
.50	7.22	10.20	1.23		4.80
				Av.	4.79 ± 0.3
1.50	6.40	10.20	0.00	log $\beta_{Ca(Hpy)}$	
1.50	6.29	10.20	1.12		2.40 ± 0.3
D. Calcium and triphosphate ($\mu = 2.00$)					
0.50	8.90	12.35	0.00		
.50	7.03	12.35	1.02	log $\beta_{Ca(tp)}$	5.32
.50	7.08	12.35	1.12		5.26
				Av.	5.29 ± 0.3
1.50	5.91	12.35	0.00		
1.50	5.46	12.35	0.977	log $\beta_{Ca(Htp)}$	3.27 ± 0.3

[a] These are concentrations of the aquo ion calculated on the basis of equilibration with solid $CaSO_4 \cdot 2H_2O$.

solution of 0.1 M $CaCl_2$ with 0.1 M $((CH_3)_4N)_2SO_4$. The precipitate was filtered on a fine fritted Pyrex crucible, washed repeatedly and air dried. Portions of the freshly precipitated calcium sulfate were shaken for several hours with a solution containing various concentrations of $((CH_3)_4N)_2SO_4$ and enough $(CH_3)_4NCl$ to adjust the ionic strength to unity. The solutions were filtered as before and analyzed for calcium ion using the Beckman D.U. spectrophotometer equipped with the flame photometer attachment. Known solutions of calcium ion in the same electrolyte were used to obtain a working curve for the calcium concentrations. The absence of polyphosphate in the solid phase after the equilibrium was established by treating the precipitate with hot nitric acid, after washing thoroughly with ethanol, and testing for phosphate by the phosphomolybdate test. No phosphate was detected when the solutions contained more than about one millimolar polyphosphate.

The data and results obtained in calculating K_{sp} for $CaSO_4 \cdot 2H_2O$ are given in Table I. The mean value of $10^{-3.16 \pm 0.08}$ for the solubility product is consistent with the results of Cameron and Brown[8] in 1 M NH_4Cl. These authors found that the solubility of calcium sulfate varies greatly with the nature and concentration of the extraneous electrolyte.

In Table IIA and IIB are given the measured pH values at the mid-point of the first two plateaus, namely, after adding $^1/_2$ and $^3/_2$ equivalents of hydrogen ion per mole of pyro- and triphosphate, respectively, as indicated in the column "a." The equilibrium concentrations of calcium ion and the polyphosphate concentrations are also given. The corresponding values with no metal ion present are included since these correspond to the logarithms of the corresponding acidity constants. Substituting the data for "a" = $^3/_2$ into equation 1 yields the following values for the complexity constants of the acid complexes $CaHP_2O_7^-$ and $CaHP_3O_{10}^{2-}$ at $\mu = 1$ and 25°

$$\beta_{Ca(HP_2O_7)} = \frac{(CaHP_2O_7^-)}{(Ca^{2+})(HP_2O_7^{3-})} = 10^{2.30 \pm 0.15}$$

$$\beta_{Ca(HP_3O_{10})} = \frac{(CaHP_3O_{10}^{2-})}{(Ca^{2+})(HP_3O_{10}^{4-})} = 10^{3.01 \pm 0.15}$$

The formation of one acidic complex of calcium with both pyrophosphate and triphosphate accounted within experimental error for all of the data in the "a" range of 1 to 2.

In the "a" range 0 to 1 complexes of the types Ca_2L, CaL and CaL_2 are possible. However, all of the experimental data could be accounted for by assuming the presence of only the (1:1) complex CaL. This was true even when the complete series of experiments was performed in the presence of 0.333 M sulfate ion at the necessarily increased ionic strength of 2 as shown in Table IIC and IID. The absence of (2:1) complex Ca_2L is to be expected under these experimental conditions since the polyphosphates are present in excess. The absence of experimentally detectable concentrations of CaL_2 indicates that the charge density about the calcium ion is effectively neutralized by one polyphosphate ion.

Substituting the data for "a" = $^1/_2$ into equation 3 yields the following values for the complexity constants of the (1:1) complexes at $\mu = 1$

$$\beta_{CaP_2O_7} = \frac{(CaP_2O_7^{2-})}{(Ca^{2+})(P_2O_7^{4-})} = 10^{4.95 \pm 0.25}$$

$$\beta_{CaP_3O_{10}} = \frac{(CaP_3O_{10}^{3-})}{(Ca^{2+})(P_3O_{10}^{5-})} = 10^{5.44 \pm 0.25}$$

Our value of 5.44 for log β_{Catp} is somewhat larger than the value 4.95 reported by Martell and Schwarzenbach. This difference is reasonable since their experiments were performed in 0.1 M KNO_3 and at 20°. Our value of 3.01 for log $\beta_{Ca(Htp)}$ is close to their value of 3.1. Potassium forms no detectable concentration of acidic complex in the pH range in which this constant is calculated. The logarithms of the constants for the calcium complexes are about 0.40 of a unit smaller than those for magnesium with the exception of $\beta_{Ca(Hpy)}$. In this case, the value for calcium is about 0.8 unit smaller. These differences are consistent with the effect one would predict for ionic bonding due to differences in the ionic radii of calcium and magnesium. Similar effects

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[8] F. K. Cameron and B. E. Brown, *J. Phys. Chem.*, **9**, 210 (1905).

were observed in the polyphosphate complexes of sodium and potassium. The larger effect in the acidic pyrophosphate complex of calcium probably is due to the closer approach of the hydrogen ion in the pyrophosphate complex in contrast to its approach in the triphosphate complex. This effect should be greater in the case of calcium which is already less firmly bound than magnesium.

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

Ceric Reduction and the Radiolytic Hydrogen Yield[1]

BY H. A. MAHLMAN

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The hydrogen yields observed in the cobalt-60 γ-ray irradiation of sulfuric acid solutions of ceric ions indicate an acid independence to 0.8 M H_2SO_4. The suppressive action of the solute may be expressed by the equation $G(H_2) = -0.21 [Ce^{IV}]^{1/3} + 0.44$. The scavenging effect of ceric ion indicates that the theoretical cerous yield may be obtained only in infinitely dilute ceric solutions.

The hydrogen yields in cobalt-60 γ-ray irradiation of 0.4 M H_2SO_4 solution and dilute H_2SO_4 solution pH 2 have been generally accepted to be 0.40 and 0.45, respectively.[2] In disagreement it was reported that in 0.4 M H_2SO_4 and 0.5×10^{-3} to 0.5×10^{-6} M H_2SO_4 solutions,[3] containing 10^{-3} M KBr to protect the molecular hydrogen formed from radical attack, the hydrogen yield was the same and equal to 0.45. The presence of HSO_4^- and $SO_4^{=}$ has been shown to have no effect on the hydrogen yield from cobalt-60 irradiated solutions.[4] The purpose of this paper is to present confirmatory evidence that the $G(H_2)$ in a 0.4 M H_2SO_4 solution is 0.45, that this yield is constant to 0.8 M H_2SO_4 and to show that the $G(Ce^{III})$ in an 0.4 M H_2SO_4–Ce^{IV} solution can approach 2.34 only when the concentration of Ce^{IV} approaches zero.

The chemicals were Baker and Adamson C.P. grade sulfuric acid and G. Frederick Smith analytical reagent ceric acid sulfate. Water from a Barnstead still was purified and stored in silica vessels. All irradiations were made in a 900 curie cobalt-60 γ-ray source. The dose rate was determined by the Fricke dosimeter assuming that 15.60 ferrous ions were oxidized per 100 e.v. of absorbed energy.[5] The additional energy absorption due to the added solute was calculated.[6] The yield, G(product), defined as the number of ions formed per 100 e.v. of absorbed energy, was calculated from the total absorbed energy. Analytical measurements of ferric ion concentrations were made directly on a Cary Recording Spectrophotometer at 3050 Å. using a molar extinction coefficient of 2240 at 25.°[5] Determination of the S.T.P. volume of the molecular hydrogen formed was made by ignition with oxygen on a platinum filament. The volume of solutions irradiated was determined by weight after the irradiation and hydrogen analysis.

The hydrogen yields were determined at two doses, 0.6×10^{20} e.v. and 1.2×10^{20} e.v. in solutions 0.001, 0.003, 0.008, 0.026, 0.064 and 0.10 molar Ce^{IV} and two acidities 0.4 and 0.8 M H_2SO_4. The data in Table I illustrate the suppressive effect of ceric ion concentration on the hydrogen yield and may be expressed by the least squares determined equation $G(H_2) = -0.21 [Ce^{IV}]^{1/3} + 0.44$. The concordance of the data indicates that the hydrogen yields in 0.4 and 0.8 M H_2SO_4 solutions containing Ce^{IV} ions are the same. The hydrogen yields reported for oxygenated 0.4 M H_2SO_4 solutions containing 0.01 and 4×10^{-4} M ceric ion[7] are in agreement with these experimentally determined values when corrections are made for the suppressive effect of oxygen. Recalling the mechanism of ceric reduction in 0.4 M H_2SO_4 solution[8] and that ions reducible by H atoms lower the hydrogen yield one may see readily that a decrease in the hydrogen yield will cause an equivalent increase in the cerous yield. Appropriate calculations for 400 and 1000 micromolar ceric solutions 0.4 M H_2SO_4 show that the $G(Ce^{III})$ should be 2.37 and 2.38, respectively. These calculated values for the Ce^{III} formation in 400 and 1000 micromolar ceric solutions are in agreement with the values $G(Ce^{III}) = 2.39$ (Sworski)[9] and $G(Ce^{III}) = 2.37$ (Masters and Challenger).[10] Since the extrapolated hydrogen yield at zero solute concentration is 0.44 ± 0.01 one may conclude that the $G(H_2)$ is the same and equal in 5×10^{-6} to 0.8 M H_2SO_4 solu-

TABLE I

HYDROGEN YIELDS OBSERVED IN Ce^{IV}–H_2SO_4 SOLUTION

Initial Ce^{IV}	0.4 M H_2SO_4	0.8 M H_2SO_4
None	0.45[a]	0.44[a]
0.001	.41[b]	.41[b]
.003	.40[b]	.40[b]
.008	.40	.40
.026	.38[b]	.39[b]
.064	.34	.35
.10	.34	.34

[a] Contained 10^{-4} M KBr. [b] Single determinations.

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(1) Work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation.

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(3) H. A. Mahlman and J. W. Boyle, THIS JOURNAL, **80**, 773 (1958).

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