TABLE I

COPPER-CATALYZED REACTIONS OF PHENYLSILANE WITH ALCOHOLS

Alcohol	Alcohol, moles	Phenylsilane, moles	Products	B.p., °C. Product fractions	Yield, %	$n^{25}D$	d^{25}_4	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Methyl	0.3	0.3	$C_6H_5SiH_2OCH_3$	60–65 (10 mm.)	26.0	1.4845	1.0051	60.87	59.04	7.24	7.15
			$C_6H_5SiH(OCH_3)_2$	78–84 (10 mm.)	12.0	1.5400	1.0298	57.14	58.24	7.14	7.32
Ethyl	.3	.3	$C_6H_5SiH_2OC_2H_5$	60–67 (10 mm.)	11.1	1.4771	0.9350	63.15	63.55	7.84	7.65
			$C_6H_5SiH(OC_2H_5)_2$	80–84 (10 mm.)	5.0	1.4814	.9533	61.22	62.45	8.11	8.08
n-Propyl	.5	.5	$C_6H_5SiH_2OC_3H_7$	44–48 (5 mm.)	34.1	1.4838	.9430	65.06	64.69	8.43	8.57
			$C_6H_5SiH(OC_3H_7)_2$	90–96 (1.4 mm.)	8.0	1.4781	.9545	65.29	64.50	8.93	8.67
n-Butyl	.5	.5	$C_6H_5SiH_2OC_4H_9$	52–57 (0.7 mm.)	47.4	1.4820	.9408	66.66	65.91	8.88	8.87
			$C_6H_5SiH(OC_4H_9)_2$	90–96 (0.7 mm.)	14.3	1.4785	.9662	66.66	64.90	9.52	8.95

Discussion

This work serves to emphasize the lability of Si–H bonds, particularly in the presence of alkoxyl groups. Their instability in the presence of bases such as OH^- and OR^- is well known. Only by the exercise of extreme care to eliminate moisture and alcohols can an Si–Br bond be replaced with an Si–OR bond in the presence of Si–H. The Si–OR bond is very susceptible to hydrolysis, but this susceptibility appears on the basis of the instability of $H_2Si(OR)_2$ compounds to be enhanced by the existence of Si–H bonds on the same silicon atom. No satisfactory explanation is advanced for the apparent inertness of monobromosilane toward sodium alkoxides.

The action of copper in catalyzing reaction of Si–H bonds with alcohols is not only interesting but makes possible a certain degree of control in the synthesis of silicon alkoxides, so that by proper regulation of the rate of addition of the alcohol one can favor the formation of partially alkoxylated compounds where several hydrogen atoms are attached to the same silicon atom. It was observed that the alkoxylation reactions attempted all took place readily at room temperature but that the vigor of the reaction increased in the order MeOH < EtOH < *n*-PrOH < *n*-BuOH. There was also a detectable tendency to form a higher percentage of the monoalkoxy derivative with the higher alcohols than with those of lower molecular weight.

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BLOOMINGTON, INDIANA

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

The Complexes of Magnesium Ion with Pyrophosphate and Triphosphate Ions

BY SHELDON M. LAMBERT[1] AND JAMES I. WATTERS[2]

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The stabilities of the complexes of magnesium ion with pyrophosphate ion and triphosphate ion have been calculated from the *p*H lowering due to an excess of magnesium ion during the titration of pyrophosphate ion and triphosphate ion with hydrogen ion. The following complexes and their corresponding over-all complexity constants were obtained at 25° using tetramethylammonium chloride to adjust the ionic strength to unity: $Mg_2P_2O_7$, $\beta_{Mg2py} = 10^{7.75}$; $MgP_2O_7^{2-}$, $\beta_{Mgpy} = 10^{5.41}$; $Mg(HP_2O_7)^{2-}$, $\beta_{Mg(Hpy)} = 10^{3.06}$; $Mg_2P_3O_{10}^{-}$, $\beta_{Mg2tp} = 10^{7.96}$; $MgP_3O_{10}^{3-}$. $\beta_{Mgtp} = 10^{5.83}$; $Mg(HP_3O_{10})^{2-}$, $\beta_{Mg(Htp)} = 10^{3.34}$.

Introduction

This is the fourth paper of a series on the acidity and complexes of polyphosphates.[3–5] A different procedure was used to study the Ca^{2+} complexes due to the lower solubility of the calcium polyphosphates. These results will be reported in a separate paper. That complex formation occurs between calcium and magnesium ions and higher phosphates is well known. However, as indicated by Quimby[6] the evaluation of the complexity constants has been hampered by the limited range of solubility especially in the systems containing calcium ion. Quimby discussed experiments by Gray and Lemmerman[7] in which conductivity measurements were performed according to Job's method of continuous variations. This evidence indicated a 1:1 complex for the complex of calcium ion with triphosphate having a dissociation constant of the order of 3.1×10^{-7} at 30°.

Van Wazer and Campanella[8] have investigated the complexes of magnesium and calcium with higher phosphates with a mean chain length of five phosphate tetrahedra. Their results indicate the dissociation constants for both magnesium and cal-

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[1] Abstracted 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] To whom communications should be directed.

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[4] J. I. Watters, S. M. Lambert and E. D. Loughran, *ibid.*, **79**, 3651 (1957).

[5] S. M. Lambert and J. I. Watters, *ibid.*, **79**, 4262 (1957).

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

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

[8] J. R. Van Wazer and D. A. Campanella, THIS JOURNAL, **72**, 655 (1950).

cium complexes to be similar to those of Fe^{2+} and Mn^{2+}. Bobtelsky and Kertes[9] performed titrations of pyro- and triphosphates with Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} by turbidity, *p*H and conductivity measurements to obtain evidence for 1:1 complexes having electrostatic bonding. Martell and Schwarzenbach[10] used techniques similar to those described in this paper but without eliminating alkali metal ions to study the complexes of calcium and magnesium ions with triphosphate and adenosine triphosphate. Their results indicate 1:1 complexes with triphosphate having a complexity constant of $10^{5.80}$ for Mg^{2+}, and $10^{4.95}$ for Ca^{2+}. They also reported acidic complexes of calcium and magnesium ions with $HP_3O_{10}{}^{4-}$ having constants of $10^{3.7}$ and $10^{3.1}$, respectively. No previous values have been reported for the magnesium complexes with pyrophosphate and complexes containing two metal ions have not been detected previously.

Theory

The principle used in the investigations of alkali complexes[4,5] is applicable for the magnesium complexes of both triphosphate and pyrophosphate although the *p*H effect is much greater. The following equations, used to calculate the complexity constants, were derived by combining equations having the forms of (1), (2) and (3) of the previous papers[4,5] with *m* values of 1 or 2 which were required to describe the equilibria

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

$$K'_v = \frac{[H^+][(L) + (ML) + (M_2L)]}{(HL) + (MHL)} = \frac{K_v[1 + \beta_{ML}(M) + \beta_{M_2L}(M)^2]}{1 + \beta_{MHL}(M)} \quad (2)$$

The symbol, L, indicates the pyrophosphate or triphosphate ligand, K_{v-1} and K_v are the last two acidity constants of pyrophosphoric acid and triphosphoric acid, and K'_{v-1} and K'_v are the corresponding apparent acidity constants. β_{ML}, β_{M_2L} and β_{MHL} are the complexity constants for the complexes ML, M_2L and M(HL). These equations differ from those in previous papers in that one additional species M_2L was required.

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.[4,5] A stock solution of 0.5 *M* $MgCl_2$ was prepared from Mallinckrodt Analytical reagent and standardized by determining the chloride content volumetrically with silver nitrate. The general experimental procedure consisted of titrating the solutions containing various concentrations of magnesium and polyphosphate ions with a solution containing the same concentrations of magnesium and polyphosphate ions to avoid dilution and an excess of hydrogen ion, added as hydrochloric acid. 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.

Results and Discussion

The titration curves obtained were similar to those for lithium ion in the previous papers[4,5] except that the *p*H change was greater and the inflection after adding the first equivalent of acid was less pronounced but still evident. All of the curves showed the presence of an acidic complex. In Table I are given the measured *p*H values at the midpoints of the first two plateaus, namely, after adding $^1/_2$ and $^3/_2$ equivalents of hydrogen ion per mole of ligand as indicated in the column "*a*." The total concentrations of magnesium and ligand also are given. The corresponding values with no metal ion present also are included since these correspond to the logarithms of the corresponding acidity constants. Substituting the data for "*a*" = $^3/_2$ into equation (4) yielded the values given in Table I for the complexity constants of the acid complexes.

TABLE I

DATA AND RESULTS FOR THE TITRATION OF SOLUTIONS CONTAINING VARIOUS CONCENTRATIONS OF MAGNESIUM 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_{Mg} is the total magnesium ion concentration. Numerical values obtained for the logarithm of the stepwise formation constants follow the designated constant.

A. Magnesium and pyrophosphate

"a"	*p*H	$C_L \times 10^3$	$C_{Mg} \times 10^3$	log *K*	
				K_{Mgpy}	K_{Mg_2py}
0.50	8.93	2.5	0.00		
.50	6.24	2.950	9.934	5.44	2.32
.50	6.20	2.900	9.934	5.38	2.36
.50	5.93	2.950	19.87	5.40	2.34
			Av.	5.41	2.34
				K_{MgHpy}	
1.50	6.13	2.5	0.000		
1.50	5.08	2.950	9.934	3.08	
1.50	5.12	2.968	9.934	3.08	
1.50	4.76	2.950	19.87	3.02	
			Av.	3.06	

B. Magnesium and triphosphate

"a"	*p*H	$C_L \times 10^3$	$C_{Mg} \times 10^3$	log *K*	
				K_{Mgtp}	K_{Mg_2tp}
0.50	8.81	2.5	0.00		
.50	6.08	2.553	9.934	5.84	2.14
.50	5.84	2.710	19.86	5.81	2.12
.50	5.18	2.553	99.34	5.85	2.13
			Av.	5.83	2.13
				K_{MgHtp}	
1.50	5.83	2.5	0.00		
1.50	4.50	2.553	9.934	3.37	
1.50	3.30	2.710	19.86	3.30	
1.50	4.51	2.553	9.934	3.36	
			Av.	3.34	

$$\beta_{MgHP_2O_7} = \frac{(MgHP_2O_7{}^-)}{(Mg^{2+})(HP_2O_7{}^{3-})} = 10^{3.06 \pm 0.06}$$

$$\beta_{MgHP_3O_{10}} = \frac{(MgHP_3O_{10}{}^{2-})}{(Mg^{2+})(HP_3O_{10}{}^{4-})} = 10^{3.34 \pm 0.06}$$

The formation of one acidic complex accounted within experimental error for all of the experimental data in the "*a*" range of 1 to 2.

When eq. 2 was used without including the species Mg_2L the value for the complexity constant β_{MgL} increased from $10^{5.79}$ to $10^{6.08}$ for the

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[9] M. Bobtelsky and S. Kertes, *J. Appl. Chem.*, **4**, 419 (1954).

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

pyrophosphate complex with a twofold increase in the total magnesium ion concentration and from $10^{6.10}$ to $10^{6.97}$ for the triphosphate complex with a tenfold increase in the total magnesium ion concentration. These variations which are much greater than the experimental deviation of $10^{\pm 0.06}$ can only be accounted for by the presence of a Mg_2L complex. Including this species in eq. (2) and solving pairs of equations simultaneously for both complexity constants yielded constant values for both complexity constants. The presence of a complex Mg_2L under these experimental conditions is not surprising since the experiments are performed with an excess of magnesium ion present. These experiments do not deny the existence of a species MgL_2 which might be obtained in the presence of a large excess of ligand. Martell and Schwarzenbach[10] mentioned $Mg_2P_3O_{10}^-$ as a possible complex species under these experimental conditions.

Our agreement with Martell and Schwarzenbach for the complexity constants of $MgP_3O_{10}^{3-}$ and $MgHP_3O_{10}^{2-}$ is fortuitous. Their supporting electrolyte was 0.1 M KCl with sodium ion added during the titration at 20° while our supporting electrolyte was close to 1.0 M $(CH_3)_3HCl$ at 25° with no alkali metal ion present since previous studies in this Laboratory have shown that alkali metals form stable complexes with pyro- and triphosphate ion.

$$\beta_{MgP_2O_7} = \frac{(MgP_2O_7{}^{2-})}{(Mg^{2+})(P_2O_7{}^{4-})} = 10^{5.41 \pm 0.06}$$

$$\beta_{Mg_2P_2O_7} = \frac{(Mg_2P_2O_7)}{(Mg^{2+})^2(P_2O_7{}^{4-})} = 10^{7.75 \pm 0.09}$$

$$\beta_{MgP_3O_{10}} = \frac{(MgP_3O_{10}{}^{3-})}{(Mg^{2+})(P_3O_{10}{}^{5-})} = 10^{5.83 \pm 0.06}$$

$$\beta_{Mg_2P_3O_{10}} = \frac{(Mg_2P_3O_{10}{}^{-})}{(Mg^{2+})^2(P_3O_{10}{}^{5-})} = 10^{7.96 \pm 0.09}$$

The effect of their larger acidity constants is cancelled by their finding no $Mg_2P_3O_{10}^-$ complex. This may have been the result of their varying the metal ion concentration over a smaller range of concentrations or the effect may have been masked as a result of the formation of mixed complexes containing both magnesium and alkali metal ions.

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Chelate Compounds of Nickel(II) with Picolinic Acid

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A spectrophotometric method has been used to demonstrate the existence of a tris-picolinato chelate of nickel(II) and to determine the three stability constants in aqueous solutions of ionic strength not exceeding 10^{-3}. The values found were log K_1, 6.68; log K_2, 5.98; log K_3, 5.12. Reasons are discussed for preferring these values to the slightly smaller figures given by the pH titration method.

A stable chelate compound of picolinic acid and nickel, having the formula $Ni(C_6H_4NO_2)_2 \cdot 2H_2O$, was prepared by Cox, Wardlaw and Webster[1]; and stability constants of the mono- and bis-picolinato derivatives recently have been determined by Holmes and Crimmin[2] and by Suzuki, Yasuda and Yamasaki.[3] In spite of the well-known hexacovalency of nickel(II), there appears to be no record of a tris-picolinato chelate. The system has been investigated here by a spectrophotometric method to which the high molar extinction of picolinic acid[4] is particularly favorable. The results are compared with those obtained by the pH titration method.

Experimental

Materials.—Picolinic acid, supplied by Hopkin and Williams, Ltd., was resublimed at 100° *in vacuo*. Its equivalent weight was checked by pH titration with standard alkali. A filtered solution of Analar nickel(II) chloride in boiled-out water was analyzed for nickel by electrodeposition and gravimetrically for chloride, the two values agreeing within 0.1%. The pH of the 0.1 M solution was 5.8.

Spectrophotometric Method.—Appropriate volumes of 0.1 M picolinic acid and 0.1 M nickel(II) chloride were mixed and diluted with boiled distilled water so that the total picolinic acid concentration was 2.5×10^{-3} M. The spectrophotometric solution was then prepared by further dilution to 10^{-4} M with respect to picolinic acid, with the addition of sufficient sodium hydroxide or hydrochloric acid to produce the required pH. Absorption spectra were measured at 25° in 1 cm. cells with a Beckman Model DU spectrophotometer, using a water-jacketed cell compartment. At 2650 Å. the molar extinction of the hydrated Ni^{++} ion is negligible compared with that of picolinic acid. Nevertheless, when high concentrations of nickel were present in the test solution, they were matched by equal nickel concentrations in the blank cell.

pH Method.—Solutions for titration were 0.0025 M with respect to nickel and contained 2, 3 or 4 moles picolinic acid per mole nickel. They were titrated with carbonate-free 0.1 M NaOH while being stirred continuously with a current of purified nitrogen in a closed vessel. Measurements were made at 25° with the Beckman Model G pH meter and a glass electrode standardized at pH 4.00 with M/20 potassium hydrogen phthalate. Because of the uncertainties associated with calculations at low pH,[2] titrations with a strong acid were not attempted.

Results and Discussion

The addition of small amounts of nickel ion to aqueous picolinic acid causes changes in the absorption spectrum of the acid between 2400 and 2800 Å. However, the wave length of the absorption maximum remains unchanged at 2650 Å. and

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