Experimental

4-Bromo-1-naphthol.—Twenty-six grams of finely divided iodine was placed in 60 cc. of glacial acetic acid and 5 cc. of bromine added. In order to facilitate formation of the iodine monobromide the solution was warmed to 50°. All of the iodine dissolved upon shaking except a trace. After the solution had cooled somewhat, it was introduced within ten minutes by means of a dropping funnel into a solution containing 14 g. of α-naphthol in 45 cc. of glacial acetic acid, kept cool by immersion in tap water. The reaction was allowed to stand for one hour during which time as much hydrogen bromide as possible was removed from the flask by a gentle air blast. The mixture was now poured into 700 cc. of water containing 16 g. of sodium bisulfite; 160 g. of sodium bicarbonate suspended in water was then added to neutralize the acetic acid and most of the hydrobromic acid. This led to a more complete precipitation of the product, which was now filtered, washed with water, and dried. The filtrate was saved for the recovery of iodine. The 20 g. of crude product was warmed with 1100 cc. of 33% alcohol, filtered, and allowed to crystallize. The yield after filtering and drying was 12 g. of a reasonably pure product (63%). After several recrystallizations from 33% alcohol (45 cc. per g.) the m. p. was 121–122°; Boudroux, 121°,[4] Reverdin and Kaufmann, 127–128°;[5] picrate, m. p. 169–170°, Boudroux 169°, Reverdin and Kaufmann 167°; acetyl derivative, m. p. 49–51°, R. and K. ~51°.

α-Bromonaphthalene.—Ten cc. of bromine (0.2 mol) was run into 100 cc. of carbon tetrachloride and 51 g. of iodine was added. To promote the formation of the iodine bromide the mixture was warmed to 50–60° and shaken until all of the iodine had dissolved. The warm solution of iodine bromide was now run into another containing 27 g. of naphthalene (slight excess of 0.1 mol) in 50 cc. of carbon tetrachloride. The apparatus was arranged to remove the hydrogen bromide which was evolved rapidly. Iodine began to precipitate from solution almost immediately. After the addition of iodine bromide was complete (ten minutes), the whole was warmed to 50–60° and allowed to stand for thirty to forty-five minutes, then filtered through glass wool into a separatory funnel. The solution was then shaken out with two portions of water to remove the remaining hydrobromic acid and with two portions of sodium hydroxide solution to remove the remaining iodine.[6] After a quick drying over calcium chloride, the carbon tetrachloride solution was refluxed for thirty minutes with 0.5 g. of zinc dust to remove compounds which slowly liberate iodine. After filtration, the carbon tetrachloride was distilled off. The remaining crude product contained naphthalene and α-bromonaphthalene. Fractionation of this at atmospheric pressure gave a fraction distilling over below 265°, and a second fraction of relatively pure α-bromonaphthalene boiling between 271 and 275° (uncorr.). The yield of the second fraction was 50–55% of the theoretical. The total yield may be increased by reworking the first fraction. The product was of a light straw color.

Summary

Iodine monobromide has been found to be a mild brominating agent for substitution on the aromatic ring.

In the preparation of 4-bromo-1-naphthol and α-bromonaphthalene, iodine monobromide presents advantages over the regular bromination procedures.

LINCOLN, NEBRASKA RECEIVED NOVEMBER 26, 1937

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(4) Boudroux, *Bull. soc. chim.*, [3] **31**, 35 (1904).

(5) Reverdin and Kaufmann, *Ber.*, **28**, 3054 (1895).

(6) The total recovery of iodine is almost quantitative.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Hydration of Diammonium Dihydrogen Pyrophosphite to Orthophosphite at 30°

BY SAMUEL J. KIEHL AND MANUEL FOSTER MOOSE

In 1888 Amat[1] discovered that pyrophosphites are unstable in aqueous solution and that they hydrate to orthophosphites. He followed the course of the hydration by titrating the solution by means of sodium hydroxide with phenolphthalein as an indicator. For justification of the method he says:

"The monosodium phosphite is, in fact, neutral to methyl orange and acid to phenolphthalein; the pyrophosphite of sodium is neutral to these two reagents."

Since his researches no work has been published upon the hydration of pyrophosphites although for many years, from time to time, the hydration of pyrophosphate in aqueous solution has been investigated and conditions which prevent, retard or promote its occurrence have been partially established.[2] As yet, little is known concerning the conditions which effect the hydration of pyrophosphites. There is an analogy of

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(1) Amat, *Compt. rend.*, **106**, 1400 (1888).

(2) Graham, *Phil. Trans.*, **123**, 53 (1833); Sabatier, *Compt. rend.*, **106**, 63 (1888); Montemartini and Egidi, *Gazz. chim. ital.*, **31**, I, 394 (1901); Balareff, *Z. anorg. Chem.*, **67**, 234 (1909); *ibid.*, **68**, 288 (1910); *ibid.*, **96**, 103 (1916); Berthelot and André, *Compt. rend.*, **123**, 776 (1896); *ibid.*, **124**, 261 (1897); *ibid.*, **124**, 265 (1897); Giran, *ibid.*, **135**, 961–63, 1333–35 (1902); Holt and Meyers, *J. Chem. Soc.* **99**, 385 (1911); Abbott, THIS JOURNAL, **31**, 763 (1909); Kiehl and Hansen, *ibid.*, **48**, 2902 (1926); Kiehl and Coats, *ibid.*, **49**, 2180 (1927); Kiehl and Hill, *ibid.*, **54**, 1332 (1932); Kiehl and Claussen, *ibid.*, **57**, 2284 (1935).

behavior, moreover, between the corresponding phosphorus compounds on these two different oxidation levels in some respects, but the extent and character of this analogy with reference to its hydration is unknown save for the work of Amat.

Consequently some data and information have been secured upon the hydration of diammonium dihydrogen pyrophosphite.

Materials.—The preparation and purification of salts and reagents have been described by the authors[3] in a previous paper.

Procedure

To follow the course of the hydration and to study controlling conditions it was necessary to develop a method whereby the orthophosphite could be determined in the presence of pyrophosphite or *vice versa*. As methods based upon titration with indicators are not satisfactory in mixtures of either phosphates or phosphites in different states of hydration, a method based upon the oxidation of orthophosphite to orthophosphate was developed. Since iodine oxidizes orthophosphite quantitatively and has little, if any, effect upon pyrophosphite, the procedure was based upon this difference of property.

During any determination of orthophosphite in the presence of pyrophosphite some hydration of the latter occurs. Conditions to make this hydration a minimum were determined. Preliminary studies indicated that the hydration proceeded at a minimum rate at a *p*H near 6.5. The rate of oxidation of orthophosphite by iodine, moreover, had been shown to fall off rapidly below 7, whereas from 7 to 10 it slowly increased.[3] Furthermore, the rate of the hydration increases far more rapidly than the rate of oxidation as the *p*H is increased from 7 to 10; hence the most accurate determination may be made at a *p*H near 7. To allow the minimum hydration on this *p*H level conditions whereby the oxidation could be made in shortest time were established as follows:

To 25 cc. of an approximately 0.05 N orthophosphite solution were added 60 cc. of a buffer (0.5 M H_3BO_3–0.05 M KOH) and then 50 cc. of 0.05 N iodine; at the end of a definite interval of time the solution was made acid and the excess iodine determined. All operations except the titration of the excess iodine were performed at 30°. Thus by successively increasing or decreasing the time allowed for the reaction of iodine and orthophosphite, the minimum time for quantitative oxidation was determined.

This series of experiments was repeated at 25°. Also, the whole series was repeated at both temperatures with 0.01 N orthophosphite and iodine solutions instead of 0.05 N solutions. From these results the quantitative oxidation of orthophosphite at a *p*H of 7 by approximately 100% excess iodine is accomplished:

In 25 minutes by 0.01 N I_2 at 30°
In 7.5 minutes by 0.05 N I_2 at 30°
In 40 minutes by 0.01 N I_2 at 25°
In 12.5 minutes by 0.05 N I_2 at 25°

The Determination of Orthophosphite in the Presence of Pyrophosphite.—As a consequence of the foregoing experiments, all determinations of orthophosphite in the presence of pyrophosphite were made under the following conditions: *p*H, 7; temperature, 30°; oxidizing agent, 100% excess iodine; time, ten minutes for 0.05 N iodine and thirty minutes for 0.01 N iodine.

To test the accuracy of the method, an orthophosphite was analyzed in the presence and in the absence of pyrophosphite. To a mixture of 60 cc. of buffer (0.18 M Na_2HPO_4–0.072 M NaH_2PO_4) and 50 cc. of iodine solution were added 10 cc. of an orthophosphite solution of such concentration as to require less than 25 cc. of the solution of iodine for its oxidation. Weighed portions of $(NH_4)_2H_2P_2O_5$ were added to some of the mixtures; and at the end of the respective required times discussed above the solutions were made acid and the excess iodine determined.

Determinations were made with 0.05 N iodine, when all of the phosphorus was in the ortho form, when 50% was pyro, and when 70% was pyro under conditions prevailing in solutions undergoing investigation below; with 0.01 N iodine when all of the phosphorus was as orthophosphite and when 90% of it was as pyrophosphite. The results of these experiments indicated that the presence of the pyrophosphite leads to high results, the magnitude of which is in the order of

0.3% when 50% of the P is pyro and 0.05 N I_2 is used
.6% when 70% of the P is pyro and .05 N I_2 is used
5.1% when 90% of the P is pyro and .05 N I_2 is used

These errors were calculated assuming that no orthophosphite was contained in the samples of pyrophosphite added. Experiments indicate, however, that the samples of pyrophosphite added contained 0.2% of orthophosphite. Consequently, the actual errors of determination are 0.1, 0.2, and 3% instead of 0.3, 0.6, and 5%, respectively.

Methods of Preparing and Analyzing the Solutions.—In the study of the hydration of $(NH_4)_2H_2P_2O_5$, duplicate experiments were made with solutions of the pyrophosphite which contained 0.1000 gram molecular weight of the pyrophosphite per 1000 g. of the final solution and which had for the respective solvent

Solution I,	0.1000 M NaOH
Solution II.	.01000 M NaOH
Solution III,	Distilled water
Solution IV,	.1000 M $HC_2H_3O_2$
Solution V,	.1000 M $KHSO_4$
Solution VI,	.1000 M HCl

Expressed in terms of molality these solutions have the following concentrations

I,	0.1022 molal $(NH_4)_2H_2P_2O_5$	0.1003 molal NaOH
II,	.1019 molal $(NH_4)_2H_2P_2O_5$	.01003 molal NaOH
III,	.1018 molal $(NH_4)_2H_2P_2O_5$	
IV,	.1025 molal $(NH_4)_2H_2P_2O_5$	.1008 molal $HC_2H_3O_2$
V,	.1032 molal $(NH_4)_2H_2P_2O_5$	.1007 molal $KHSO_4$
VI,	.1022 molal $(NH_4)_2H_2P_2O_5$	.1005 molal HCl

The times required for the hydration in solutions I, II and III were so great that oxygen had to be excluded to prevent oxidation of the phosphite. The apparatus shown in Fig. 1 was so designed that the solvent might be freed of air and the solution prepared in an atmosphere free of oxygen.

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(3) Kiehl and Moose, THIS JOURNAL, **60**, 47 (1938).

Flask B was used to free the solvent of air. It was rinsed with the solvent, allowed to drain, and weighed. The quantity of the solvent needed in the hydration was introduced and the flask again weighed. Purified hydrogen, which previously had been passed through three gas wash bottles containing the same liquid as in B, was bubbled through the solvent in B for several hours. The weight of the flask and its contents was again ascertained, and the flask then set in the constant temperature bath.

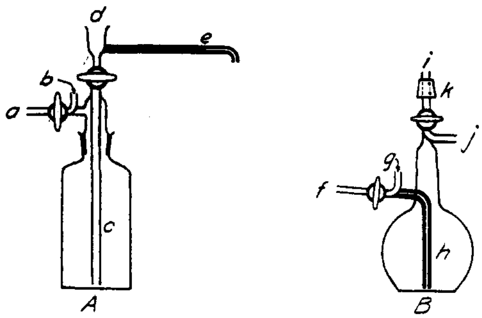

Fig. 1.

In the meantime the quantity of $(NH_4)_2H_2P_2O_5$ required to prepare a solution of the desired concentration when dissolved in the solvent contained in B was placed in flask A which was in turn swept free of air by hydrogen. Flask B was then inverted over A and the stopper k fitted into d. Hydrogen entering at a passed through c, d, i and out at j, thus sweeping the air out of pocket d. Stopcocks where then opened so as to allow the solvent to flow into A from B. The solvent in tube c was forced down into the main body of the solution where it was well mixed.

Flask B was again weighed in order to check the weight of the solvent used (weight 4 minus weight 3 less a correction due to the added buoyancy of hydrogen) against the value used in determining the quantity of $(NH_4)_2H_2P_2O_5$ to be taken (weight 2 minus weight 1). In all cases the two agreed within 0.05%.

Portions of the solution were withdrawn from flask A, from time to time, through e by means of a pressure of hydrogen introduced at a into a Bailey buret from which weighed samples were taken for analysis.

The cup d was fitted with a two-hole rubber stopper with two glass tubes, one of which was connected with b. Thus after each sampling the solution in the upper portion of e could be returned to the bottle.

In hydrations IV, V, and VI the time of the reaction was so short that it was found unnecessary to protect the solution from oxygen. However, the rate was so rapid that the time consumed by the weighing of the sample taken for analysis would introduce a serious error unless the rate of the reaction of the sample could be materially diminished. Consequently, in a stoppered Erlenmeyer flask were placed 15 cc. of a buffer (0.18 *M* Na_2HPO_4–0.072 *M* NaH_2PO_4 or 0.5 *M* H_3BO_3–0.05 *M* KOH) and a sufficient quantity of 0.1 *N* sodium hydroxide to neutralize roughly the sample removed. The weight of the flask and its contents without the sample was ascertained. The sample was withdrawn from the solution under investigation by a Mohr pipet and added to the contents of the Erlenmeyer flask. Again the weight of the flask and its contents was determined and the contents analyzed for orthophosphite in the usual manner. Thus the hydration of the sample was, for all practical purposes, cut short at the time of the sampling.

The Measurement of the *p*H During the Course of the Hydration.—The hydration of pyrophosphite to orthophosphite produces available hydrogen ions and, in most cases lowers the *p*H of the solution

$$H_2P_2O_5^{=} + H_2O \longrightarrow 2HPO_3^{=} + 2H^+$$

The resulting changes in *p*H were followed by means of a glass electrode according to the method and with the instrument designed and described recently.[4]

Results

The course of the hydrations and the change of *p*H which accompanies the hydration are shown in Table I. The hydrations were studied in duplicate.

Figures 2, 3, 4 and 5 represent graphically the data from solutions II, III, IV and VI, respectively. The "tabs" on the circles which represent the points on the graphs indicate duplicate experiments; the one extending upward one experiment the one downward the other.

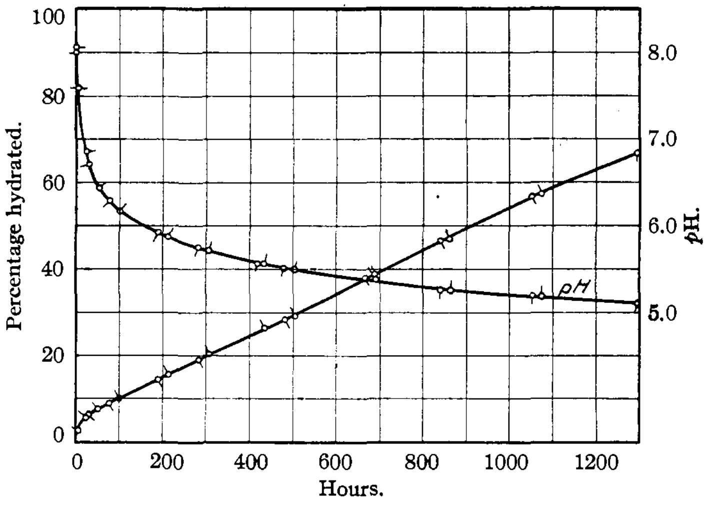

Fig. 2.—0.1000 molar $(NH_4)_2H_2P_2O_5$–0.0100 molar NaOH.

The rate of hydration was so much greater in the solutions of low *p*H that separate samples had to be taken and separate times had to be recorded for solutions IV, V and VI in the determination of the *p*H values.

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[4] Ellis and Kiehl, *J. Sci. Instruments*, **4**, 131–138 (1933); Ellis and Kiehl, THIS JOURNAL, **57**, 2139 (1935).

TABLE I

THE HYDRATION OF $(NH_4)_2H_2P_2O_5$ AT 30°

Solution I, 0.1022 molal $(NH_4)_2H_2P_2O_5$ 0.1003 molal NaOH
Solution II, .1019 molal $(NH_4)_2H_2P_2O_5$ 0.01003 molal NaOH
Solution III, .1018 molal $(NH_4)_2H_2P_2O_5$
Solution IV, .1025 molal $(NH_4)_2H_2P_2O_5$ 0.1008 molal $HC_2H_3O_2$
Solution V, .1032 molal $(NH_4)_2H_2P_2O_5$ 0.1007 molal $KHSO_4$
Solution VI, .1022 molal $(NH_4)_2H_2P_2O_5$ 0.1005 molal HCl

Sample	Time, hours	Sample, g.	Equiv. of I_2 per g. of soln. × 10^4	Per cent. hydrated	*p*H	
			Solution I			
	0.0				9.27	
1	2.0	4.888	0.3940	9.85	9.10	
2	7.5	3.229	.8495	21.24	8.79	
3	18.0	4.844	1.143	28.58	8.56	
4	32.0	7.160	1.338	33.45	8.56	
5	46.0	7.319	1.515	37.88	8.34	
6	75.5	6.552	1.770	44.25	8.12	
7	128.0	7.543	2.000	50.00	7.51	
8	238.5	6.045	2.206	55.15		
9	359.0	5.466	2.374	59.35	6.84	
10	527.5	5.401	2.553	63.83	6.68	
11	671.0	5.540	2.694	67.35	6.62	
12	839.0	5.496	2.829	70.73	6.54	
13	1298.0	5.508	3.136	78.40	6.43	
			Solution II			
0	0				8.00	
1	30.5	9.510	0.2448	6.12	6.72	
2	78.5	6.113	.3578	8.95	6.29	
3	191.5	3.150	.5777	14.44	5.93	
4	285.5	1.740	.7642	19.11	5.76	
5	410.5	1.561			5.57	
6	481.5	4.969	1.137	28.43	5.51	
7	669.5	4.999	1.519	37.98	5.38	
8	841.5	5.629	1,867	46.68	5.27	
9	1052.5	5.584	2.274	56.85	5.20	
10	1294.0	5.024	2.688	67.20	5.11	
11	1542.0	4.582	3.039	75.98	5.06	
12	1821.5	3.737	3.346	83.65	5.01	
			Solution III			
0	0.1				4.14	
	1.5				4.11	
1	6.5	10.088	0.1934	4.84	4.04	
2	17.5	5.348	.5807	14.52	3.93	
3	28.0	2.252	.9572	23.93	3.88	
4	40.5	1.543	1.389	34.72	3.84	
5	53.0	6.377	1.768	44.20	3.82	
6	65.0	5.401	2.105	52.63	3.81	
7	77.0	4.722	2.390	59.75	3.81	
8	89.5	4.649	2.651	66.28	3.79	
9	101.5	4.260	2.862	71.55	3.78	
10	125.5	3.880	3.207	80.18	3.78	
11	149.0	3.421	3.440	86.00	3.77	
12	187.0	3.173	3.691	92.28	3.77	
			Solution IV			Time for *p*H, hours
1	0.23	10.094	0.1064	2.66	2.92	0.02
2	.43	7.516	.1923	4.81	2.93	.15
3	1.31	9.945	.5115	12.79	2.93	.38
4	2.25	9.960	.8309	20.77	2.95	1.20
5	3.52	9.077	1.185	29.63	2.99	2.37
6	5.00	10.360	1.540	38.50	2.99	3.88
7	6.75	6.781	1.880	47.00	3.03	6.38
8	9.25	5.235	2.273	56.83	3.07	9.33
9	12.25	5.560	2.639	65.98	3.08	12.33
10	16.00	4.420	2.981	74.53	3.08	15.90
11	22.50	4.083	3.375	84.38	3.10	22.63
12	32.75	3.664	3.705	92.63	3.12	32.60
13	47.00	3.228	3.894	97.35	3.12	47.50
			Solution V			
	Time, min.					Time, min.
1	1.0	15.751	0.3318	8.29	1.49	1.0
2	4.4	9.222	1.157	28.93	1.55	6.0
3	9.0	5.560	1.856	46.40	1.60	10.0
4	12.8	5.081	2.303	57.58	1.61	13.0
5	17.2	4.907	2.632	65.80	1.65	24.0
6	25.0	4.258	3.053	76.33	1.68	33.5
7	35.0	3.638	3.398	84.95	1.68	44.0
8	45.8	3.590	3.612	90.30	1.70	56.0
9	55.0	3.374	3.731	93.28	1.70	78.0
10	86.2	3.261	3.872	96.80		
11	144.7	3.080	3.988	99.70		
			Solution VI			
1	0.6	15.894	0.4753	11.88	1.29	1.0
2	2.5	8.047	1.405	35.13	1.38	4.5
3	4.6	5.955	2.057	51.43	1.42	7.5
4	6.7	4.600	2.478	61.95	1.44	10.5
5	9.0	3.983	2.810	70.25	1.45	13.5
6	13.0	3.855	3.197	79.93	1.47	16.0
7	20.0	3.260	3.577	89.43	1.49	24.5
8	28.5	3.318	3.798	94.95	1.51	35.5

Discussion of Results

The hydration of pyrophosphite to orthophosphite manifests a very striking behavior with respect to change of rate at the different *p*H levels as the results in the foregoing table and the curves in Figs. 2, 3, 4 and 5 indicate. In a solution of 0.1003 molal sodium hydroxide, the rate is very rapid during the period where the *p*H ranges from 9.3 to 8.8. As the reaction proceeds and the *p*H drops, the rate decreases considerably more than is to be accounted for solely on the basis of the decrease in the concentration of the pyrophosphite. Moreover, in the same solution, a very slow conversion of the pyrophosphite to orthophosphite at *p*H values of 7 to 6.5 is revealed by the 1000 hours required for the reaction to proceed from 56 to 78% completion.

Furthermore, the hydration in a solution of 0.01 molal sodium hydroxide proceeds very rapidly for the short time during which the *p*H is relatively high. The low concentrations of the sodium hydroxide, however, allow the *p*H to fall rapidly. This change is accompanied by the rather sudden break in the hydration curve (Fig. 2). Moreover, after fifty hours there is an almost linear relationship. These phenomena can be interpreted only by the fact that the decrease in *p*H is now materially favoring the conversion of the pyrophosphite to orthophosphite, whereas heretofore it was hindering the change.

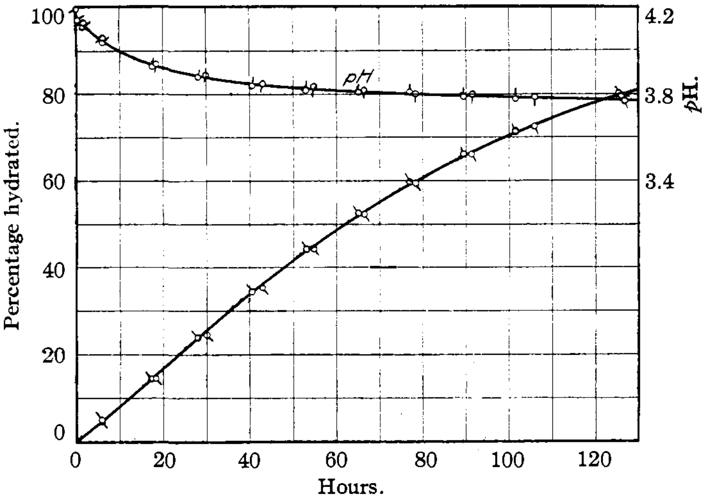

Fig. 3.—0.1000 molar $(NH_4)_2H_2P_2O_5$.

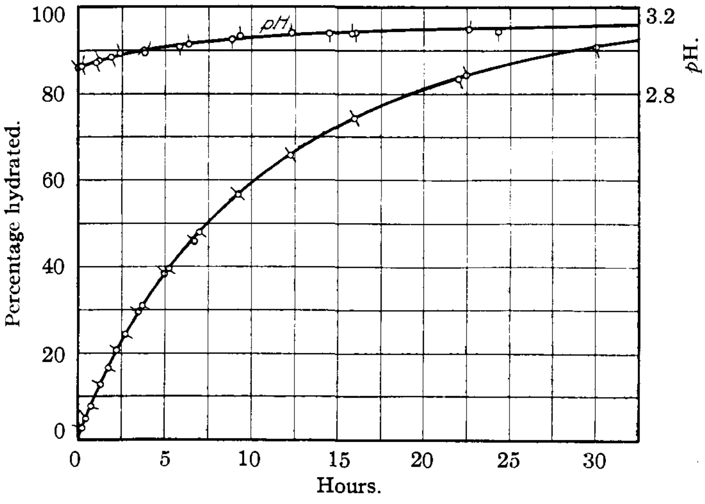

Fig. 4.—0.1000 molar $(NH_4)_2H_2P_2O_5$–0.1000 molar $HC_2H_3O_2$.

The hydration in water alone is 50% complete in sixty-two and one-half hours, 75% in one hundred eleven hours, and 87.5% in one hundred fifty-eight hours. A unimolecular reaction which is 50% complete in sixty-two and one-half hours would require one hundred twenty-five hours for 75% completion and one hundred eighty-seven and one-half hours for 87.5% completion. The most plausible explanation for this behavior is that the decrease in the *p*H which accompanies the reaction favors the hydration of the pyrophosphite.

The hydrations in solutions of 0.1 molal acetic acid, 0.1 molal potassium hydrogen sulfate, and 0.1 molal hydrochloric acid require more than twice their respective half-times for 75% completion and more than thrice these half-time values for 87.5% completion. If these hydrations are considered individually, one possible explanation is that the increase of *p*H hinders the conversion of the pyrophosphite to orthophosphite or that a decrease in *p*H favors the conversion. If the hydrations are considered collectively, the tremendous effect of *p*H on the reaction is much better shown by the fact that, with the same initial concentration of $(NH_4)_2H_2P_2O_5$, 50% of it is hydrated in

7.4 hours at a *p*H of 2.92 to 3.04
10.2 minutes at a *p*H of 1.48 to 1.60
4.4 minutes at a *p*H of 1.24 to 1.38

From the data for the six solutions in Table I it may be seen that the rate of hydration is very rapid at a *p*H of 9, very slow at *p*H values from 5 to 7, and exceedingly rapid at a *p*H value of about 1.3 or below. Above a *p*H of 6.5 a decrease in *p*H hinders the hydration of the pyrophosphite; below 6.5 a decrease of *p*H favors the hydration. Hence the shapes of the hydration curves are considerably dependent upon any change of *p*H which occurs during the experiment. Whenever the *p*H changes very greatly and rapidly, significant variations in the shape of the hydration curves are likely to follow.

In solution III the results reveal to some extent at least the acidic nature of both the $(NH_4)_2H_2P_2O_5$ and the $NH_4H_2PO_3$ formed by the hydration

$$(NH_4)_2H_2P_2O_5 + H_2O \rightleftarrows 2NH_4H_2PO_3$$

because there is neither additional acid nor additional base in the solution. After the reaction had proceeded for one hour the *p*H value was 4.14, which indicates by extrapolation that the initial value for 0.1 molar $(NH_4)_2H_2P_2O_5$ is near

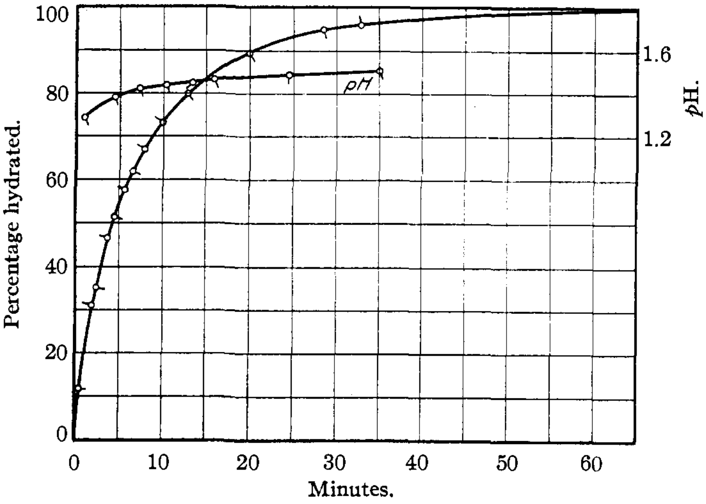

Fig. 5.—0.1000 molar $(NH_4)_2H_2P_2O_5$–0.1000 molar HCl.

4.3. This fact, moreover, reveals that the third hydrogen for the poly-basic pyrophosphorus acid must be definitely acidic. Furthermore, after the hydration had proceeded for one hundred eighty-seven hours and had reached 92.28% completion the *p*H value had decreased to 3.77. The solution became more acidic, which may be interpreted to mean that the second hydrogen of orthophosphorous acid is still more acidic than the third hydrogen of the pyrophosphorous acid. These facts are shown graphically in Fig. 3. The final *p*H value, disclosed by extrapolation, for the 0.2 *M* $NH_4H_2PO_3$ formed seems to lie somewhere near 3.7 at 30°.

The characteristics manifested in the hydration of pyrophosphite are similar to those shown in the case of pyrophosphate at *p*H values below 6.5 only. The pyrophosphate is stable in an alkaline solution. No hydration occurs.[5] Hydration of pyrophosphite does occur in alkaline solution. The rate increases as the *p*H increases. This is the characteristic difference in behavior of the respective compounds of phosphorus concerning hydration.

Summary

1. A method for the determination of orthophosphites in the presence of pyrophosphites has been developed.

2. Data are presented on the hydration of $(NH_4)_2H_2P_2O_5$ in the following solutions

Solution I,	0.1000 *M* NaOH	0.1000 *M* $(NH_4)_2H_2P_2O_5$
Solution II,	.01000 *M* NaOH	.1000 *M* $(NH_4)_2H_2P_2O_5$
Solution III,	Distilled water	.1000 *M* $(NH_4)_2H_2P_2O_5$
Solution IV,	.1000 *M* $HC_2H_3O_2$	.1000 *M* $(NH_4)_2H_2P_2O_5$
Solution V,	.1000 *M* $KHSO_4$	.1000 *M* $(NH_4)_2H_2P_2O_5$
Solution VI,	.1000 *M* HCl	.1000 *M* $(NH_4)_2H_2P_2O_5$

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(5) Kiehl and Coats, THIS JOURNAL, **49**, 2180 (1927).

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The Standard Potential of the Silver-Silver Azide Electrode

BY ALICE C. TAYLOR AND LESLIE F. NIMS

The standard potentials of a stable reproducible silver-silver azide electrode, prepared electrolytically, have been obtained from electromotive force measurements of the cell

$$Ag\text{-}AgCl/NaCl(m)/KCl(satd.)/NaN_3(m)/AgN_3\text{-}Ag(+)$$

over the temperature range from 5 to 45°. The electromotive force of such a cell is represented by an equation of the form

$$E = E^0{}_{AgN_3} - E^0{}_{AgCl} - \frac{RT}{F}\log\frac{m_{N_3^-}\ \gamma_{N_3^-}}{m_{Cl^-}\ \gamma_{Cl^-}} + E_D \quad (1)$$

At infinite dilution the sum of the diffusion potentials, E_D, would be very small and can be neglected. Consequently, for equal concentrations of azide and chloride, the potential at infinite dilution is related to the standard potentials of the electrodes in the following manner

$$E^0{}_{AgN_3} = E_{(inf.\ dil.)} + E^0{}_{AgCl} \quad (2)$$

Experimental Details

Sodium azide (Eimer and Amend) was twice recrystallized from an aqueous solution saturated at 90° by cooling it to 10° and adding an equal volume of alcohol. A colored impurity was then removed by treatment with charcoal (Norite A) and a third crystallization was effected, this time with an equal volume of acetone. The resulting crystals were well washed with acetone and the product was dried at room temperature. Weighed samples dried at 110° were taken for analysis. These were converted to sodium sulfate and the results indicated that a satisfactory degree of purity of the sodium azide had been obtained. Sodium chloride was twice recrystallized from