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The Preparation of Diammonium Dihydrogen Pyrophosphite

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Amat[1] in a series of papers has reported the preparation of six pyrophosphites by gently heating the respective dihydrogen orthophosphite in a closed evacuated tube so constructed that concentrated sulfuric acid could be placed in one end to absorb the water liberated by the following reaction

$$2M'H_2PO_3 \rightleftarrows M'_2H_2P_2O_5 + H_2O$$

In these preparations it was difficult to dehydrate the salt completely without causing another decomposition. In any case the loss of water occurs slowly and if the temperature is raised to hasten the reaction phosphates are formed with the liberation of phosphine. Attempts by Amat to prepare the ammonium pyrophosphite were unsuccessful. He reports that, upon the heating of ammonium dihydrogen orthophosphite, water vapor and ammonia evolved simultaneously were absorbed by the sulfuric acid.

By the substitution of a selective absorbing agent, barium oxide for water alone, instead of sulfuric, the preparation of the diammonium dihydrogen pyrophosphite may be realized as the following account will show.

Preparation and Analysis of Materials.—Ammonium dihydrogen orthophosphite was prepared from concentrated ammonium hydroxide and the highest grade crystalline phosphorous acid obtainable. Concentrated solutions of the two were mixed by the dropwise addition of small portions of first one and then the other till neutral to methyl orange. The salt obtained by concentrating this solution was recrystallized from distilled water and dried in a desiccator over concentrated sulfuric acid. Analyses for ammonia, phosphorus, and oxidation titer were made.

In the determination of ammonia, the standard methods were used. To prevent loss, samples were not added to the alkali in the Kjeldahl flask till all the dissolved air had been expelled.

For the determination of phosphorus two methods were used, one gravimetric and the other oxidimetric. In the gravimetric determination the phosphite was oxidized to orthophosphate by boiling it with potassium permanganate. The manganese dioxide formed was reduced by sulfur dioxide and the phosphate separated as ammonium phosphomolybdate. After it was twice precipitated as $MgNH_4PO_4 \cdot 6H_2O$, it was ignited to and weighed as $Mg_2P_2O_7$.

Because of the importance of the oxidation of the orthophosphite by iodine in this analysis and the subsequent analysis of $(NH_4)_2H_2P_2O_5$ for purity and extent of hydration, it was necessary to determine the optimum conditions with respect to the *p*H of the solution for the quantitatively complete oxidation in the shortest time. Consequently, by means of a series of fifteen carefully prepared buffers, extending from a *p*H of 3 to 13.2, the completeness of oxidation in a period of three minutes upon each of the fifteen *p*H levels was determined. The results of these analyses are summarized by the curve in Fig. 1. The abscissa represents the *p*H; the ordinate the percentage of orthophosphite oxidized to orthophosphate in a time period of three minutes by iodine. In the determination of phosphorus, therefore, by the oxidimetric method the samples were analyzed in solutions buffered between a *p*H of 7 and 9; excess iodine solution was added; after twenty minutes, the solutions were made acid and the excess iodine determined by titrating with thiosulfate.

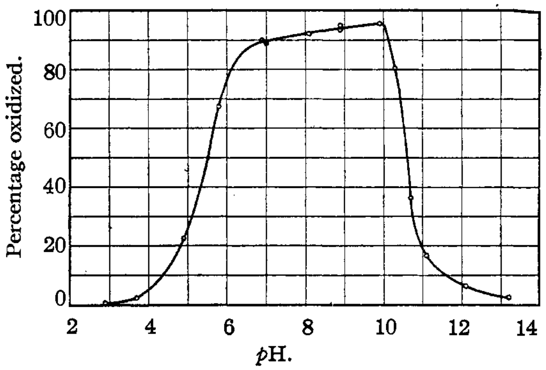

Fig. 1.—The effect of *p*H on the percentage of orthophosphite oxidized at 25° in three minutes by 100% excess 0.05 *N* I_2.

The results of these analyses are shown in Table I.

The sodium hydroxide solutions used in ammonia determinations, in making buffers, and in standardization of acids, were made from saturated and filtered sodium hydroxide solutions with water free of carbon dioxide. They were standardized against Bureau of Standards potassium acid phthalate.

The sodium thiosulfate was purified carefully and its solutions kept free from oxygen and carbon dioxide.

A high grade of iodine was ground with one-fifth its weight of potassium iodide, and from this mixture iodine was sublimed. It was resublimed without the addition of potassium iodide. All of the iodine solutions contained 4% potassium iodide and they were kept in amber colored bottles.

Boric acid, monosodium and disodium phosphates used in making buffers were twice crystallized from distilled water.

Apparatus.—For the preparation of $(NH_4)_2H_2P_2O_5$, the apparatus represented in Fig. 2 was constructed. The

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(1) Amat (a) *Compt. rend.*, **106**, 1400 (1888); (b) **108**, 1056 (1889); (c) **110**, 901 (1890); (d) **112**, 527 (1891); (e) **112**, 614 (1891); (f) *Ann. chim. phys.*, **304**, 289 (1891).

TABLE I

ANALYSIS OF $NH_4H_2PO_3$

Sample, g.	Equiv. H_2SO_4 required	NH_3, %	Sample, g.	$Mg_2P_2O_7$, g.	P, %	Sample, g.	Cc. of 0.1004 N I_2 required	P, %
0.2943	0.002969	17.18	0.2569	0.2878	31.22	0.2035	40.60	31.06
.3096	.003132	17.23	.1573	.1752	31.04	.2025	40.45	31.10
.3246	.003281	17.20	.1592	.1778	31.12	.2024	40.49	31.12
			.1541	.1720	31.10			
Average		17.20			31.12			31.10
Theoretical		17.19			31.31			31.31
Ratio NH_3/P		1.006/1.						

glass tube C, about 35–40 cm. long, was fitted with a No. 50 ground glass joint, the inner member of which projected beyond the ground surface of the cap to prevent grease from falling into containers A and B. The salt to be dehydrated was contained in weighing bottle A. Vial B, supported just above the top of the electric furnace D, contained the dehydrating agent, barium monoxide. The tube and contents were heated in an electric furnace whose temperature was so controlled that it fell within the limits of plus or minus three degrees.

The Preparation of Diammonium Dihydrogen Pyrophosphite

Method.—The preparation of diammonium dihydrogen pyrophosphite from ammonium dihydrogen orthophosphite requires the removal of one mole of water for every two moles of orthophosphite.

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

The reaction is reversible; hence the water must be removed as it is formed if the reaction is to go to completion in the direction desired.

The apparatus in Fig. 2 made this possible. The orthophosphite was placed in weighing bottle A and the dehydrating agent, barium monoxide, in Vial B. After the system had been evacuated, the temperature was brought to and maintained at 100–110°. Until the salt lost most of its moisture, it caked and had to be crushed every day or so. If the temperature was kept below 110° during the period when the salt caked badly, this operation could be performed most readily by crushing it against the walls of the weighing bottle by means of a steel spatula. After the caking had ceased, the salt was ground in a mortar, and the heating continued at 115–120° until constant weight was obtained for three successive days.

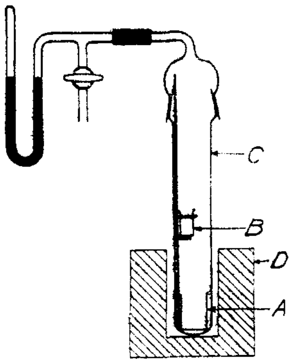

Fig. 2.

Properties of $(NH_4)_2H_2P_2O_5$

The salt thus obtained is a white powder. Prolonged heating above 130° produces a decomposition to phosphine and phosphate and imparts a yellow color to the solid which remains. The salt is very soluble in water and, because of its deliquescence when the humidity is moderately high, weighings had to be made in a closed system free from moisture.

To confirm the formula, samples of three different preparations of the salt were analyzed for ammonia, phosphorus, and oxidation titer as in the case of ammonium dihydrogen orthophosphite. A modification of the procedure, moreover, was necessary in the determination of the oxidizable phosphorus because iodine reacts extremely slowly, if at all, with pyrophosphites. It was therefore necessary to boil it for two hours in 0.4 molar sulfuric acid to hydrate it to orthophosphate.

The results of these analyses are shown in Table II.

Criteria of Purity

Although the analyses (Table II) correspond very favorably with the theoretical, they are not conclusive in proving the absence of the orthophosphite, for a mixture of ninety-nine parts of the pyrophosphite and one of the orthophosphite would contain 18.89% ammonia and 34.42% phosphorus instead of 18.91 and 34.45%, respectively, for the pure pyrophosphite. A mixture of ninety-five parts of the pyrophosphite and five of the orthophosphite would contain 18.82% ammonia and 34.30% phosphorus, or only five parts in a thousand lower than theory demands for the pure pyrophosphite.

The loss of water in the conversion of the ammonium dihydrogen orthophosphite to pyrophosphite would be a good indication as to the contamination by orthophosphite were this loss easy to follow. The necessity of crushing the salt during the course of its dehydration makes this determination exceedingly difficult. However, the loss in weight was followed on two small samples, the crushing of which was all done in the weighing bottle. The results are shown in Table III.

The most satisfactory criterion of purity is based upon the difference in the behavior of orthophosphite and pyrophosphite with iodine. At a pH of 7 where the rate of hydration is a minimum and at 30° a 100% excess 0.05 N iodine quantitatively oxidizes orthophosphite to phosphate in ten minutes, but has little effect on pyro-

TABLE II

ANALYSIS OF $(NH_4)_2H_2P_2O_5$

1.5179 g. of Salt III was dissolved in 100 cc. of 0.4 *M* H_2SO_4. The solution was swept free of air by H_2 and boiled for two hours. It was diluted to 500.0 cc. and aliquots taken for analysis

Salt	Sample, g.	Equiv. H_2SO_4 required	NH_3, %	Sample, g.	$Mg_2P_2O_7$, g.	P, %	Solution taken, cc.	Cc. of $0.1027\ N\ I_2$ required	P, %
I	0.2673	0.002982	19.00	0.2220	0.2725	34.20			
	.3203	.003999	18.92	.2063	.2537	34.27			
	.2834	.003156	18.96	.2304	.2838	34.32			
	Average		18.96			34.26			
	0.3160	0.003508	18.90	0.2083	0.2563	34.29			
II	.2457	.002738	18.98	.2266	.2786	34.26			
	.3020	.003351	18.90	.1400	.1719	34.22			
				.1394	.1716	34.30			
				.1388	.1705	34.23			
	Average		18.93			34.26			
	0.2544	0.002842	19.02	0.2074	0.2547	34.22	49.95	32.72	34.40
III	.2708	.003007	18.91	.2211	.2718	34.26	49.46	32.71	34.38
	.2825	.003152	19.00	.2437	.3001	34.31	49.96	32.76	34.44
	.2569	.002852	18.91						
	Average		18.96			34.26			34.41
	Theoretical		18.91			34.45			34.45
	Ratio NH_3/P					1.008/1.			1.004/1.

TABLE III

LOSS OF WEIGHT OF $NH_4H_2PO_3$ WHEN HEATED

Wt. of sample, g.	Loss of wt., g.	Loss of wt., %
2.0779	0.1904	9.18
1.7082	0.1554	9.10
	Theoretical	9.09

phosphite as will be shown by another piece of work which the authors have in progress. To estimate the amount of orthophosphite with which the pyrophosphite may be contaminated, samples of the $(NH_4)_2H_2P_2O_5$ were treated with 25 cc. of 0.05 *N* iodine under the above specified conditions. In no case did the amount of phosphorus found as orthophosphite exceed 0.6% of the total phosphorus present as orthophosphite and pyrophosphite; the low was 0.2% and the average for all of the samples 0.4%. Subsequent experiments indicate that these results are high by a value of 0.1% due to the hydration which took place during the determination. Results for a typical analysis are shown in Table IV.

TABLE IV

ANALYSIS FOR ORTHOPHOSPHITE IN $(NH_4)_2H_2P_2O_5$

Sample, g.	Cc. of $0.05535\ N\ I_2$ consumed	Cc. of $0.05535\ N\ I_2$ needed for complete oxidation	% of P as orthophosphite
0.1437	0.14	58.0	0.23
.1070	.15	43.2	.35
.1185	.16	47.8	.33
		Average	.31

Summary

1. A new salt diammonium dihydrogen pyrophosphite $(NH_4)_2H_2P_2O_5$ has been prepared and its formula confirmed by analysis.

2. Some properties and the degree of purity have been given.

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