347. *The Preparation, Stability, and X-Ray Powder Diffraction Data for Eleven Condensed Ammonium Phosphates.*

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The preparation and stability of eleven condensed ammonium phosphates are described. *X*-Ray powder diffraction data, obtained on a Geiger-counter diffractometer, are included to permit identification and rapid analysis of these phosphates. Their stability was mainly investigated on a high-temperature holder on the diffractometer.

MOST of the previous work on the condensed phosphates was carried out on the sodium salts,[1a] no doubt because relatively pure compounds are easily prepared by thermal methods. Very few data of any kind exist for the ammonium and potassium salts, in which we are interested.

X-Ray powder diffraction [2] and paper chromatography [3] were used with success to analyse condensed phosphates. Both methods have the advantage of using a very small sample, but the *X*-ray method, using a diffractometer, is the quicker and necessarily gives the crystallographic phases present.

X-Ray powder diffraction data for eleven pure condensed ammonium phosphates are given, which will permit the rapid analysis of these compounds. Most of the information on the thermal stability has been obtained by heating the phosphates on the diffractometer.

EXPERIMENTAL

X-*Ray Apparatus and Preparation of Specimens.*—The *X*-ray powder diffraction data were obtained with a Geiger-counter diffractometer of 24 cm. radius, using Cu K_α-radiation (Ni filter) at 30 Kv and 20 mA, and a scanning speed of 1° Bragg/min. In order to increase the crystallite randomisation in the sample it was oscillated $\pm 2°$ at 100 c./sec. about the diffractometer axis. Samples could be heated on the diffractometer up to 200° using a hot-air blast; the required air temperature was obtained by a Variac controlled heater coil. The sample was placed in a non-vibrating asbestos holder and surrounded by an asbestos container having a 0·001 in. Melinex window. The phosphate was ground to pass a 300 B.S.S. sieve and, for work at room temperature, made into a 1 in. square slab using a mould and Lakeside 70C resin binder (Cutrock Eng. Co.), dissolved in dry acetone. The acetone was evaporated off at 40° on a heater unless there was a danger of dehydrating the sample. Samples to be examined at elevated temperatures were pressed into discs. A flat side was cut on the disc so that it could be mounted in the high-temperature holder, and a small hole drilled in it through which a thermocouple lead was threaded so that the junction was in the irradiated surface.

Paper Chromatography.—The method used was essentially the same as that used by Kollof [3] but was not used for quantitative analysis. The major differences were that the molybdate and reducing sprays of Heinert [4] were used and, as a standard procedure, the aqueous phosphate solution was put on the paper at 3 different concentrations.

Ion Exchange Columns.—Amberlite IR-120(H) resin in 30 × 3·5 cm. columns was used to prepare the fully ammoniated phosphates from the sodium salts. The resin was most rapidly reconditioned by treatment with the following reagents in order: dilute hydrochloric acid (1 : 1, concentrated acid : water) (130 ml.); concentrated hydrochloric acid (170 ml.); water (until the effluent was neutral); ammonium hydroxide (1 : 3, 0·880 ammonium hydroxide : water) (150 ml.); water (300 ml.). These liquids were run through the column at approximately 5 ml./min.

[1] Van Wazer, " Phosphorus and its Compounds," Interscience, New York, 1958, (*a*) Vol. 1; (*b*) Vol. I, p. 648.

[2] Mabis and Quimby, *Analyt. Chem.*, 1953, **25**, 1814.

[3] Kollof, *Analyt. Chem.*, 1961, **33**, 373.

[4] Heinert, *Z. analyt. Chem.*, 1959, **166**, 37.

Preparation of Condensed Phosphates.—$Na_4P_2O_7,10H_2O$. Analytical grade tetrasodium pyrophosphate decahydrate was commercially available.

$Na_5P_3O_{10},6H_2O$. Commercial anhydrous pentasodium triphosphate was purified by four to six recrystallisations, using the method described by Van Wazer.[1b]

$Na_3P_3O_9,H_2O$. Anhydrous trisodium trimetaphosphate was prepared by the standard method.[5] It was dissolved in water, filtered from higher insoluble phosphates, and precipitated with Industrial Methylated Spirit (I.M.S.). An oil formed which quickly solidified as the monohydrate.

$Na_4P_4O_{12},10H_2O$. Tetrasodium tetrametaphosphate decahydrate was prepared by the method of Bell *et al.*[6] The tetrametaphosphate was precipitated with I.M.S.; a thick opaque oil formed, and was stirred with an equal volume of water. This mixture was filtered and the solid was impure sodium tetrametaphosphate.

$(NH_4)_4P_2O_7$. A saturated solution of tetrasodium pyrophosphate (90 ml.) was run through the conditioned ion-exchange column at a rate of 1·5 ml./min. The ammonium pyrophosphate solution was collected and the tetra-ammonium salt precipitated with I.M.S.

$(NH_4)_3HP_2O_7,1H_2O$. Triammonium monohydrogen pyrophosphate monohydrate was prepared by recrystallising equimolar amounts of diammonium dihydrogen pyrophosphate and tetra-ammonium pyrophosphate from water.

$(NH_4)_3HP_2O_7$. Anhydrous triammonium monohydrogen pyrophosphate was prepared by dehydration of the monohydrate in a vacuum oven at 50° for 48 hr.

γ-$(NH_4)_2H_2P_2O_7$. Tetra-ammonium pyrophosphate (1 g.) was shaken for 4 hr. with acetic acid (10 ml.; glacial acetic acid–water, 4 : 1 v/v). The solid in equilibrium with this solution was γ-di-ammonium dihydrogen pyrophosphate.

β-$(NH_4)_2H_2P_2O_7$. Tetra-ammonium pyrophosphate (1 g.) was dissolved in acetic acid (30 ml.; glacial acetic acid–water, 3 : 2 v/v) and precipitated with I.M.S. Occasionally an oil formed but this crystallised, on rapid stirring, to β-diammonium dihydrogen pyrophosphate.

α-$(NH_4)_2H_2P_2O_7$. Tetra-ammonium pyrophosphate (1 g.) was shaken with glacial acetic acid (10 ml.). After 48 hr. the solid phase in equilibrium with this solution was α-diammonium dihydrogen pyrophosphate.

$(NH_4)_5P_3O_{10},H_2O$. A 13 wt. % solution of pentasodium triphosphate hexahydrate (80 ml.) was passed through the conditioned ion-exchange column at a rate of 1·5 ml./min. From the resultant solution, penta-ammonium triphosphate was precipitated with I.M.S.

$(NH_4)_4HP_3O_{10}$. Penta-ammonium triphosphate monohydrate (1 g.) was shaken for 3 hr. with dilute acetic acid (25 ml.; glacial acetic acid–water, 1 : 2 v/v). Tetra-ammonium monohydrogen triphosphate was the solid phase in equilibrium with this solution.

$(NH_4)_3H_2P_3O_{10}$. Penta-ammonium triphosphate (1 g.) was shaken for 3 hr. with glacial acetic acid (5 ml.). Triammonium dihydrogen triphosphate was the solid phase in equilibrium with this solution.

$(NH_4)_3P_3O_9$. A 20 wt. % solution of trisodium trimetaphosphate (50 ml.) was passed through the conditioned ion-exchange column. From the collected solution, triammonium trimetaphosphate was precipitated with I.M.S.

$(NH_4)_4P_4O_{12}$. A 13 wt. % solution of tetrasodium tetrametaphosphate (60 ml.) was passed through the conditioned ion-exchange column. From the collected solution, tetra-ammonium tetrametaphosphate was precipitated with I.M.S. It did not contain the ortho- and pyrophosphates which were present as impurities in the sodium tetrametaphosphate.

The purity of the sodium salts used as starting materials was checked by paper chromatography, and against complete *X*-ray powder diffraction data.[7] Chemical analyses of the ammonium salts for nitrogen and phosphorus agreed with the calculated values to within 1%, except for tetra-ammonium pyrophosphate which lost ammonia at room temperature. However, it was essential to check the absence of other types of condensed phosphate by paper chromatography, as quite often a few percent of another type did not make any appreciable change in the N and P contents. Less than 1% by weight of an ammonium phosphate present as an impurity could be detected.

The concentrations used in the preparations were often very critical, particularly in the experiments using acetic acid, as mixtures of products were easily obtained.

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[5] Bell, *Inorg. Synth.*, 1950, **3**, 103.

[6] Bell, Audrieth, and Hill, *Ind. Eng. Chem.*, 1952, **44**, 570.

[7] Corbridge and Tromans, *Analyt. Chem.*, 1958, **30**, 1101.

RESULTS

X-Ray Powder Diffraction Data.—All the spacings quoted in the Table are subject to an arbitrary cut-off at approximately 1·45 Å. The values below 10 Å are correct to 0·01 Å. The intensities are based on peak heights and are expressed as a percentage of the strongest, (I/I_1) in accordance with the A.S.T.M. *X*-ray powder data file.

X-Ray powder diffraction data.

$(NH_4)P_2O_7$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6·55	5	2·71	13	1·97	2
5·60	50	2·63	8	1·89	2
5·47	76	2·58	3	1·87	12
4·98	50	2·52	13	1·85	5
4·62	31	2·48	4	1·82	6
3·86	30	2·38	20	1·80	1
3·70	17	2·32	6	1·75	5
3·35	20	2·30	16	1·73	1
3·30	98	2·25	2	1·66	8
3·23	100	2·20	4	1·63	1
3·16	41	2·15	1	1·56	3
3·03	51	2·10	3	1·55	5
2·96	6	2·09	3	1·52	1
2·90	4	2·05	17	1·50	6
2·83	1	2·02	13		

$(NH_4)_3HP_2O_7,H_2O$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6·45	12	2·79	10	1·95	1
5·90	94	2·75	20	1·91	5
5·85	51	2·70	4	1·86	5
5·27	65	2·63	10	1·82	1
4·48	100	2·60	6	1·80	1
4·27	13	2·49	6	1·79	1
4·19	6	2·45	3	1·76	3
4·04	14	2·28	8	1·73	3
3·84	5	2·25	14	1·72	5
3·28	77	2·22	6	1·66	3
3·21	37	2·19	15	1·64	4
3·18	69	2·12	12	1·58	3
3·14	36	2·09	6	1·56	1
3·09	27	2·07	4	1·54	1
3·01	74	2·03	12	1·53	5
2·95	24	1·98	1	1·51	5
2·85	44				

$(NH_4)_5P_3O_{10},H_2O$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
7·49	19	2·92	29	1·89	6
5·90	2	2·71	15	1·85	2
5·53	58	2·65	24	1·82	3
5·21	5	2·51	9	1·79	3
4·87	30	2·43	3	1·73	3
4·67	14	2·34	24	1·71	3
4·00	18	2·30	8	1·65	1
3·86	14	2·26	3	1·62	2
3·77	23	2·19	3	1·60	2
3·56	1	2·15	5	1·59	3
3·42	6	2·08	2	1·57	2
3·30	100	2·03	11	1·56	1
3·28	44	2·01	4	1·53	1
3·21	37	1·97	2	1·51	2
3·06	54	1·93	5	1·50	2

$(NH_4)_4P_4O_{12}$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6·48	92	2·79	4	1·84	1
6·32	19	2·70	12	1·82	2
5·47	43	2·61	57	1·79	5
4·98	3	2·42	15	1·78	3
4·11	30	2·31	7	1·73	1
4·00	31	2·27	4	1·71	3
3·68	38	2·15	3	1·68	1
3·59	29	2·09	12	1·66	4
3·30	26	2·05	5	1·64	1
3·22	100	2·01	4	1·60	1
3·16	4	1·96	4	1·59	5
3·00	12	1·91	9	1·56	4
2·94	9	1·88	1	1·50	2

$(NH_4)_3HP_2O_7$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
9·82	9	2·79	39	1·97	6
6·23	25	2·71	4	1·95	4
5·47	89	2·63	1	1·94	8
4·92	68	2·59	9	1·89	2
4·67	5	2·56	8	1·87	2
4·52	8	2·53	5	1·85	2
4·27	18	2·52	5	1·83	4
3·95	4	2·48	5	1·82	1
3·86	30	2·44	4	1·76	3
3·83	34	2·41	9	1·75	1
3·70	4	2·32	9	1·73	1
3·62	8	2·30	4	1·72	1
3·48	16	2·27	9	1·70	9
3·40	30	2·26	8	1·67	1
3·30	80	2·22	3	1·64	2
3·24	100	2·20	1	1·61	1
3·10	48	2·15	8	1·56	4
3·08	13	2·13	1	1·55	5
2·95	6	2·08	8	1·54	1
2·84	39	2·01	5	1·52	4

$(NH_4)_4HP_3O_{10}$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6·51	11	2·73	17	1·95	1
6·10	100	2·70	12	1·92	1
5·90	16	2·67	34	1·91	1
5·40	41	2·64	10	1·86	1
4·74	12	2·56	11	1·81	3
4·04	11	2·50	3	1·78	2
3·98	9	2·48	6	1·75	5
3·83	80	2·44	2	1·73	6
3·71	8	2·38	22	1·72	1
3·65	19	2·31	15	1·70	1
3·56	2	2·19	2	1·67	1
3·44	4	2·15	9	1·65	1
3·32	3	2·13	4	1·63	4
3·26	47	2·10	2	1·61	1
3·14	17	2·08	10	1·59	2
3·07	12	2·07	3	1·57	1
3·00	7	2·05	2	1·56	1
2·94	2	2·01	2	1·50	1
2·85	8	1·97	3		

$(NH_4)_3H_2P_3O_{10}$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
7·02	5	2·86	39	1·96	9
5·98	74	2·79	1	1·94	4
5·40	100	2·73	12	1·90	7
5·30	89	2·65	53	1·87	2
4·77	3	2·57	15	1·85	3
4·72	3	2·53	26	1·83	1
4·31	42	2·48	8	1·80	1
4·05	95	2·42	3	1·78	3
3·71	42	2·32	13	1·75	2
3·59	18	2·31	11	1·73	1
3·53	16	2·29	12	1·72	2
3·45	38	2·25	4	1·71	2
3·42	68	2·23	5	1·67	1
3·35	43	2·19	27	1·65	1
3·23	62	2·15	11	1·63	7
3·10	12	2·07	5	1·59	5
3·05	46	2·04	7	1·56	1
3·00	22	2·01	7		
2·93	15	2·00	5		

α-$(NH_4)_2H_2P_2O_7$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6·32	20	2·53	3	1·93	2
5·68	92	2·47	12	1·89	8
4·57	25	2·35	10	1·88	7
3·80 (Broad)	62	2·26	3	1·79	3
3·57	100	2·25	12	1·76	2
3·48	39	2·23	12	1·73	3
3·35	3	2·21	12	1·72	3
3·16	85	2·19	16	1·64	3
2·99	10	2·16	7	1·57	3
2·82	26	2·09	2	1·56	3
2·64	8	2·04	3	1·50	2
2·55	3	1·99	7		

β-$(NH_4)_2H_2P_2O_7$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
6·38	9	2·83	36	1·90	1
5·47	62	2·51	6	1·83	8
4·92	2	2·48	5	1·80	3
4·67	63	2·38	8	1·77	5
3·59	100	2·32	17	1·75	6
3·50	65	2·28	10	1·73	5
3·42	25	2·23	6	1·71	3
3·37	36	2·21	5	1·64	3
3·23	27	2·16	3	1·60	1
3·18	58	2·14	6	1·57	1
3·06	11	2·11	9	1·55	6
3·02	57	2·00	3	1·54	1
2·98	43	1·97	10		
2·86	26	1·93	2		

γ-$(NH_4)_2H_2P_2O_7$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
7·31	30	2·67	19	2·04	1
5·60	87	2·65	27	2·03	1
4·44	11	2·62	9	1·94	4
4·35	35	2·58	5	1·89	1
4·30	41	2·54	5	1·86	5
3·67	100	2·49	52	1·84	7
3·42	82	2·43	12	1·80	3
3·41	79	2·35	5	1·71	10
3·28	11	2·33	5	1·67	4
3·23	9	2·26	6	1·64	1
3·07	99	2·21	6	1·61	4
2·94	41	2·17	1	1·55	1
2·90	15	2·13	2	1·51	1
2·82	7	2·12	2	1·50	1
2·79	22	2·07	4		

$(NH_4)_3P_3O_9$

d (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
8·34	1	3·30	100	2·14	4
6·91	9	3·28	50	2·10	9
6·41	20	3·21	16	2·05	7
6·15	9	3·17	36	2·04	6
5·82	63	3·16	24	2·00	16
5·68	34	3·03	1	1·96	3
5·40	16	2·96	4	1·94	3
5·20	6	2·89	17	1·92	3
4·77	6	2·81	6	1·89	9
4·62	19	2·76	26	1·83	5
4·50	6	2·73	9	1·80	3
4·21	21	2·64	13	1·73	1
3·90	6	2·48	1	1·70	3
3·83	3	2·45	1	1·65	1
3·67	19	2·38	1	1·63	1
3·59	20	2·32	9	1·55	1
3·53	27	2·31	14	1·53	1
3·48	30	2·25	4	1·51	3
3·42	14	2·17	4	1·46	7

Stability of Condensed Ammonium Phosphates.—$(NH_4)_4P_2O_7$. Tetra-ammonium pyrophosphate lost ammonia and was hydrated at room temperature, to give triammonium monohydrogen pyrophosphate monohydrate. When heated, tetra-ammonium pyrophosphate slowly lost ammonia and became amorphous. The amorphous solid melted at ~170°, losing more ammonia. Paper chromatography showed that the melt, $\frac{1}{4}$ hr. after fusion, contained ortho-, pyro-, tri-, and trimeta-phosphate. The melt took 3 months to crystallise in a desiccator, and *X*-ray analysis showed that α-diammonium dihydrogen pyrophosphate was the predominant phase.

$(NH_4)_3HP_2O_7,H_2O$. Triammonium monohydrogen pyrophosphate monohydrate slowly lost its water of crystallisation at 40°.

$(NH_4)_3HP_2O_7$. At room temperature in a moist atmosphere, triammonium monohydrogen pyrophosphate was hydrated to the monohydrate. When heated no phase changes occurred until it melted at ~165°. The properties of the melt were very similar to those of molten tetra-ammonium pyrophosphate.

γ-$(NH_4)_2H_2P_2O_7$. When γ-diammonium dihydrogen pyrophosphate was heated, no phase changes occurred until it melted at 162°. The melt had properties very similar to those of molten tetra-ammonium pyrophosphate. It was shown by chemical analysis that the melt from γ-diammonium dihydrogen pyrophosphate still slowly lost ammonia.

β-$(NH_4)_2H_2P_2O_7$. β-Diammonium dihydrogen pyrophosphate was stable in dry air at room temperature but recrystallised to the γ-form in a moist atmosphere. The dry β-di-ammonium dihydrogen pyrophosphate was not converted into the γ-form when heated. Its melting point and melt properties were similar to those of the γ-form.

α-$(NH_4)_2H_2P_2O_7$. α-Diammonium dihydrogen pyrophosphate was unstable in air at room temperature, and in 30 days had been completely converted into the γ-form. By pressing the α-phase at 10 tons/sq. in. at room temperature it was converted into the γ-phase.

$(NH_4)_5P_3O_{10},H_2O$. On heating penta-ammonium triphosphate monohydrate on the diffractometer a new phase, H3, slowly appeared at 75°, and after $1\frac{1}{2}$ hr. none of the original triphosphate remained. This new phase was stable at room temperature but has not been identified. At higher temperatures the penta-ammonium triphosphate lost ammonia and softened. As soon as softening had occurred ortho-, pyro-, trimeta-, and higher phosphates could be detected.

$(NH_4)_4HP_3O_{10}$. Tetra-ammonium monohydrogen triphosphate lost ammonia at 100°, and after 1 hr. at this temperature had formed crystalline triammonium dihydrogen triphosphate.

$(NH_4)_3H_2P_3O_{10}$. Tri-ammonium dihydrogen triphosphate melts at 132°. Ortho-, pyro-, tri-, trimeta-, and higher phosphates were present in the melt after 1 hr.

$(NH_4)_3P_3O_9$ *and* $(NH_4)_4P_4O_{12}$. Triammonium trimetaphosphate and tetra-ammonium tetrametaphosphate did not melt but slowly polymerised at 175°. Traces of lower phosphates were also formed at this temperature.

DISCUSSION

Ion Exchange.—When new resin was used it was essential to give the columns a lengthy conditioning with concentrated hydrochloric acid, as there was a considerable amount of calcium on the resin. The columns were used in the NH_4^+ form, as tri-, trimeta-, and tetrameta-phosphates hydrolysed within the time they took to run through the column if the resin was in the acid form. Nearly saturated solutions were passed through the columns simply to reduce the volume of methylated spirit needed to precipitate the ammonium phosphate.

Paper Chromatography.—The dioxan solvents and Whatman ET 31 paper used by Kollof[3] gave good separation of traces of impurities from nearly pure materials, and the sprays of Heinert[4] gave the strongest colour with the separated phosphates and hence kept the detection limits relatively low. The use of three concentrations of aqueous phosphate solution on the chromatographic paper ensured that all relevant information that could be gained from paper chromatography was obtained immediately, trace components were easily detected, and major components different by only one phosphorus atom were separated. Descending chromatography was examined but the separation was not good and the running time required was much longer than with ascending chromatography.

The Influence of Pressure, Temperature, and Humidity.—It was suspected that anhydrous penta-ammonium triphosphate was the unknown phase, H3, formed from the monohydrate when it was heated at 75° on the diffractometer; the major diffraction lines were 6·06, 4·67, and 3·17 Å. Despite many attempts, a pure sample of anhydrous penta-ammonium salt could not be prepared either by dehydration of the monohydrate or by ammoniation of an acid salt in non-aqueous solvents. It was possible to get a pure *X*-ray pattern on the diffractometer because the outside of the pressed disc was soft and glassy and hence did not contribute to the pattern, and the penetration of the *X*-ray beam was not sufficient to reach the unconverted monohydrate at the centre of the disc. The solubility of triphosphate was tested in the following non-aqueous solvents: glacial acetic acid, tri-n-butyl phosphate, liquid ammonia, dioxan, nitromethane, pyridine, tri-n-butylamine, *NN*-dimethylformamide, ethyl methyl ketone, n-butanol, and tetramethylene sulphone. Only glacial acetic acid dissolved triphosphate, but attempts to ammoniate the anhydrous triammonium salt in this solvent to the penta-ammonium salt failed because the solubility product of ammonium acetate was exceeded. Triphosphate was soluble in liquid ammonia and tri-n-butylphosphate if traces of water were present but in these cases the monohydrate was formed from the ammoniation of an acid salt. This ammonium salt has an exceptional affinity for its water of crystallisation.

As it was not possible to convert one diammonium dihydrogen pyrophosphate into another by heating or cooling it was not immediately obvious which was the most stable phase. However, both the α- and the β-form crystallised from aqueous solution to give the γ-form. The β-form was quite stable in a dry atmosphere but the α-form was converted into the γ-form even in a dry atmosphere or under pressure. The α-, β-, and γ-forms were so designated on the basis of these results.

All the pyrophosphates give very similar melts, any ammonia above the diammonium level being rapidly lost on melting. On cooling the melts, a glass formed which very slowly recrystallised to α-diammonium dihydrogen pyrophosphate. The reason for the α-phase's crystallising at room temperature where it is unstable may be that the crystal structure is formed which has the ionic co-ordination most similar to that found in the glass. The ionic rearrangement to form a more stable structure may be hindered by the lack of mobility of the pyrophosphate ion in the glass. The following facts are evidence that this may be the case. (a) Some chain phosphates cannot be crystallised from aqueous solution, and this is usually explained by the inability of the large anion to re-orientate itself sufficiently easily for a crystalline structure to be built up. (b) When impure tri-, trimeta-, and tetrameta-phosphates are precipitated with I.M.S. an oil often forms, whereas in the pure system crystals are formed, showing that crystallisation of these phosphates is easily hindered.

Unlike the pyro- and tri-phosphates the trimeta- and tetrameta-phosphates did not melt but slowly decomposed in the solid state, to give mainly higher phosphates.

Degradation as well as polymerisation occurred in all the melt phases and complex equilibria between the phosphates are undoubtedly present.

Efforts to prepare acid trimeta- and tetrameta-phosphates from acetic acid were unsuccessful.

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