The observations noted here concerning the finding that simple Cu(I) complexing agents can reverse the oxidation of Cu(I) by O_2 afford a possible explanation for the ability of Cu(I), under oxidizing conditions, to serve as an effective source of univalent copper for the reconstitution of the copper-free proteins (apohemocyanin or apocytochrome *c* oxidase) as noted earlier in this communication. It is possible that the apoproteins react to reverse the autoxidation in the same fashion as the simple Cu(I) complexing agents reported here.

Acknowledgment. The author thanks Professor D. F. DeTar for making LSKIN2 available and for help in its use and Professor C. K. Mann for a gift of redistilled CH_3CN. Thanks are also due D. A. Johnson for the use of the spectrophotometer oxygen electrode. Finally the author extends his thanks to Professor E. Frieden for discussion and support of this work.

Preparation and Characterization of Crystalline Long-Chain Ammonium Polyphosphates

C. Y. Shen, N. E. Stahlheber, and D. R. Dyroff

Contribution from the Research and Development Department,
Inorganic Chemicals Division, Monsanto Company, St. Louis, Missouri 63166.

Received July 22, 1968

Abstract: Crystalline ammonium polyphosphates with a chain length greater than 50 were characterized for the first time. Control of the ammonia vapor pressure is the key to producing these compounds at elevated temperatures. Five forms were identified. Single crystals of forms II, IV, and V were isolated and their cell parameters determined. The long-chain crystalline ammonium polyphosphates are quite insoluble in cold water and show a slower degradation rate than Graham's salt.

It is well known that thermal dehydration of ammonium orthophosphates, instead of producing crystalline condensed phosphates, produces an amorphous mixture of polyphosphates,[1] from which most of the ammonia has been lost.[2,3] Early attempts to produce $(NH_4PO_3)_x$ varied from treating a copper or lead polyphosphate with ammonium sulfide[4,5] to tempering ammonium trimeta- or tetrametaphosphate at 200–250°. The products from these approaches, however, were impure as revealed by paper chromatograms and chemical analysis.[6]

Relatively pure and highly polymerized ammonium polyphosphates were reported to result from heating amidophosphates[7] and from reaction of ammonia with a condensed phosphoric acid containing about 83–84% P_2O_5.[8] The X-ray diffraction pattern given in the latter work is similar to that of an ammonium polyphosphate produced by heating an ammonium orthophosphate with urea.[9–11]

In the present work much more detailed information is developed on the formation and properties of a number of crystalline long-chain ammonium polyphosphates including forms not previously reported in the literature.

Experimental Methods

All chemicals used in the preparations were reagent grade without further purification. The products were first characterized by X-ray diffraction patterns of powdered samples. In those cases where sufficiently large single crystals could be isolated, oscillation and Weissenberg photographs were obtained to determine the unit cell parameters which were then refined using the powder data.

Total nitrogen in ammonium polyphosphate samples was determined by a Kjeldahl method for nitrate-free material.[12] Ammoniacal nitrogen was determined by a formaldehyde titration technique.[12] Total P_2O_5 content and phosphate species were determined by a combination molybdenum blue colorimetric paper chromatographic procedure.[13] Nuclear magnetic resonance spectra[14] were used to test for the presence of amido or imido phosphates and to estimate the relative amounts of ortho-, end-group, and middle-group phosphates.

Preparation and Characterization of Various Crystalline Forms

General Considerations. The long-chain ammonium polyphosphates (APP) described here were prepared either by tempering other forms and quenching or by reaction of urea with a less condensed phosphate. In either case it was necessary to provide some control

---

[1] In this work, "polyphosphate" designates –P–O–P– chains and "metaphosphate" designates ring compounds.

[2] (a) G. V. Knorre, *Z. Anorg. Chem.*, 24, 369 (1900); (b) H. N. Terem and S. Akalan, *Compt. Rend.*, 228, 1437 (1949).

[3] E. V. Margulis, L. J. Beisekeeva, N. I. Kopylov, and M. A. Fishman, *J. Appl. Chem.* (USSR), 39, 2216 (1966).

[4] G. Tamman, *Z. Physik Chem.*, 6, 122 (1890); *J. Prakt. Chem.*, 45, 417 (1892).

[5] S. J. Kiehl and T. H. Hill, *J. Am. Chem. Soc.*, 49, 123 (1927).

[6] V. H. Grunze and E. Thilo, *Z. Anorg. Allgem. Chem.*, 281, 262 (1955).

[7] M. Goehring and J. Sambeth, *Ber.*, 90, 232 (1957).

[8] A. W. Frazier, J. P. Smith, and J. R. Lehr, *J. Agr. Food Chem.*, 13, 317 (1965).

[9] S. Ueda, K. Oyama, and K. Koma, *Kogyo Kagaku Zasshi*, 66, 586 (1963).

[10] P. G. Sears and H. L. Vandersall, Belgian Patent 651,782 (Aug 13, 1964), and unpublished information.

[11] E. Kobayashi, *Kogyo Kagaku Zasshi*, 69, 2065 (1966).

[12] W. Horwitz, Ed., "Official Methods of Analysis of the Association of Official Agricultural Chemists," 8th ed, Association of Official Agricultural Chemists, Washington, D. C., 1955, Procedures 2:23 and 2:26.

[13] E. K. Kroupa, *Anal. Chem.*, 28, 1091 (1956).

[14] M. Crutchfield, C. Dungan, J. Letcher, V. Mark, and J. R. Van Wazer, "Topics in Phosphorus Chemistry," Vol. 5, E. Griffith and M. Grayson, Ed., Interscience Publishers, New York, N. Y., 1967.

of the ammonia content of the atmosphere over the sample since the vapor pressures of the products and/or intermediates are appreciable at practical reaction temperatures. If the ammonia partial pressure is below the equilibrium vapor pressure, the sample tends to lose ammonia and becomes more acidic and hygroscopic. The lower pH and the absorption of water from the atmosphere can cause degradation to lower phosphates, a problem which appears to have confused the results of some earlier investigators.

All of the crystalline forms are sufficiently stable to be stored for extended periods of time in open containers at room temperature without appreciable conversion to other forms or to degradation products.

The action of urea as a dehydrating and ammoniating agent is illustrated by eq 1–4. Thus any phosphoric

$$NH_2CONH_2 + H_3PO_4 \longrightarrow (1/x)(NH_4PO_3)_x + CO_2 + NH_3 \quad (1)$$

$$NH_2CONH_2 + H_2O \longrightarrow 2NH_3 + CO_2 \quad (2)$$

$$2NH_4H_2PO_4 + NH_2CONH_2 \longrightarrow (NH_4)_4P_2O_7 + CO_2 \quad (3)$$

$$(NH_4)_4P_2O_7 + NH_2CONH_2 \longrightarrow (2/x)(NH_4PO_3)_x + CO_2 + 4NH_3 \quad (4)$$

acids or less condensed ammonium phosphates could in principle be used as raw materials to prepare $(NH_4PO_3)_x$ provided that sufficient urea is present. The rate of decomposition of urea in excess phosphoric acid at temperatures above 120° was shown to increase rapidly with phosphoric acid concentration, and it is believed that reaction of urea with free water is not rate controlling if the amount of free water is no greater than the amount present in 100% H_3PO_4 which is estimated by Van Wazer[15] as being about 5%.

Some understanding of the course of the reaction of urea with $NH_4H_2PO_4$ was obtained by differential thermal analysis using a Du Pont 900 unit with an open sample holder at a heating rate of 5°/min (see Figure 1). The processes mainly responsible for the various endotherms are believed to be as shown in Table I. If a high flow of nitrogen purge gas is used, the last two peaks merge at 350–360° since the APP is less stable when less NH_3 is present in the local atmosphere. It is believed that the endothermic nature of the peak at 330–340° is at least partly due to the fact that the breakdown of the form I crystal structure offers an opportunity for a small amount of NH_3 to vaporize with absorption of heat before the new crystal structure is established.

Table I

Temp, °C	Process	Evidence
130–135	Urea melts	Urea melting point is 132°
150	Eq 3	Analysis of evolved gas, phosphate species analysis[13], X-ray diffraction pattern
170–220	Eq 4	X-Ray diffraction pattern, analysis of evolved gas
330–340	Form I → other forms of APP plus degradation products	Related experiments in sealed tubes
400	APP → liquid degradation products	Visual observation and related experiments

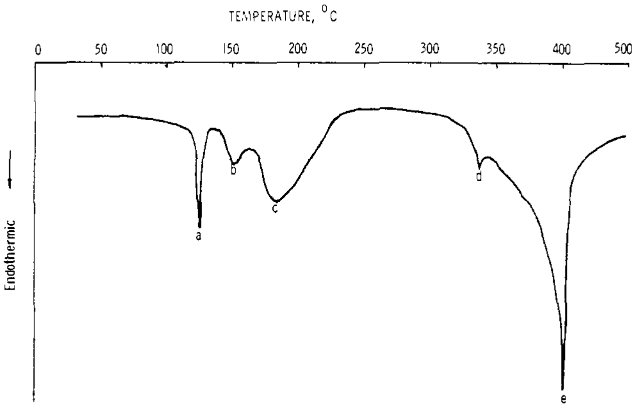


Figure 1. Differential thermal analysis of equal molar mixture of $NH_4H_2PO_4$ and NH_2CONH_2.

Form I. Form I APP was prepared by heating an equal molar mixture of $NH_4H_2PO_4$ and urea under anhydrous ammonia at 280° for 16 hr. The X-ray diffraction pattern is given in Table II, and, except for some minor differences, the pattern is the same as reported earlier.[8,10] Unit cell dimensions were not determined because of a lack of crystals large enough for single-crystal X-ray studies. The crystals are very small when first formed and could not be adequately enlarged by recrystallization or tempering without conversion to other forms. The only crystalline impurities which could be identified by X-ray diffraction were form II APP, cyanuric acid, and melamine cyanurate. The latter two compounds usually are present when a large excess of urea is used. Unconverted urea and urea cyanurate are present in products which are not heated above 180°.

Table II. X-Ray Diffraction Pattern of Form I Ammonium Polyphosphate

d, Å	I/I_0	d, Å	I/I_0
6.91	12	2.75	13
6.66	3	2.72	5
6.06	100	2.64	15
5.45	70	2.54	6
5.16	2	2.45	5
3.84	50	2.42	13
3.75	5	2.35	8
3.57	18	2.29	30
3.51	45	2.24	7
3.42	25	2.14	8
3.32	4	2.13	7
3.24	35	2.11	5
3.10	8	2.01	3
3.00	3	1.93	3
2.92	7	1.91	6
2.88	10	1.89	5
2.82	15	1.84	1
2.78	5	1.81	2

Form II. Form II APP can be easily prepared from form I by tempering at 200–375° in a well-covered container. The rate of transformation increases with temperature. At 300° about 60 hr was required to remove all traces of form I and form III, an intermediate.

The conversion of form I to form II is accelerated by the presence of an amorphous phase which can be produced by removing a small amount of ammonia or by introducing a small amount of water vapor.

---

(15) J. R. Van Wazer, "Phosphorus and Its Comounds," Vol. I, Interscience Publishers, New York, N. Y., 1958, p 750.

The largest form II single crystals found were about 0.1 mm long and were isolated from a glassy mixture formed at 300° by removing some NH_3 from form I. Orthorhombic symmetry was well established by inspection of the intensities on Weissenberg photographs. The unit cell parameters are $a = 4.256$, $b = 6.475$, $c = 12.04$ Å, all ±0.01 Å. The agreement between the calculated and observed powder patterns given in Table III is excellent. The calculated density for $4NH_4PO_3$ per cell is 1.94 g/cm³ which is in satisfactory agreement with the value of 1.90 measured by displacement of acetone. The apparent extinction rules are: $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$. The most probable space group is thus $P2_12_12_1$.

Table III. X-Ray Diffraction Pattern of Form II Ammonium Polyphosphate

	$2\theta^a$				$2\theta^a$		
Index	Calcd	Obsd	I/I_0	Index	Calcd	Obsd	I/I_0
001	7.34	...	0	122	37.95	37.98	9
010	13.67	...	0	114	39.17	39.18	2
002	14.70	14.69	47	015	39.91	...	0
011	15.52	15.52	100	024	40.89	...	0
012	20.12	20.10	5	123	41.61	41.65	<1
100	20.85	...	0	030	41.82	...	0
003	22.13	...	0	200	42.44	42.5	1
101	22.13	22.18	12	031	42.50		
110	25.01	25.07	2	105	43.12	43.10	6
102	25.60	25.63	7	201	43.13		
013	26.09	26.12	25	032	44.55	Masked	...
111	26.11			210	44.78	44.83	4
020	27.52	27.52	17	006	45.14	45.2	
021	28.52	28.55	4	202	45.14		
112	29.13	29.14	41	115	45.45	45.45	2
004	29.65	29.65	3	211	45.45		
103	30.59	30.61	28	124	46.33	46.35	1
022	31.35	...	0	025	46.99	Masked	...
014	32.78	32.79	3	130	47.17	Masked	...
113	33.64	...	0	016	47.38	47.40	2
120	34.78	34.8	1	212	47.40		
023	35.60	35.62	9	131	47.80	47.80	
121	35.60			033	47.80		
104	36.54	36.53	14	203	48.37	...	0
005	37.31	...	0	132	49.70	49.63	3

[a] Copper Kα radiation.

Form III. Form III APP was observed as an intermediate in the conversion of form I to form II at 300° or to form V at high temperatures. When form I was heated at 300° while maintaining an NH_3 pressure of about 20–50 mm above the reaction mass, the amount of form III reached a maximum at about 20 hr, but considerable amounts of forms I and II were also present. One way to prepare a reasonably pure sample of form III is to choose an ammonia pressure such that the rate of formation of form II is minimized relative to the rate of formation of form III and then quench the sample when the form III content reaches a maximum. It is possible that a more favorable situation might exist at a somewhat different temperature.

Characterization of form III APP was complicated by the lack of pure material. The X-ray diffraction peaks given in Table IV were determined by subtracting the known peaks of forms I and II from the pattern produced by a mixture of forms I, II, and III.

Table IV. X-Ray Diffraction Peaks of Form III APP

d, Å	Intensity rank[a]	d, Å	Intensity rank[a]
6.01[b]	4	3.25[b]	9
5.92	3	3.13[c]	2
5.53	1	3.00[c]	12
4.02[b]	11	2.92[b]	5
3.57[c]	8	2.45[b]	10
3.29[c]	6	2.43[c]	7

[a] The 12 strongest peaks are given with estimates of their rank after correction for contributions from forms I and II. The strongest peak is ranked 1. [b] This peak is close to a strong peak of form I or II. Both intensity and position could be influenced by the form I or II peak. [c] This peak coincides with a weak peak in form I or II, but the intensity relative to other form I or II peaks strongly indicates that it is due to form III.

Form IV. Form IV APP was obtained in a mixture with glassy impurities by rapidly cooling a melt formed by heating form I or II APP to 450–470°. The X-ray diffraction pattern of the crystalline material was very similar to that of potassium Kurrol's salt (Table V) which is probably isomorphous. Using a somewhat imperfect single crystal, oscillation and zero-layer Weissenberg photographs were obtained about the *b* axis which was parallel to the longest dimension of the crystal. Form IV is monoclinic with the approximate parameters $a = 14.5$ Å, $b = 4.62$ Å, $c = 11.0$ Å, $\beta = 100°$. The unit cell parameters for potassium Kurrol's salt as reported by Jost[16] are $a = 14.02$ Å, $b = 4.54$ Å, $c = 10.28$ Å, $\beta = 101.5°$. From IV crystals, when placed in water, rapidly disintegrate into fibers parallel to the *b* axis, similarly to the behavior of potassium Kurrol's salt.[17]

Table V. X-Ray Diffraction Pattern of Form IV APP

d, Å	I/I_0	d, A	I/I_0
6.37	50	2.70	17
5.30	18	2.60	14
5.12	25	2.41	3
4.55	14	2.28	57
3.78	19	2.23	23
3.71	8	2.06	5
3.45	83	2.03	6
3.40	100	1.95	3
3.31	15	1.90	7
3.16	24	1.88	7
3.10	12	1.85	6
2.84	13	1.80	4
2.75	27		

Form V. One good way to prepare form V APP is by heating form I or II in a sealed tube at 410° for about a day and then quenching in liquid nitrogen. Form V undergoes rapid conversion to form II at temperatures in the neighborhood of 250–350°, and unless the cooling of form V is done at a high rate the final product is a mixture containing large amounts of form II.

The largest single crystal obtained was only 0.03 × 0.04 × 0.06 mm. Oscillation and zero layer Weissenberg photographs were obtained about the *a* axis which was parallel to the longest dimension of the crystal. From V is orthorhombic with $a = 4.346$, $b = 6.135$, $c = 13.646$ Å (all ±0.02 Å).

(16) K. Jost, *Acta. Cryst.*, **16**, 623 (1963).
(17) R. K. Iler, *J. Phys. Chem.*, **56**, 1086 (1952).

The calculated powder pattern between 0 and 50° 2θ based upon the cell dimensions is presented in Table VI along with the observed 2θ values and intensities. The agreement between the calculated 2θ values and all but the weakest observed peaks is good indication that the proposed cell is either the correct one or a subcell of the correct one and that form V has been prepared as an essentially pure phase. There are a number of weak peaks unexplained by the above unit cell, which could be due to small amounts of other phases or to superlattice lines. The calculated density for $4NH_4PO_3$ per cell is 1.77 g/cm^3 compared to 1.80 g/cm^3 measured by flotation in a CCl_4–CH_3I mixture.

Table VI. X-Ray Diffraction Pattern of Form V Ammonium Polyphosphate

Index	2θ[a] Calcd	2θ[a] Obsd	I/I_0[b]
001	6.47	...	0
002	12.96	12.97	66
...	...	13.43	7
010	14.42	...	0
...	...	14.72	4
011	15.82	15.85	100
...	...	16.73	6
012	19.44	...	0
003	19.49	...	0
100	20.42	...	0
101	21.44	...	0
...	...	22.00	3
...	...	22.30	2
...	...	23.73	<3, sh
102	24.25	24.22	50
013	24.32		
110	25.08	25.17	3
111	25.93	26.07	75
004	26.08		
...	...	27.20	3
112	28.34	...	0
103	28.36	...	0
020	29.08	29.23	11
021	29.82	...	0
014	29.93	...	0
...	...	30.28	3
022	31.96	31.83	25
113	31.97	32.09	sh
005	32.78	...	0
104	33.35	33.35	22
023	35.26	...	0
120	35.80	...	0
015	35.98	36.13	2
121	36.42		
114	36.51	...	0
122	38.22	38.23	14
105	38.92	...	0
024	39.47	39.42	3
006	39.58	...	0
123	41.08	...	0
200	41.52	41.51	3
115	41.72	...	Masked
201	42.07	...	Masked
016	42.34	42.34	8
202	43.53	43.50	3
210	44.13	...	0
030	44.25	...	0
025	44.39	44.8	3
211	44.69		
031	44.78		
124	44.83		
106	44.95	45.12	3
212	46.23	45.9	2
203	46.26	...	0
032	46.30	...	0
007	46.53	...	0
116	47.43	47.5	1
213	48.70	48.6	4
033	48.79		
017	48.97		
130	49.21	...	0
125	49.32	...	0
131	49.67	49.8	1
204	49.70		
026	49.87		

[a] Copper Kα radiation. [b] sh = shoulder.

Chemistry of Polymorphic Transitions

It was found that the following transitions could be accomplished by tempering at the indicated temperature and then quenching rapidly to room temperature.

110–200°	form V → mixture of forms I and II
200–375°	form I → form II (see text)
250–300°	form V → form II
300°	form I → form III (transient intermediate) → form II
300–370°	form IV → form II
330–420°	form I → form V
385°	form II → form V
450–470°	form I or form II → form IV + glass

It should be noted that some of these transitions may be possible somewhat outside the indicated temperature ranges as well, although this was not experimentally demonstrated.

Below 300° forms I and II are rather stable in the presence of reasonably high NH_3 partial pressures, but, if the NH_3 pressure is lower, form I converts to other forms at temperatures as low as 200°. The loss of NH_3 presumably lowers the activation energy, allowing the transitions to occur at an observable rate. Form V is less stable thermodynamically than forms I and II at the lower temperatures and converts to other forms at an appreciable rate at temperatures as low as 110° even without removal of NH_3. In the conversion of form V to forms I and II at 110–200°, the proportions of the two products were unaffected by variation of H_2O or NH_3 pressures, and form II predominated. Seeding with large amounts of form I increased the percentage of the form V which converted to form I, but the highest yield of form I was only 33%.

Based upon the above information it is concluded that form I is a metastable phase with no true region of thermodynamic stability relative to the other allotropes above 110°. The only observed transformation of another form to form I, V $\rightarrow$ I + II (110–200°), can be interpreted as the trapping of a portion of the APP in the metastable form I structure as it converts from an even higher energy structure to the stable form II structure. Further evidence for the metastable nature of form I is that although form I is the product of the reaction of $NH_4H_2PO_4$ and urea in the absence of seeding, when a mixture of form I and form II seeds is present the product contains a larger proportion of form II than that in the seed material. In fact the formation of form I can be essentially eliminated in this reaction by seeding with form II.

Form II and form V appear to have considerable regions of thermodynamic stability. Form III appears to be a metastable phase. Whether or not form IV has a true region of stability has not yet been definitely established. To prepare it in pure form may require the application of very high NH_3 pressures.

Properties of Ammonium Polyphosphates

Solubility. The aqueous solubility of the long-chain ammonium polyphosphates was difficult to determine because the solubility increased with the quantity of solid phase present. The small amount of more soluble material could have been generated by grinding as was observed with $NaPO_3$-II.[18] The apparent solubility of form I APP given in Figure 2 was estimated from a series of solubility determinations with different amounts of solids using the phase-rule approach[19] used earlier in estimating the true solubility of pure proteins.[20] The heat of solution estimated from the solubility–temperature data by van't Hoff's equation is 8.8 kcal/mole of NH_4PO_3 which is in good agreement with the calorimetrically measured value. The solubility of form II APP appears to be about the same as that of form I.

---

(18) I. Motooka, G. Hashizume, and M. Kabayashi, *Nippon Kagaku Zasshi*, **87**, 953 (1966).

(19) S. P. L. Sorensen, *Compt. Rend. Trav. Lab. Carlsberg*, **18** (5), 1 (1930).

(20) M. Kunitz and J. H. Northrop, *Symp. Quant. Biol.*, **6**, 325 (1938).

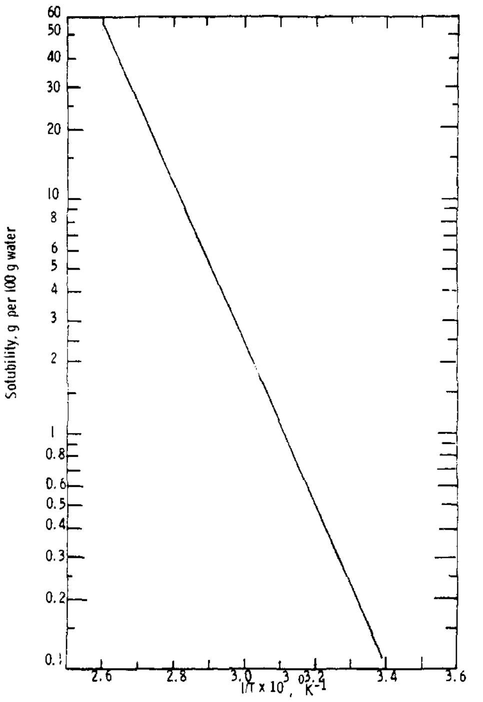


Figure 2. Apparent solubility of form I ammonium polyphosphate.

In the presence of other dissolved cations, the ammonium ion in an APP crystal undergoes an ion-exchange reaction resulting in increased solubility of the phosphate and formation of a gummy material. For example, the amount of form I APP dissolved in 100 g of water at 25° increases from 0.15 to about 3.5 g with the addition of 0.5 g of NaCl.

Thermochemical Data. The calorimeter used in these measurements was described in a previous paper[21] and is accurate to ±0.03 cal. The specific heats of forms I and II APP at 25° were measured in CCl_4 slurries to be 0.274 and 0.281 ± 0.002 cal/(g °C), respectively. The heat of formation was calculated from the measured heat of solution and hydrolysis of APP in 5 N HCl. The technique was similar to that used earlier in determining heats of formation of various crystalline polyphosphates.[22] For forms I and II the standard heats of formation from the elements at 25° are about −261 ± 2 and −256 ± 2 kcal/mole of NH_4PO_3, respectively.

Hydrolytic Degradation Rate. The hydrolytic degradation rate was determined in a 15% by weight solution of form I APP in water. The pH was held constant by addition of NH_4OH or HCl. The degradation reaction is pseudo first order as judged by the disappearance of middle groups followed by nmr analyses and the formation of end groups followed by end-group titrations. The rate constants are given in Table VII. The degradation is much slower, especially at 100°, than was observed earlier for Graham's salt.[23] The activation energy of 13.8 kcal/mole is lower than the value of about 25 for 1% Graham's salt solution, but this is consistent with the tendency for the activation energy of such reactions to decrease with increasing concentration.[24]

Vapor Pressure. The equilibrium ammonia pressure over form I APP was measured using a technique similar to that described by Mack and France.[25] The vapor pressure p (in mm) at a temperature T (°K) fits eq 5

$$\log p = 8.207 - 3230/T \qquad (5)$$

with an average error of about 3% from the measured values. The equilibrium ammonium pressure above forms II and V is somewhat lower than that of form I, but the exact numbers have not been obtained. The NH_3 pressure was assumed equal to the total vapor pressure since the water vapor pressure over long-chain polyphosphoric acid is small even at a temperature of 350°.[26]

Molecular Structure. Although individual atomic positions within the unit cells have not been determined, the following facts appear to be sufficient to conclude that the various forms of ammonium polyphosphate described in this work are long-chain polyphosphates.

1. All forms have a mole ratio of ammoniacal nitrogen to phosphorus of essentially 1.0.
2. Infrared and nmr spectra did not show any detectable amount of –P–N–P– linkages.
3. Phosphorus nmr spectra of APP solutions show a single peak corresponding to a middle group.
4. Paper chromatographic analyses show that all forms are nonmoving high molecular weight species.
5. pH titrations of solutions obtained by passing APP solutions through a column of acid-treated Amberlite IR-120 resin show a single inflection. End-group titrations indicate that the equivalent phosphate chain length is above 50.
6. The unit cell parameters of form IV APP are closely related to those of potassium Kurrol's salt. Since the ionic radii of potassium and ammonium are nearly equal, it is reasonable to assume that the crystal structures are similar. Potassium Kurrol's salt was proved to be a long-chain polyphosphate.[16]
7. Intrinsic viscosity, light scattering, and gel permeation chromatographic measurements[27] showed that the ammonium polyphosphates described here contain very long-chain anions and that forms II and V typically contain longer chains than form I.

Discussion

The very low water vapor pressure above condensed phosphoric acid indicates that it would be very difficult to produce long-chain ammonium polyphosphate (APP) by using heat to remove water from an ammonium orthophosphate. It is theoretically possible, however, to produce APP from an ammonium orthophosphate by using a stream of dry ammonia to

---

(21) R. R. Irani and T. A. Taulli, *J. Inorg. Nucl. Chem.*, **28**, 1011 (1966).

(22) T. R. Meadowcroft and F. D. Richardson, *Trans. Faraday Soc.*, **59**, 1564 (1963).

(23) J. F. McCullough, J. R. Van Wazer, and E. J. Griffith, *J. Am. Chem. Soc.*, **78**, 4528 (1956).

(24) C. Y. Shen and D. R. Dryoff, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 97 (1966).

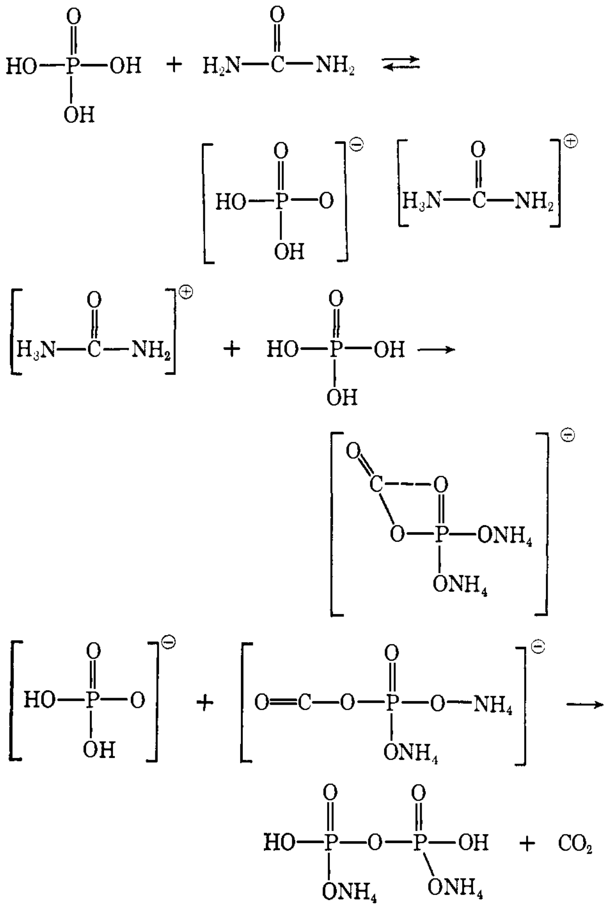
(25) E. Mack and W. G. France, "A Laboratory Manual of Elementary Physical Chemistry," 2nd ed, D. Van Nostrand Co., New York, N. Y., 1934.

(26) E. H. Brown and C. D. Whitt, *Ind. Eng. Chem.*, **44**, 615 (1952).

(27) W. A. Feiler and J. W. Lyons, paper presented at the Midwest Regional American Chemical Society Meeting, Kansas City, Kan., Oct 28, 1966; W. A. Feiler, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 3, 1968, No. M-101.

Table VII. Degradation Rate of Ammonium Polyphosphate in 15% Solutions

	100°		60°	
	pH 4.5	pH 6.0	pH 4.5	pH 6.0
First-order rate const, min^{-1}	5.5×10^{-4}	3.3×10^{-5}	4.9×10^{-5}	2.6×10^{-6}



(6)

(7)

(8)

maintain the water vapor pressure below the APP equilibrium value. This approach was tried by heating a thin layer of monoammonium orthophosphate to 350° under a flow of dry ammonia gas for a period of a week, and indeed, some form II APP was found in the product.

The use of urea as a dehydration and ammoniating agent to condense polybasic acids seems to have wide applicability. Urea is a good fluxing agent and often forms a low-temperature eutectic melt with salts. For a reaction involving solids, this property can speed up the usual slow diffusional rate-controlling step.

One conceivable mechanism for such reactions is eq 6–8, using the condensation of H_3PO_4 as an example. In any case, it seems probable that the mechanism is something other than the reaction of urea with free water to drive a simple condensation between molecules of acid because these reactions proceed at much lower temperatures than the simple acid condensations. Indeed, form I APP was prepared during this investigation by heating $NH_4H_2PO_4$ and urea at 118° in a covered dish. Other examples of these low-temperature condensations are the preparation of alkyl ammonium polyphosphate from alkyl dihydrogen phosphate and urea at 120–200°[28] and the preparation of ammonium pyrosulfate from sulfuric acid and urea at 140°.[29]

Acknowledgment. The help of Tom Taulli in obtaining the thermochemical data is appreciated.

---

(28) S. Ueda and M. Tada, *Bull. Chem. Soc. Japan*, **39**, 2395 (1966).
(29) P. G. Sears, unpublished results.

The Solid-State Deamination of Tris(ethylenediamine)- and Tris(propylenediamine)chromium(III) Thiocyanate

J. E. House, Jr., and John C. Bailar, Jr.

Contribution from the W. A. Noyes Laboratory of Chemistry, University of Illinois, Urbana, Illinois 61801. *Received June 20, 1968*

Abstract: The solid state deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$ to the corresponding dithiocyanato compounds has been studied isothermogravimetrically. The reaction is catalyzed by ammonium thiocyanate and amine hydrothiocyanates and is first order in catalyst over a wide range of catalyst/salt ratios. Activation energies for the uncatalyzed and catalyzed deamination of $[Cr(en)_3](NCS)_3$ are 47.4 ± 2.4 and 33.1 ± 1.6 kcal/mol, respectively, while those for the deamination of $[Cr(pn)_3](NCS)_3$ are 55.2 ± 2.8 and 44.6 ± 2.2 kcal/mol. The mechanism of the deamination is discussed in terms of the acid catalysis and kinetic observations.

It has been known for many years that $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$ (where en = ethylenediamine and pn = propylenediamine) each lose a molecule of ligand on heating in the solid state and are converted to *trans*-$[Cr(en)_2(NCS)_2]NCS$ and *trans*-$[Cr(pn)_2(NCS)_2]NCS$, respectively.[1,2] The study by Rollinson and Bailar showed that the solid-state reaction is catalyzed by ammonium thiocyanate. This has been,

---

(1) P. Pfeiffer, P. Koch, G. Lando, and A. Trieschmann, *Ber.*, **37**, 4255 (1904).
(2) C. L. Rollinson and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **66**, 641 (1944).