Condensation of Ammonium Phosphates with Urea at 120 °C

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The pyrolysis of $NH_4[H_2PO_4]$ and $[NH_4]_2[HPO_4]$ in the presence of urea at 120 °C has been followed by ^{31}P n.m.r. spectroscopy and shown to go through a sequence of reactions involving di- and tri-phosphates and eventually leading to ammonium hexacyclophosphate $(NH_4PO_3)_6$ as the principal product. The heating of ' urea phosphate ', $(NH_2)_2CO{\cdot}H_3PO_4$, at 120 °C has also been studied by ^{31}P n.m.r. spectroscopy.

Urea phosphate (uph) is the usual name given to the unusual chemical compound formed between urea and phosphoric acid, $(NH_2)_2CO{\cdot}H_3PO_4$. This substance is not a salt as its name implies but is an adduct held together by a pair of hydrogen bonds, of which the O · · · H · · · O bond is a very strong one, as its length and symmetry shows, (I).[1] Although uph has been known for over a century [2] it is only within the last decade that its commercial potential has been realized. Reports have appeared on its use as a fertilizer,[3] an animal feed supplement,[4] and a fire-resistant treatment.[5] Chemical Abstracts databases have over 250 citations to uph between 1967 and 1981,† and many of these refer to patents.

Heating uph results in ammonium polyphosphates, and this condensation reaction (1) occurs at much lower temperatures than are normally required to polymerize phosphoric acid or phosphates. Indeed, the formation of ammonium poly-

$$(NH_2)_2CO{\cdot}H_3PO_4 \longrightarrow \frac{1}{n}\left(NH_4PO_3\right)_n + NH_3 + CO_2 \quad (1)$$

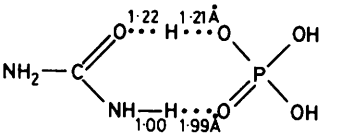
phosphates by thermal dehydration of $NH_4[H_2PO_4]$ requires temperatures in the range 200—350 °C and an atmosphere of NH_3 to prevent decomposition, which gives an amorphous material with reduced nitrogen content.[6]

Prolonged heating of uph at temperatures as low as 100 °C will produce ammonium diphosphate.[7] At higher temperatures, up to 400 °C, insoluble ammonium polyphosphates of high molecular weights are produced. A pressure of NH_3 gas was necessary to prevent decomposition of the $(NH_4PO_3)_n$ (n = *ca.* 50).[8]

At 190—250 °C soluble ammonium polyphosphates are formed.[9] Other work at lower temperatures, 120—185 °C, has shown that cyclophosphates are also produced.[10] Thermogravimetric studies indicate the reaction to be zero-order, in the temperature range 118—150 °C.[11]

McCullough *et al.*[12] have shown that the pyrolysis of uph is slow below 126 °C but above this temperature a very rapid, exothermic reaction occurs to form ammonium hydrogen monophosphates and polyphosphates $[O(PO_3)_n]^{(n+2)-}$ (n = 2—8) being identified chromatographically. It is this mixture (which also contains unreacted urea and some biuret) that is seen as a potential fertilizer.[13] These workers [12] also investigated the pyrolysis of a mixture of $NH_4[H_2PO_4]$ and uph in various ratios at 150—200 °C again producing ammonium polyphosphates.

† The Chemical Abstracts registry numbers for uph are [4861-19-2] urea phosphoric acid and [4401-74-5] urea phosphate: uph has many synonyms based on the combination of urea–carbamide with phosphoric acid–monophosphate–rock phosphate–orthophosphate. At different times some of these have had their own registry numbers.



(I)

Prebiotic phosphorylation *via* uph and its conversion to polyphosphates has been suggested.[14] It is thus of interest to determine the effects of relatively low temperatures on this substance and other monophosphate–urea mixtures. Ammonium phosphates were chosen since these share a common cation with the products of pyrolysis of uph.

The effect of heat on $NH_4[H_2PO_4]$ and $[NH_4]_2[HPO_4]$ mixtures with urea is negligible below 100 °C, but at 120 °C the rate of reaction was sufficient to allow them to be studied over periods that were not too prolonged. The reactions were sampled at regular intervals and the composition of the products determined by ^{31}P n.m.r. spectroscopy, a technique that has so far not been used to study phosphate condensations involving urea, although it has been profitably used to study H_3PO_3–carbodi-imide condensations in tetramethylurea (as solvent) at 40 °C; the products were cyclophosphates $(PO_3)_n^{n-}$ (n = 3—8).[15]

Experimental

Materials.—Analytical reagent grade H_3PO_4, $NH_4[H_2PO_4]$, $[NH_4]_2[HPO_4]$, and urea were used without further purification.

Phosphorus-31 N.M.R. Spectroscopy.—Phosphorus-31 n.m.r. spectra were recorded on a Bruker HFX 90 spectrometer operating at 36.4 MHz at 307 ± 2 K. Aqueous solutions (5% w/v) containing a few drops of D_2O were measured in 10 mm tubes with broad band decoupling and pulsed Fourier transform. Peak positions were measured in p.p.m. from 85% H_3PO_4 as external standard: pulse width 12.5 μs; 8 K data points; −1 to −2 s time constant; 6 000 Hz sweep-width; 4 500 Hz offset; 512—2 000 scans; 30° flip angle.

Reaction of $NH_4[H_2PO_4]$ *and Urea.*—$NH_4[H_2PO_4]$ (23.2 g, 0.2 mol) and $(NH_2)_2CO$ (24 g, 0.4 mol) were ground together and heated. Ammonia gas was evolved at 115 °C and the mixture melted and swelled due to the evolved gases. The temperature was held at 120 °C over a period of 25 h during which time samples were withdrawn for ^{31}P n.m.r. analysis. After *ca.* 10 h the viscous mixture slowly solidified.

Reactions with lower ratios of urea were more viscous and some solidified shortly after melting. Nevertheless, heating was continued at 120 °C after the solid aggregate had been

Table 1. Reaction of $NH_4[H_2PO_4]$ and urea on heating

Temp. (°C)	Ratio reactants $NH_4[H_2PO_4]$: urea	t/h	Composition (%) P_1	P_2	P_3	cP_3	cP_6	Other P
120	1 : 1	5	29	70	1			
		10	9	68	12		11	
		15	12	61	4		16	7 *
		20	9	24			66	1
		25	24	20			56	
110	1 : 1	5	58	42				
		15	38	62				
		25	5	95				
		35		100				
		65		95			5	
		100		86			14	
		125		80			20	
120	1 : 2	2	31	69				
		5	13	87				
		10	2	86	12			
		15	1	51	34	4	10	
		20		<1	<1	11	89	

* Three small signals at δ +1.98, +1.09, and +0.81 p.p.m. appeared in this spectrum suggestive of esters or compounds with a P–N link: see text.

broken up. Reactions of $[NH_4]_2[HPO_4]$ and urea were carried out in a similar manner.

Mixing equimolar ratios of phosphoric acid and urea at room temperature resulted in an exothermic reaction and finally a solid crystalline mass of uph. This softened on heating at 90 °C and melted at 117.5 °C. At 120 °C the liquid became gradually more viscous as NH_3 was evolved and solidified slowly after *ca.* 15 h.

Analysis.—In addition to analysis by ^{31}P n.m.r. spectrum integration, samples were also analysed by conventional acid-base titration to check the composition terms of mono-, end group-, and middle group-phosphate links.[16] Thin layer chromatography (t.l.c.) was used to check the identity of individual polyphosphates. The most suitable solvent for this purpose was found to be a 5 : 4 : 1 mixture of propan-1-ol–NH_3–H_2O.[17] The best results were obtained with anion exchange t.l.c. using 0.3 mol dm^{-3} LiCl aqueous solution as the solvent.[18] Zones were detected with Hans and Isherwood reagent [19] ($HClO_4$–$NH_4[MoO_4]$–acetone). The R_f values for the principal species are: monophosphate 0.86; diphosphate 0.79; triphosphate 0.62; cyclotriphosphate 0.85; cyclohexaphosphate 0.40; long-chain polyphosphate 0.02—0.06.

Results and Discussion

These investigations show that heating a mixture of an ammonium hydrogen phosphate (P_1) and urea at 120 °C produces first diphosphate (P_2) then triphosphate (P_3) which cyclises to cyclotriphosphate (cP_3). This subsequently condenses to cyclohexaphosphate (cP_6) which is presumed to be the species preferred and formed by equilibration–rearrangement under these reaction conditions.

Phosphorus-31 n.m.r. spectroscopy is the ideal investigative tool for these reactions. The spectrum separates the three types of phosphate in clearly defined regions: monophosphate appears as a singlet at $\delta = 0 \pm 2$, diphosphate appears as a singlet at $\delta = -9 \pm 2$; end group phosphates appear as multiplets in the same region; middle group phosphates appear as multiplets in the region $\delta = -21 \pm 2$ but cyclophosphates appear as sharp singlets in this region.[20] Moreover, while the mono-, di-, and end group-phosphates are sensitive to pH the cyclophosphates are not, and can be directly identified by their chemical shift.[15,21] Thus cP_3 at δ −21.4 and cP_6 at δ −22.8 p.p.m. are readily observed: cP_4 and cP_5 have δ −23.6 and −23.7 but no sharp signals were observed at these resonances. Linear phosphates middle groups which occur in this part of the spectrum have multiplet structure due to POP coupling and corresponding end group phosphates appear at *ca.* δ 9 as doublets.

$NH_4[H_2PO_4]$ *and Urea.*—The composition of the reaction mixture is shown in Table 1. The reaction mixture melted at 115 °C but after 1.5 h solidified, which may explain the irregularities in the composition after this time.

To study the reaction more closely a lower temperature (110 °C) was employed but this resulted in a very slow reaction (Table 1) although this clearly showed the steps through which this reaction proceeds in its early stages, reaction (2). At this temperature there was no evidence of triphosphate formation;

$$P_1 \longrightarrow P_2 \longrightarrow cP_6 \qquad (2)$$

diphosphate appears to be converted to cyclohexaphosphate without detectable amounts of other phosphates (linear or cyclic) being observed. Clearly at this temperature equilibration strongly favours cP_6.

As an alternative method the temperature was returned to 120 °C but the quantity of urea doubled so that the reaction mixture remained liquid over the period of heating. The results (Table 1, Figure 1) show rapid formation of P_2 and its slower conversion to P_3 which in turn forms cP_3 and thence cP_6 which reaches a yield of *ca.* 90%. This reaction clearly establishes the intermediate formation of triphosphates, something which the lower temperature reaction did not show.

$[NH_4]_2[HPO_4]$ *and Urea.*—Table 2 gives the results of three reactions in which $[NH_4]_2[HPO_4]$ was heated with various mol ratios of urea.

When a 1 : 1 mixture of these reactants was left at 90 °C for a week it was found that 10% diphosphate had been formed and a trace of triphosphate was detectable in the spectrum.

When a similar mixture was heated at 120 °C it remained molten for only a short time but heating was continued for 25

Table 2. Reaction of $[NH_4]_2[HPO_4]$ and urea on heating

Temp. (°C)	Ratio reactants $[NH_4]_2[HPO_4]$: urea	t/h	Composition (%) P_1	P_2	P_3	cP_3	cP_6	P_n	Other P
120	1 : 1	5	19	81					
		10	7	91	2				
		11	10	68	16		6		
		12	12	63	14		11		
		13	15	56	12		17		
		14	18	38	15			29	
		15	9	21	10			60	
		20	10	20				70	
		25	15	21				64	
120	1 : 2	1	91	9					Trace [a]
		2	72	28					Trace
		3	45	55					
		4	10	90					
		5		64	16	8	12		
		6		48	16	14	22		
		8		26	4	30	40		
		10		15		33	52		
		15		5		19	76	Trace	
		20				10	90		
		25					96	3	
120	1 : 3	1	92	8					
		2	49	37	5				7 [b]
		3	35	57	6				
		4	3	89	9				
		5	3	88	9				
		10	0	96	2	2			
		15	2	85	13				Trace
		20	6	83	7	1	3		
		25	0	82		4	14		

[a] δ 75.98 and −27.45 p.p.m. (<1% of either). [b] δ −30.4 p.p.m.

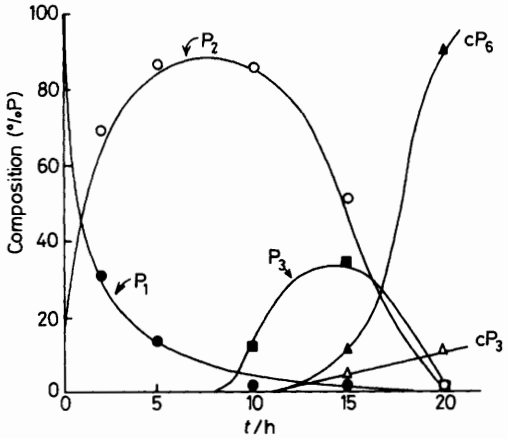


Figure 1. $NH_4[H_2PO_4]$ and urea (1 : 2) at 120 °C: ● = P_1; ○ = P_2; ■ = P_3; △ = cP_3; and ▲ = cP_6

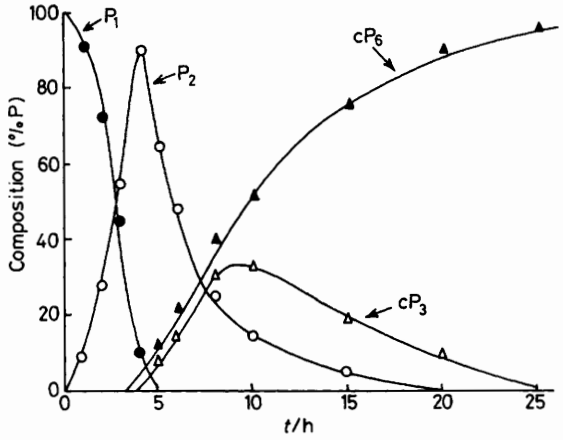


Figure 2. $[NH_4]_2[HPO_4]$ and urea (1 : 2) at 120 °C: ● = P_1; ○ = P_2; △ = cP_3; and ▲ = cP_6

h and the reaction sampled at hourly intervals during the period 10—15 h when P_2 is converted to higher polymers. Table 2 shows that during this period the products are initially P_3 and cP_6 but these form higher polymeric material and the final composition is mainly a high polymer. The numerical values show that during the conversion of P_2 to P_3 the amount of P_1 increases as would be expected for (3).

$$2P_2 \longrightarrow P_3 + P_1 \qquad (3)$$

By doubling the amount of urea compared to $[NH_4]_2[HPO_4]$ the mixture remained liquid over a longer period of time and the results (Table 2, Figure 2) show clearly the same rapid rate of formation of P_2 as observed with $NH_4[H_2PO_4]$ (Figure 1) but it also shows an equally rapid disappearance, being transformed to P_3 which in turn is converted either directly or *via* cP_3 into cP_6. Figure 2 shows this step $cP_3 \longrightarrow cP_6$ clearly between 10 and 25 h whereas the reaction with $NH_4[H_2PO_4]$ did not.

Further diluting the $[NH_4]_2[HPO_4]$ by adding a two-fold

Table 3. Reaction of H_3PO_4 and urea on heating

Temp.(°C)	Ratio reactants H_3PO_4 : urea	t/h	Composition (%) P_1	P_2	P_3	P_n	cP_3	cP_6	Other P
90	1 : 1	5	96	4					
		20	90	10					
		40	76	24					
		100	61	39					
		135	37	63					
105	1 : 1	5	67	33					
		10	54	46					
		15	29	70	1				
		20	24	58	18				
120	1 : 2	2	45	30	20		5		
		4	13	32	44		11		
		5	6	38	46		9		
		10	4	33		54	9		
		15	2	24		60	9	5	
		20	2	25		56	5	11	
		25	8	32		35	5	20	

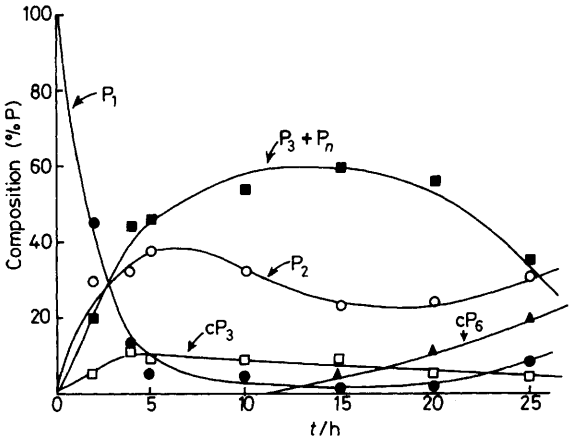


Figure 3. H_3PO_4 and urea (1 : 2; *i.e.* uph and urea) at 120 °C: ● = P_1; ○ = P_2; ■ = P_3 and P_n; □ = cP_3; and ▲ = cP_6

excess of urea slows down the higher polymerization although not the rate of formation of diphosphate (Table 2).

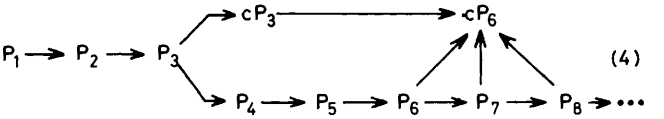
Comparison of Figures 1 and 2 show that there is a small but important difference between these reactions in their intermediate stage but after 20 h they both give high yields of $(NH_4PO_3)_6$ which is presumably the most stable polymer under these conditions. The difference is the rate at which P_2 is consumed in the formation of higher polymers. Why this difference should depend on the concentration of NH_4^+ in the mixture cannot be explained.

H_3PO_4 *and Urea.*—At 90 °C uph is slowly converted to P_2 without melting (Table 3) and at a more rapid rate than $[NH_4]_2[HPO_4]$ and urea. The explanation for this lies with the nature of the two mixtures. Urea phosphate is a chemical adduct where the reactants are held in close proximity by a strong hydrogen bond. Urea and $[NH_4]_2[HPO_4]$ do not form such an adduct and the sample is simply a finely ground mixture of reactants.

At 105 °C uph is converted to P_2 at seven times the rate at which this occurs at 90 °C. There is also some triphosphate formed (Table 3).

Repeating the reaction at 120 °C but with a 1 : 2 ratio of H_3PO_4 : urea *i.e.* a mol ratio of 1 : 1 uph : urea gave the results shown in Table 3 plotted in Figure 3. These show some significant differences from Figures 1 and 2. Firstly the formation of P_2 is not a very large percentage of the total mixture before P_3 appears which rapidly builds up to become the main component after 4 h. After 10 h there is also evidence of other short-chain linear polyphosphates and these continue to accumulate until the appearance of cP_6 after which they decrease; an increase in P_1 and P_2 during this phase suggests that cyclization of cP_6 is from P_7 and P_8 chains which then lose one or two phosphate groups from the end of the cyclizing chain. Some cP_3 is also present in the reaction from near the start but its concentration is low and gradually decreases as presumably it is converted to cP_6.

The mechanism for the pyrolysis of uph + urea is shown by sequence (4).



(4)

The pyrolysis of uph has been shown to result in ammonium polyphosphates and there is a lack of NH_4^+ in the system which may lead to amorphous products. Loss of NH_3 from the system at high temperatures is responsible but even at 120 °C the polymerization favours linear polymers although ultimately these equilibrate to cP_6. Clearly the formation of cyclophosphates is favoured if the phosphate sub-units do not carry acidic protons whereas linear polymerization is favoured if they do. This in turn can be related to the ability of end group phosphate as $-PO_3H_2$ to hydrogen bond to urea, as in (I), a process that favours chain growth rather than cyclization.

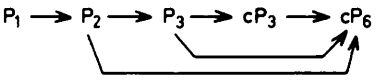
'*Ultraphosphates*'. In some ^{31}P n.m.r. spectra, signals were observed in the upfield region −27 to −30 p.p.m. which is characteristic of the grouping $OP(OPO_3^{2-})_3$.[22] Similar intermediates were observed in the condensation reaction of H_3PO_4 and dicyclohexylcarbodi-imide.[23] Normally, ultraphosphates are rapidly hydrolysed in water and since our samples were dissolved in water for ^{31}P n.m.r. analysis it seems unlikely that they could persist in solution unless particularly favoured by pH or protected as part of another molecule.

Peaks in other spectra at *ca.* 2 p.p.m. seem likely to be esters or P–N compounds and these might be ureido-derivatives containing $POCONH_2$ or $PNHCONH_2$ groupings, which can be envisaged as likely intermediates in these condensation reactions, for example reaction (5).

$$NH_4[H_2PO_4] + (NH_2)_2CO \longrightarrow NH_4[NH_2CO{\cdot}O{\cdot}PO_3H] + NH_3(g) \quad (5)$$

Conclusion

Urea will promote the condensation of phosphate below 100 °C but very slowly. Even at 120 °C the reaction is slow but rapid enough for its course to be plotted by ^{31}P n.m.r. spectroscopy. At 126 °C the reaction becomes too rapid to be followed by such techniques.[11] The condensation of $NH_4[H_2PO_4]$ and $[NH_4]_2[HPO_4]$ at 120 °C can be summed up by sequence (6).



(6)

The condensation of H_3PO_4 as uph produces mainly linear polyphosphates although these also form cyclohexaphosphate as in (4). If these reaction pathways are the same at higher temperatures then the conflicting reports of the type of ammonium polyphosphate obtainable from uph can be understood: short periods of heating would favour linear products,[12] long periods cyclic ones.[9,10]

Acknowledgements

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