Phosphate Condensation and Amination in Dilute Aqueous Solution; Reaction of Sulphamide with Triphosphate and Diphosphate

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Sulphamide promotes a net intramolecular cyclocondensation of triphosphate to trimetaphosphate in dilute aqueous solution at pH 8—10, as well as the formation of amidophosphates from diphosphate and triphosphate; the relatively saturated character of the reactive S–N bond of sulphamide contrasts that of previously examined aqueous-phase phosphate condensing agents.

The phosphoric anhydride linkage (P–O–P) is susceptible to hydrolytic degradation and only a few examples have been reported of non-enzymatic, net phosphate condensation in dilute aqueous solution.[1,2] Other reported examples of phosphate condensation in dilute aqueous solution generally involve rearrangements,[3] controlled hydrolysis of derivatized phosphates such as amidophosphates,[4,5] halophosphates, or phosphate esters,[6] or condensation concurrent with a more prominent phosphate hydrolysis.[7] We now report that sulphamide directly effects a net phosphate condensation in dilute aqueous solution. Sulphamide is unlike previously reported phosphate condensing agents in that the bond order of the reactive S–N moiety is thought to be *ca.* 1.2 (solid state),[8] in contrast to the fully unsaturated C=N or C≡N linkages in carbodiimides, cyanoguanidine, and other more extensively examined condensing agents.[1,2,7] We also report the novel conversion of short-chain condensed phosphates directly to the corresponding amidophosphates.

An aqueous solution of sulphamide (0.21 M) and sodium triphosphate (0.05 M) was heated at 60 °C. The pH was maintained at a constant value of 9.0 (±0.1) by periodic adjustment with conc. NaOH, HCl, or H_2SO_4, and the reaction was monitored for several days by ^{31}P NMR spectroscopy and ion chromatography. In addition to the expected hydrolytic degradation products of triphosphate and sulphamide [equations (1) and (2), respectively], the cyclic trimetaphosphate was also formed [equation (3)]. The yield of equation (3) exceeds that of equation (1), indicating that overall more phosphoric anhydride linkages are formed in the reaction medium than destroyed.† The reaction of sulphamide and triphosphate therefore results in a net formation of P–O–P linkages in the dilute solution and the appearance of trimetaphosphate cannot be considered as arising simply from a phosphate rearrangement. As the pH was maintained constant, an observed increased in sulphamate yield in the presence *vs.* the absence of triphosphate is ascribed to reaction (3) and not to a buffering effect by the phosphate on reaction (2).

$$P_3O_{10}{}^{5-} + H_2O \rightarrow HP_2O_7{}^{3-} + HPO_4{}^{2-} \qquad (1)$$

$$2\,H_2N\text{-}SO_2\text{-}NH_2 \rightarrow NH_4{}^+H_2N\text{-}SO_2\text{-}N\text{-}SO_2\text{-}NH_2{}^- \xrightarrow{+2H_2O} 2\,NH_4{}^+H_2N\text{-}SO_3{}^- \qquad (2)$$

$$P_3O_{10}{}^{5-} + SO_2(NH_2)_2 \xrightarrow{[+2H^+]} P_3O_9{}^{3-} + NH_4{}^+H_2N\text{-}SO_3{}^- \qquad (3)$$

Reaction (3) occurs only between pH 8 and 10. Near pH 10 additional ^{31}P NMR signals are observed which correspond to amidotriphosphate, $H_2N\text{–}P_3O_9{}^{4-}$, and amidodiphosphate,

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† After 48 h: 13% trimetaphosphate, 3% orthophosphate and diphosphate. After 142 h: 18% trimetaphosphate, 12% orthophosphate and diphosphate; orthophosphate : diphosphate molar ratio *ca.* 1:1.

$H_2N\text{-}P_2O_6{}^{3-}$.‡ The latter is formed by the reaction of diphosphate and sulphamide [equation (4)]. Orthophosphate does not react with sulphamide to yield appreciable quantities of new stable phosphorus-containing species, but does catalyse the formation of sulphamate.

$$P_2O_7{}^{4-} + SO_2(NH_2)_2 \rightarrow H_2N\text{-}P_2O_6{}^{3-} + H_2N\text{-}SO_3{}^{-} \qquad (4)$$

The conversion of sulphamide to sulphamate apparently provides much of the thermodynamic driving force for the reaction between sulphamide and the phosphates. Unfortunately, a reliable value for the free energy of hydrolysis for sulphamide does not appear to be available from the literature.

A few comments may be made regarding the mechanism. The narrow pH range over which reactions (3) and (4) occur is indicative of an opposing effect of pH on the concentrations of the reacting species. The acid dissociation constants of sulphamide (pK_1 ~10), and the polyphosphates (diphosphate pK_4 9.6, triphosphate pK_5 9.2)[9] are comparable, indicating the coexistence of more than one species for both the sulphamide and the phosphate at pH 8—10. Nucleophilic attack of the sulphamide anion ($H_2N\text{-}SO_2\text{-}NH^-$) on an incompletely deprotonated phosphate, or, conversely, the attack of phosphate on sulphamide are possible initial steps. Analogous to reaction (4), it may be surmised that amidotriphosphate is the initial product of reaction (3) and that it is subsequently equilibrated with trimetaphosphate.[5]

Work is in progress to establish the generality of phosphate condensation by sulphamide and related compounds. A more detailed understanding of the reaction mechanism is also being sought.

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‡ ^{31}P NMR (ref. to 1.62% H_3PO_4 in D_2O) amidotriphosphate: δ −0.5 (d), −6.1 (d), and −23.1 (t) ppm; amidodiphosphate: δ −1.0 (d) and −6.1 (d) ppm.

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