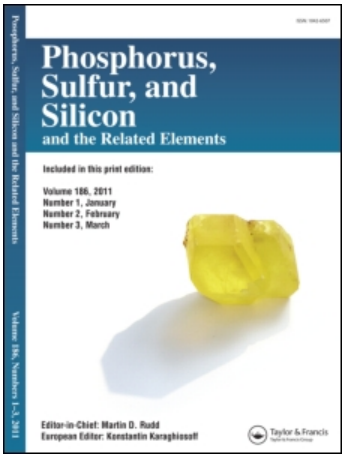

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Non-Enzymatic Phosphate Condensation in Dilute Aqueous Media-the Effect of Alkyl Substituents on Sulfamide

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NON-ENZYMATIC PHOSPHATE CONDENSATION IN DILUTE AQUEOUS MEDIA - THE EFFECT OF ALKYL SUBSTITUENTS ON SULFAMIDE

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Abstract The reactions of alkyl-substituted sulfamides with diphosphate and triphosphate in dilute aqueous solution are examined to determine the reaction requirements with respect to the relative position of amino hydrogens. A nucleophilic attack by the sulfamide anion on the phosphate is postulated, resulting in the cyclocondensation of triphosphate to trimetaphosphate and the formation of amidophosphates. The major reaction pathway leads to the formation of sulfamate.

The triphosphate ion undergoes intramolecular cyclocondensation to trimetaphosphate in mildly alkaline aqueous solutions of sulfamide.[1] This reaction is believed to be the first example of a net, non-enzymatic phosphate condensation in dilute aqueous media. Amidodiphosphate is formed by a similar reaction of sulfamide with diphosphate, thereby effecting direct formation of a P-N bond in aqueous media without sacrificing a P-O-P linkage. Alkyl-substituted sulfamides are examined in this communication to determine the effect of the substitution pattern as a requirement for the reaction with phosphates.

The products observed from the reactions of sulfamides and phosphates are given in TABLE I with pertinent yields listed in TABLE II. The reaction solutions are prepared with approximately 2 wt% each sulfamide and phosphate and are heated at 60°C for 142 hr. Analyses are accomplished by ^{31}P NMR and ion chromatography. The chromatographic detection limits are sufficiently low to determine that no significant quantities of ammonia or substituted sulfamates are formed in the reactions of substituted sulfamides.

Except for sulfamate, yields of the sulfamide and the phosphate degredation products are not appreciably affected by the presence of both reactants. Although not fully characterized, the lack of ammonia generation from the reactions of the substituted sulfamides strongly indicates the general structure of the imidodisulfamide byproducts to be $(R_1)(R_2)NSO_2NSO_2NH_2^-$ (R_1 = alkyl; R_2 = H or alkyl).

TABLE I Reactions Between Substituted Sulfamides and Phosphates.

Reactants		Products
$BuNH\text{-}SO_2\text{-}NH_2$ +	$P_3O_{10}^{5-}$ ⟶	$P_3O_9^{3-}$, $H_2N\text{-}SO_3^-$, $BuNH_2$
$Me_2N\text{-}SO_2\text{-}NH_2$ +	$P_3O_{10}^{5-}$ ⟶	$P_3O_9^{3-}$, $H_2N\text{-}SO_3^-$, Me_2NH
$BuNH\text{-}SO_2\text{-}NH_2$ +	$P_2O_7^{4-}$ ⟶	$BuNH\text{-}P_2O_6^{3-}$, $H_2N\text{-}SO_3^-$, $BuNH_2$
$Me_2N\text{-}SO_2\text{-}NH_2$ +	$P_2O_7^{4-}$ ⟶	$H_2N\text{-}P_2O_6^{3-}$, $H_2N\text{-}SO_3^-$, Me_2NH
$MeNH\text{-}SO_2\text{-}NHMe$ +	$P_3O_{10}^{5-}$ or $P_2O_7^{4-}$ ⟶	No Reaction

The reactivity pattern indicates the need for one unsubstituted amino group on the sulfamide. Yields of phosphorus-containing products are generally lower if the sulfamide is substituted. The substituted sulfamides are estimated to range from 5-10% reacted at pH 8 to ~50% reacted at pH 10 compared to ~50% and ~100%, respectively, for sulfamide. After 142 hr. the bulk of the phosphate remains as the starting material.

The substituted sulfamides do not form significant quantities of amidotriphosphates, a fact probably related to the shift in the trimetaphosphate - amidotriphosphate equilibrium with the pK_a of the corresponding ammonium ion.[2] With sulfamide, the product distribution shifts to

TABLE II Reaction of Sodium Phosphates With Sulfamides at 60°C; Each Reactant at ~2% (Wt/Wt).

		% Yield (Based on Phosphate)		Mole Ratio*	
Sulfamide	pH	Tri-phosphate	Di-phosphate	Tri-phosphate	Di-phosphate
Sulfamide	8	18 P3	6 NP2	5.5	16.6
	10	3 P3;9 NP3; 1 NP2	21 NP2	5.4	3.7
N-Butyl-sulfamide	8	1 P3	-	5.7	-
	10	4 P3	5 BuNP2	6.2	6.7
N,N-Dimethyl-sulfamide	8	1 P3	-	6.1	-
	10	2 P3	4 NP2	9.2	6.3

Legend: P3 trimetaphosphate; NP3 aminotriphosphate; NP2 aminodiphosphate; BuNP2 butylamino-diphosphate

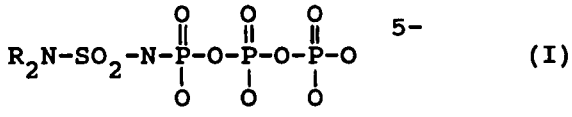
$$\text{Mole Ratio}^{*} = \frac{\text{(sulfamate formed in presence of phosphate - sulfamate formed in absence of phosphate)}}{\text{(trimetaphosphate + amidophosphates)}}$$

the amidotriphosphate as the pH is increased. The yield of amidodiphosphate increases with pH.

The yield of sulfamate is substantially higher in all reactions containing phosphate compared to that for controls without phosphate. The incremental sulfamate yield can be attributed to the reaction of sulfamide with phosphate and is considerably higher than that of the phosphorus-containing products. Either the products revert to the original phosphates under the reaction conditions or more than one reaction pathway is possible, the predominant one generating sulfamate. The relative hydrolytic stability of trimetaphosphate and amidotriphosphate[3,4], the apparent stability of the amidodiphosphates, and the similar product ratios at pH 8 and 10 support the latter case.

The mechanism proposed for the reaction of phosphate and sulfamide involves the nucleophilic attack of the sulfamide anion, $H_2N\text{-}SO_2\text{-}NH^-$, at the terminal phosphorus atom with

elimination of water to form an unstable intermediate or transition state resembling (I) (R = H and/or alkyl) in a process similar to the formation of imidodisulfamide from sulfamide.[5]



(I)

The dissociation of two protons from a single nitrogen in forming (I) accounts for the requirement of one unsubstituted amino group on the sulfamide. Structure (I) would necessarily be unstable to account for the fact it is not directly observed. In comparison, the hydrolysis rates of the structurally similar imidophosphates[6-8] and acyl-N-phosphoryl compounds[9] are such that they would not be observed in significant concentrations if formed under identical reaction conditions.

A sulfamidobisphosphoric acid ester is known to readily hydrolyze to yield the phosphate ester, the amidophosphate ester, and sulfamate.[10] Work is continuing to more definitively elucidate the reaction mechanism.

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