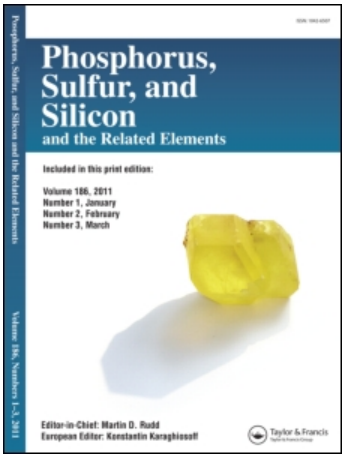

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Thermal Property of Hydrated Sodium Tetra-μ-Imido-Cyclo-Tetraphosphate

Makoto Watanabe[a]; Makoto Sakurai[a]
[a] Chubu University, Kasugai, Japan

To cite this Article Watanabe, Makoto and Sakurai, Makoto(1994) 'Thermal Property of Hydrated Sodium Tetra-μ-Imido-Cyclo-Tetraphosphate', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 369 — 370
To link to this Article: DOI: 10.1080/10426509408021861
URL: http://dx.doi.org/10.1080/10426509408021861

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 369-370
Reprints available directly from the publisher
Photocopying permitted by license only

THERMAL PROPERTY OF HYDRATED SODIUM TETRA-μ-IMIDO-CYCLO-TETRAPHOSPHATE

MAKOTO WATANABE AND MAKOTO SAKURAI
Chubu University, Kasugai, Aichi 487, JAPAN

Abstract Hydrated tetrasodium tetra-μ-imido-cyclo-tetraphosphate has been prepared. The tetraphosphate reorganized to tri-μ-imido-cyclo-triphosphate and then changed to chain and ring condensed phosphates upon heating in air.

INTRODUCTION

Imidopolyphosphates are very interesting compounds, since they can be used as flame retardants, precursors of phosphate glass containing nitrogen, biochemical materials, chemical fertilizers, etc.

PREPARATION

Octachlorocyclotetraphosphazene was made by reacting phosphorus pentachloride with ammonium chloride in 1,2-tetrachloroethane. The phosphazene was reacted with sodium acetate in an aqueous dioxane solution at 45 to 50 °C for 3 h. The product was recrystallized by dissolving in water and then adding sodium chloride in the solution. According to chemical analysis, HPLC method and ^{31}P NMR measurement, the product was concluded as hydrated tetrasodium tetra-μ-imido-cyclo-tetraphosphate, $(NaPO_2NH)_4 \cdot 2.5H_2O$.

THERMAL BEHAVIOR

TG and DTA curves of the product are given in FIGURE 1. The tetra-μ-imido-cyclo-tetraphosphate reorganized to produce anhydrous trisodium tri-μ-imido-cyclo-triphosphate and then changed to give chain and ring condensed phosphates containing imino groups upon heating above 180 °C in air according to the following reactions:

$$(NaPO_2NH)_4 \cdot 2.5H_2O \longrightarrow 4/3(NaPO_2NH)_3 + 2.5H_2O$$

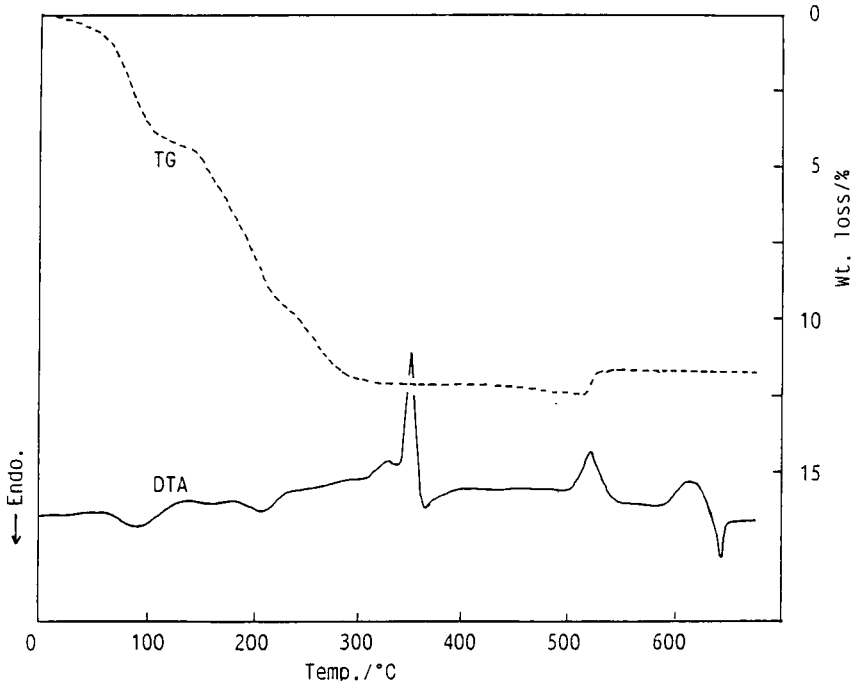

FIGURE 1 TG and DTA curves of $(NaPO_2NH)_4 \cdot 2.5H_2O$.

$$(NaPO_2NH)_3 + H_2O \longrightarrow Na_3P_3O_7(NH)_2$$

$$(NaPO_2NH)_3 + 2H_2O \longrightarrow Na_3P_3O_8NH$$

$$n(NaPO_2NH)_3 + mH_2O \longrightarrow Na_{3n}P_{3n}O_{6n+m}(NH)_{3n-m} + mNH_3$$

All kinds of the imidopolyphosphates were finally converted to sodium cyclo-triphosphate above 550 °C by the substitution of imino groups for bridging oxygens and reorganization of the thermally produced condensed phosphates. The processes may be exhibited by the following equations:

$$Na_3P_3O_8NH + H_2O \longrightarrow (NaPO_3)_3 + NH_3$$

$$Na_3P_3O_7(NH)_2 + 2H_2O \longrightarrow (NaPO_3)_3 + 2NH_3$$

$$Na_{3n}P_{3n}O_{6n+m} + (3n-m)H_2O \longrightarrow n(NaPO_3)_3 + (3n-m)NH_3$$

The overall conversion of the tetra-μ-imido-cyclo-tetraphosphate to sodium cyclo-triphosphate is written by the equation:

$$(NaPO_2NH)_4 + 4H_2O \longrightarrow 4/3(NaPO_3)_3 + 4NH_3$$