

Synthesis, crystal structure and vibrational spectra of the new strong and eco-friendly reducing agent $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_2)_2$

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Abstract

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Introduction

Materials and Methods

Materials

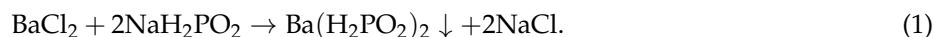
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ($\geq 98\%$, Sigma-Aldrich, Milwaukee, WI, USA); $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ($\geq 99\%$, Sigma-Aldrich, Milwaukee, WI, USA); H_2SO_4 ; $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ (64-65%, $\geq 97\%$, reagent grade Sigma-Aldrich, Milwaukee, WI, USA). All chemicals were used as purchased without further purification.

Synthesis

Hydrazinium bishypophosphite $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_2)_2$ was synthesized in two steps. Firstly a fresh aqueous solution of hypophosphorous acid is prepared from $\text{Ba}(\text{H}_2\text{PO}_2)_2$ and H_2SO_4 . Then the acid is neutralized with hydrazine hydrate.

Preparation of the precursor $\text{Ba}(\text{H}_2\text{PO}_2)_2$

Initially barium hypophosphite $\text{Ba}(\text{H}_2\text{PO}_2)_2$ was synthesized by mixing freshly prepared saturated aqueous solutions of BaCl_2 and NaH_2PO_2 at 90°C . After cooling to $\sim 5^\circ\text{C}$ the reaction mixture was left for 2-3 h. Under these conditions $\text{Ba}(\text{H}_2\text{PO}_2)_2$ precipitates as a white crystalline product with high yield. The obtained white crystals were recrystallized from water, washed with cool water and dried in a desiccator.



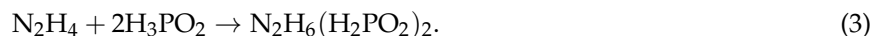
Preparation of H_3PO_2 and $\text{N}_2\text{H}_6(\text{H}_2\text{PO}_2)_2$

Aqueous solution of hypophosphorous acid H_3PO_2 was prepared by dissolving barium hypophosphite $\text{Ba}(\text{H}_2\text{PO}_2)_2$ in cool water and slowly adding stoichiometric amount of H_2SO_4 under constant stirring. A white crystalline product of BaSO_4 precipitated immediately.



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The mixture was cooled down to $\sim 5\text{ }^{\circ}\text{C}$ and left for 48 h to promote the Ostwald ripening of the small BaSO_4 crystals. Then the solution was filtered using a vacuum pump and the filtrate was used for the next step when stoichiometric amount of hydrazine hydrate was added to it under constant stirring.



The obtained hydrazinium hypophosphite salt is highly soluble in water and thus no visible change in the solution appearance was observed. The solution was evaporated slowly under vacuum ($\sim 400\text{ mbar}$) at temperature of $55 \pm 5\text{ }^{\circ}\text{C}$.