

STUDIES ON SODIUM HYPOPHOSPHATES

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The oxidation of red phosphorus into sodium hypophosphate with an aqueous extract of bleaching powder was carried out at 12–15°C. and an increase in the yield by 15% was noticed. However, when the oxidation was undertaken with sodium chlorite solution, having a small proportion of sodium hypochlorite, the yield was found to be higher than that achieved by the previous methods. Infrared spectra and magnetic susceptibility were determined to elucidate the structure of $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$.

Introduction

Red phosphorus can be oxidised to hypophosphate with different catalysts such as copper nitrate solution¹, aqueous extract of bleaching powder^{2,3}, sodium chlorite⁴ and hypochlorite⁵ solutions. None of these methods however give satisfactory yield. It has now been found that the use of aqueous extract of bleaching powder at lower temperatures gives 15% increase in the yield of the hypophosphate. Further improvement has been observed by using a mixture of sodium chlorite and hypochlorite. In the case of the latter the disodium salt $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ was converted into the tetra-sodium salt $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$. The structure of the hypophosphates has been elucidated by studying the infrared spectra and the magnetic susceptibility values of the anhydrous salts.

Experimental

12g. of red phosphorus were taken in a round-bottomed flask which 120 ml. each of water and 3M acetic acid were added at 12–15°C. The aqueous extract of bleaching powder (prepared by dissolving 150 g. of bleaching powder in 500 ml. of water at 10°C. containing 101.53 g./l. of $\text{Ca}(\text{OCl})_2$, was poured slowly in the flask. The reaction was complete in about 75 minutes, which could be tested with the litmus paper (if it was bleached in a few seconds, it showed that the reaction was not yet completed). To the colourless filtrate from this, a 15% solution of sodium hydroxide was slowly added (38–39 ml.) until a persistent turbidity appeared. 45 g. of hydrated sodium acetate were added to get a white precipitate of calcium hypophosphate, $\text{Ca}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$. This was filtered and the precipitate was introduced in a mixture of 80 ml. of each of 3N sulphuric acid and ethyl alcohol. The whole mixture was shaken for a few minutes when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was precipitated. It was filtered and hypophosphoric acid was obtained as filtrate. The precipitate was washed with 15 ml. each of 2 N sulphuric acid and ethyl alcohol.

45 g. of hydrated sodium acetate were dissolved in the filtrate and a crystalline product, Na_2H_2

$\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, was precipitated along with a little of sodium sulphate. All the orthophosphate remained in the solution as NaH_2PO_4 . The product, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, was filtered off and all the orthophosphate was retained in the filtrate. The compound, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$, was dissolved in 120 ml. of hot water at 70–80°C. and the solution cooled to 40°C. To the solution 15 g. of sodium hydroxide was added. The solution was then allowed to cool gradually which resulted in the precipitation of sodium hypophosphate, $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$. This was filtered and washed first with cold dilute sodium hydroxide and finally with ethyl alcohol. The yield was 16.52 g.

In another attempt sodium chlorite (47.23%) containing a small proportion of sodium hypochlorite (9.13%) was used as an oxidant for the preparation of sodium hypophosphate. The apparatus used in this method was of the under-mentioned design.

An outer glass tube called the 'reaction column' was 1" in diameter and 12" in length, and another glass tube 25" long and 1 cm. in diameter was inserted in to it. Cold water was circulated through this inner tube to control the reaction. There was a small side-arm opening towards the lower end of the outer tube which was connected to the flask receiving the reaction mixture. Suction may be applied to the flask to draw the solution conveniently. Porcelain chips were placed at the bottom of the reaction chamber followed by an asbestos layer. Alternate layers of red phosphorus and glass beads were then placed over it.

30 g. of red phosphorus was placed in alternate layers with glass beads in the reaction column 500 ml. of sodium chlorite solution containing (236.15 g. NaClO_2) and 45.65 g. NaOCl was taken in dropping funnel clamped above the reaction column. The sodium chlorite solution was poured slowly at the rate of 30–38 drops per minute. In order to maintain the temperature in the reaction chamber at 18–25°C. cold water was passed through the central tube throughout the course of the reaction. The flask collecting

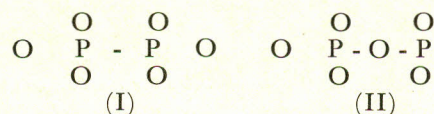
the reaction mixture could be connected to a suction pump to draw the solution and at the same time 5-6 ml. of the solution should be kept above the upper most layer of phosphorus. The sodium chlorite solution must not be drawn too fast, because it results in spattering and evolution of chlorine dioxide. When the whole of the sodium chlorite solution was consumed, the flask was taken out. 12-15 g. of decolorizing carbon were added in the flask containing the reaction mixture and the mixture was allowed to stand overnight. The solution was filtered to remove carbon. To the filtrate 15% sodium hydroxide solution was added to bring the pH from 3 to 5.4. At this stage, the impurities were precipitated as phosphates and on standing disodium dihydrogen hypophosphate $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ started to precipitate. The solution was also boiled later on to complete the precipitation and coagulation of the impurities and to dissolve $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$ as it was soluble in hot water. The solution was again filtered to remove the impurities (mostly phosphates) and a clean solution containing $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ was obtained. The solution was cooled and kept overnight when crystals of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ were formed. These were removed and washed with ice-cold water. The compound was recrystallized with water and the yield was 35-36 g. of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ which could be converted into tetrasodium hypophosphate. The disodium salt was dissolved in 240 ml. of hot water at 70-80°C. and cooled to 40°C. 30 g. of sodium hydroxide was dissolved. On cooling the solution gradually, pure crystals of $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ were obtained. These were filtered and washed first with dilute cold sodium hydroxide and finally with ethyl alcohol. The yield was 40 g. of tetra sodium salt, $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$.

The following studies were adopted in order to show that the compound was $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$.³

- (i) Oxidation of the hypophosphate with iodic acid at 100°C. in the presence of 40% H_2SO_4 .
- (ii) Precipitation as $\text{Ag}_4\text{P}_2\text{O}_6$. Sodium hypophosphate was covered into the corresponding silver hypophosphate in the presence of nitric acid on treatment with silver nitrate solution.
- (iii) Precipitation of zinc hypophosphate followed by conversion into silver hypophosphate. Sodium hypophosphate can be precipitated first into zinc hypophosphate, $\text{Zn}_2\text{P}_2\text{O}_6$, at PH_4 and was further converted into silver hypophosphate.
- (iv) Preparation of ceric hypophosphate. When equal volumes of equimolar solution of sodium hypophosphate and ceric ammonium nitrate were mixed in the presence of dilute nitric acid, a yellow jelly-like precipitate of ceric hypophosphate, $\text{CeP}_2\text{O}_6 \cdot \text{XH}_2\text{O}$, was obtained.
- (v) Oxidation with aqueous bromine (acting as HOBr). The

results obtained in these experiments were close to those in the literature according to which the compound is $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$.

For the determination of the structure of the hypophosphate infrared spectra were studied. The compound, $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$, was rendered anhydrous ($\text{Na}_4\text{P}_2\text{O}_6$) and 'Nujol' was used to mull the salt. Infrared spectra were observed first in NaCl plate and then in KBr plate. The results recorded were found to be the same as those obtained by W.G. Palmer.⁶ Thus these findings supported structure (I) and not (II) for $\text{Na}_4\text{P}_2\text{O}_6$.



The magnetic susceptibility of the compound $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ was determined after rendering it anhydrous at 32°C. and the value in several operations was found to be -0.455×10^{-6} g. suscept., showing the compound as diamagnetic which supports structure (I).

Results and Discussions

Palmer³ employed an aqueous extract of bleaching powder to oxidise red phosphorus for the preparation of sodium hypophosphate. He gave 45 minutes at 15-25°C. for the completion of the reaction, but the yield was on the low side. When the oxidation was done at 12-15°C., the reaction was completed in 75 minutes and the yield was increased by 15% as compared to the former method. During the precipitation of $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ rapid cooling was avoided so as to obviate the co-deposition of sodium sulphate. E. Leininger and T. Ghulaski⁶ used sodium chlorite only for the oxidation of red phosphorus and prepared the disodium salt only, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$. However, when the oxidation with sodium chlorite (47.23%) in the presence of a small proportion of sodium hypochlorite (9.13%) solution was done, a 20% increase in the yield of the product was noticed because the lower oxychloro compounds have proved stronger oxidizing agents. Moreover, the disodium salt $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ has been successfully converted into tetrasodium salt, $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ when the former was reacted with sodium hydroxide after dissolution in hot water. On gradually cooling the solution $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ was precipitated. After treating the red phosphorus with sodium chlorite the solution was filtered and sodium hydroxide was added to bring the pH of the solution from 3 to 5.4 when the disodium salt along with other

phosphates was precipitated. This was dissolved in hot water. The disodium salt remained in solution and insoluble phosphates were removed by filtration. On cooling the filtrate, crystals of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ came down which were dissolved in hot water and reacted with sodium hydroxide to get $\text{Na}_4\text{P}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ on gradual cooling. The presence of the small quantity of sodium hypochlorite affected the increase in the yield by about 20%.

The methods used for the determination of hypophosphate gave results adhering very closely to those available in literature. The infrared spectra of $\text{Na}_4\text{P}_2\text{O}_6$ were taken to elucidate its structure. Palmer showed the resemblance of hypophosphate ion, $\text{P}_2\text{O}_6^{-4}$, to that of dithionate ion, $\text{S}_2\text{O}_6^{-2}$, by taking the infrared and Raman spectra of both the salts. He proved that P-P link in hypophosphate is similar to that of S-S link in dithionates.⁶ The infrared spectra of anhydrous salt $\text{Na}_4\text{P}_2\text{O}_6$ were observed using Nujol to mull the salt, and the NaCl and KBr plates were used to observe the spectra.

The double formula of the hypophosphate was suggested beyond any doubt by Bell and Sugden.⁷ They argued that since H_2PO_3 and its ions contain an odd number of extranuclear electron (hence paramagnetic) while $\text{H}_4\text{P}_2\text{O}_6$ and its ions do

not. Thus the hypophosphates should be paramagnetic, provided they exhibit the simple structure. But it has been found experimentally that $\text{Na}_4\text{P}_2\text{O}_6$ and a number of other hypophosphates are diamagnetic which proved that the hypophosphates are derivatives of the polymer of a simple empirical formula i.e. H_2PO_3 . The experimental value for the magnetic susceptibility of $\text{Na}_4\text{P}_2\text{O}_6$ was -0.455×10^{-6} g. suscept. (diamagnetic), which proves the dimeric structure (T) for the hypophosphate.

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