# The Oxidation of Red Phosphorus with Hydrogen Peroxide and the Isolation of Disodium Dihydrogen Hypophosphate

By Norimasa YOZA and Shigeru OHASHI

(Received January 16, 1965)

Hypophosphate has been prepared by the wet oxidation of elementary phosphorus with various oxidizing agents, i. e., hypochlorite,[1] chlorite,[2-5] bleaching powder,[6] copper nitrate,[7,8] permanganate,[9] iodine,[10] and hydrogen peroxide.[9,11]

Remy and Falius[4] pointed out that hypophosphate prepared by Vogel's method,[9] i. e., by oxidizing red phosphorus with hydrogen peroxide in a solution of sodium hydroxide, contained several oxo acids of phosphorus as impurities and that the further purification of it was very difficult. On the other hand, Dragulescu et al.[11] reported a method for the preparation of hypophosphate by the oxidation of red phosphorus with hydrogen peroxide in aqueous ammonia. In this case ammonium ions must be removed by passing the reaction products through ion exchange resin in order to isolate sodium hypophosphate.

The present work was undertaken in order to examine the oxidation products of red phosphorus with hydrogen peroxide in a solution of sodium carbonate or in a solution free from other electrolytes, and to isolate disodium dihydrogen hypophosphate by crystallization from a mixture of ethyl alcohol and water.

## Experimental

**The Preparation of Disodium Dihydrogen Hypophosphate.** — Ten grams of red phosphorus is suspended in 200 ml. of water (in a 1 l.-beaker), and then 30 ml. of a solution of hydrogen peroxide is added. After an hour 120 ml. more of the solution of hydrogen peroxide is added. (If 150 ml. of hydrogen peroxide is added at one time, a drastic reaction will occur.) The mixture is allowed to stand for 3 days at room temperature, after which

---

[1] J. Probst, *Z. anorg. u. allgem. Chem.*, **179**, 155 (1929).
[2] E. Leininger and T. Chuluski, *J. Am. Chem. Soc.*, **71**, 2385 (1949).
[3] H. Remy and H. Falius, *Naturwissenschaften*, **43**, 177 (1956).
[4] H. Remy and H. Falius, *Z. anorg. u. allgem. Chem.*, **306**, 211 (1960).
[5] J. A. R. Genge, B. A. Nevette and J. E. Salmon, *Chem. & Ind.*, **1960**, 1079.
[6] W. G. Palmer, *J. Chem. Soc.*, **1961**, 1079.
[7] W. Jung, *Anales asoc. quim. argentina*, **30**, 99 (1942).
[8] A. Rosenheim and J. Pinsker, *Ber.*, **43**, 2003 (1910).
[9] F. Vogel, *Z. angew. Chem.*, **42**, 263 (1929).
[10] T. Milobedzki, J. H. Kolitowska and J. Berkan, *Roczniki Chem.*, **17**, 620 (1937).
[11] C. Dragulescu, M. Enache, and T. Simonescu, *Acad. Rep. Populare Romine, Baza Cercetari Stiint. Timisoara, Studdi Cercetari, Stinnte Chim.*, **10**, 23 (1963) ; *Chem. Abstr.*, **61**, 331 (1964).

time the small, unreacted portion of red phosphorus is filtered off with Toyo No. 5B filter paper. After the pH of the filtrate is adjusted to 4.5 with a solution of sodium hydroxide, a half volume of ethyl alcohol is added. The precipitate, almost free from other oxo acids of phosphorus, is recrystallized by the same procedure and dissolved in 400 ml. of water. (It may be warmed to accelerate the dissolution of the precipitate.) The solution is adjusted to pH 5.2 and filtered off, if necessary, to remove such insoluble hypophosphates as alkaline earth hypophosphates. Finally, disodium dihydrogen hypophosphate hexahydrate, $Na_2H_2P_2O_6 \cdot 6H_2O$, is recrystallized from 1 : 2 ethyl alcohol. The crystals are filtered off, washed with 1 : 2 ethyl alcohol, and air dried. The yield is about 23% on the basis of the weight of the red phosphorus used.

Large crystals are obtained by dissolving the salt in hot water (60°C) with subsequent cooling in a refrigerator overnight.

The chemical composition of the final product was confirmed to be $Na_2H_2P_2O_6 \cdot 6H_2O$ by the following methods: I) the qualitative identification by paper chromatography[12] and spectrophotometry (hypophosphoric heteropoly blue[13]); II) the release of hydrated water at 110°C; III) the determination of the hydrogen ions released by precipitation reaction with silver nitrate ($Ag_4P_2O_6$) and IV) the determination of the total phosphorus by gravimetry as $Mg_2P_2O_7$.

## Discussion

The known method of preparing hypophosphate from red phosphorus and hydrogen peroxide in a solution of sodium hydroxide is complicated because of the necessity of suppressing the rise in temperature due to the heat of the reaction. The present work was undertaken to overcome this disadvantage. The new method for the preparation of hypophosphate described in the Experimental section does not need any special cooling apparatus. As will be mentioned below, the reaction of red phosphorus with hydrogen peroxide in a solution of sodium carbonate has some disadvantages, i. e., the violent evolution of heat and the difficulty of the complete removal of by-products.

**The Reaction in a Solution of Sodium Carbonate.**—Hydrogen peroxide reacts with red phosphorus in a solution of sodium carbonate with the evolution of the heat of the reaction. The products obtained by the oxidation of 10 g. of red phosphorus with 150 ml. of 30% hydrogen peroxide in a solution of sodium carbonate (10 g. of $Na_2CO_3$ in 200 ml. of water) include at least six oxo acids of phosphrus. The $R_f$ values of the species on paper chromatogram correspond to phosphite, phosphate, diphoshate, hypophosphate, $\overset{5}{P}$-O-$\overset{4}{P}$-$\overset{4}{P}$-, and $\overset{4}{P}$-$\overset{3}{P}$-$\overset{4}{P}$-anions in the order of decreasing $R_f$. Some of them can be removed from hypophosphate by crystallization from 1 : 2 ethyl alcohol at pH 4.5. However, this procedure is not satisfactory in eliminating the phosphorus compounds with lower $R_f$ values than that of hypophosphate.

**The Reaction in a Neutral or Acid Solution.**—As has been described in the Experimental section, red phosporus is also oxidized with hydrogen peroxide in the absence of other electrolytes to form hypophosphate. The solution is neutral at the start of the reaction, while the acidity of the solution increases with the formation of oxo acids of phosphorus. The hypophosphate thus produced contains two components as impurities, i. e., phosphite and phosphate, which are easily removed from the hypophosphate by treatment with 1 : 2 ethyl alcohol at pH 4.5. The reaction under the conditions described in the Experimental section proceeds so slowly that it is not necessary to cool the reaction vessel.

*Department of Chemistry*
*Faculty of Science*
*Kyushu University*
*Hakozaki, Fukuoka*

---

[12] E. Thilo and D. Heinz, *Z. anorg. u. allgem. Chem.*, **281**, 303 (1955).

[13] N. Yoza and S. Ohashi, This Bulletin, 37, 33 (1964).