

value 93. A sample prepared by the method of Kosolapoff⁴ melted at 136.5–138° and did not depress the melting point of the compound prepared from ethylbenzene.

Diphenylmethanephosphonic Acid.—An approximately 2% yield of this acid was obtained by the usual procedure from diphenylmethane. It melted at 234–237° and titration indicated an equivalent weight of 123 compared with the calculated value of 124.

Anal. Calcd. for $C_{18}H_{18}O_3P$: P, 12.48. Found: P, 12.2, 12.55.

When triphenylmethane was treated in the same way, it was recovered unchanged and no phosphonic acid could be isolated.

Neopentane phosphonic Acid and Neopentane diphosphonic Acid.—The reaction of neopentane⁶ was carried out at 0° and gave rise to a 22% yield of the monophosphonic acid. After crystallization from carbon tetrachloride it melted at 140–141.5°. Titration gave an equivalent weight of 79 compared with the calculated value of 76.

Anal. Calcd. for $C_5H_{10}O_3P$: P, 20.37. Found: P, 20.27, 20.46.

The aqueous filtrate remaining after removal of the monophosphonic acid was evaporated to dryness. The residue was an oil which slowly solidified. No suitable solvent was found for crystallization, but successive ex-

(6) A sample of neopentane of 99% purity was supplied by the California Research Corporation.

tractions at the boiling point of the solvent with ether, benzene, and acetone, followed by solution in dioxane and precipitation with ether gave a white product that melted at 160–167°. It behaved like cyclohexanediphosphonic acid on potentiometric titration, and the observed equivalent weight was 61. The calculated value is 58.

Anal. Calcd. for $C_6H_{14}O_6P_2$: P, 26.69. Found: P, 26.92, 26.86.

Summary

In the reaction of cyclohexane and neopentane with phosphorus trichloride and oxygen, diphosphonyl chlorides are formed in addition to the monosubstitution products. When mixed aromatic aliphatic hydrocarbons react, substitution in the aliphatic side chain takes place. The ease of substitution on the methane carbon atom as determined by the yield of monophosphonic acid decreases with increasing number of aryl groups. In the case of ethylbenzene substitution takes place on the β -carbon atom of the side-chain. With larger alkyl side chains mixtures appear to be formed.

STANFORD, CALIF.

RECEIVED FEBRUARY 15, 1949

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

A New Method for the Preparation of Disodium Dihydrogen Hypophosphate

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Hypophosphates offer the possibility of a number of analytical applications particularly to the separation and determination of some of the quadrivalent elements including thorium, since their hypophosphates are very insoluble in acid solution.

These applications would be greatly facilitated if good methods for the preparation and determination of hypophosphates were available. While investigating these possibilities it was noted that red phosphorus reacts vigorously with a solution of sodium chlorite. The only reference to this reaction found in the literature was the statement that a solution of chlorous acid instantly dissolves red phosphorus.² However, the products formed were not mentioned. Therefore the solution resulting from the reaction of red phosphorus with a sodium chlorite solution was tested and found to contain hypophosphorous, phosphorous, hypophosphoric and orthophosphoric acids. A relatively high yield of hypophosphoric acid was apparent upon neutralization with sodium hydroxide by the precipitation of crystalline disodium dihydrogen hypophosphate hexahydrate. On the basis of this reaction, a new method for the preparation of this salt has been developed. Volumetric methods for the determination of hypophosphate will be presented in another paper.

(1) Present address: Lindsay Light and Chemical Company, West Chicago, Ill.

(2) Schiel, *Ann.*, **109**, 317 (1859).

Most of the methods found in the literature for the formation of hypophosphates depend upon the oxidation of yellow or red phosphorus. In these reactions some of the phosphorus is oxidized to each of the higher oxidation states and the yield of hypophosphate is low.

Yellow phosphorus may be oxidized by air³ or by cupric nitrate.^{4,5} The air oxidation is slow and the cupric nitrate method involves the evolution of large quantities of phosphine.

Red phosphorus may be oxidized by hypochlorites,^{6,7} alkaline permanganate,⁸ hydrogen peroxide⁸ or iodine.⁹ The use of red phosphorus is more desirable; however none of these reactions has been adapted to the preparation of hypophosphate in quantity.

The phosphorus trihalides, upon hydrolysis and treatment with iodine, yield some hypophosphate.⁹ A method involving the electrolytic oxidation of a metallic phosphide to hypophosphate has been reported.⁵

Experimental

Apparatus and Materials.—Since the reaction between red phosphorus and sodium chlorite may become very

(3) Van Name and Huff, *Am. J. Sci.*, **46**, 587 (1918).

(4) Jung, *Asoc. quim. Argentina*, **30**, 99 (1942).

(5) Rosenheim and Pinsker, *Z. anorg. Chem.*, **64**, 327 (1909).

(6) Probst, *Z. anorg. u. allgem. Chem.*, **179**, 155 (1929).

(7) Speter, *Rec. trav. chim.*, **46**, 588 (1927).

(8) Vogel, *Z. angew. Chem.*, **42**, 263 (1929).

(9) Kollitowska, *Roczniki Chem.*, **16**, 313 (1936); **17**, 616 (1937); *Z. anorg. u. allgem. Chem.*, **230**, 310 (1937).

vigorous, it must be controlled properly. This may be done conveniently in the reaction vessel (A) shown in Fig. 1. It may be prepared from the water jacket of a Liebig condenser by cutting a 15-cm. length from one end, thus including one tubulature. The end of the section is closed with a one-hole rubber stopper through which a 30-cm. length of glass tubing (1 cm. inside diameter) is inserted. Cold water is circulated through this central tube in order to control the reaction.

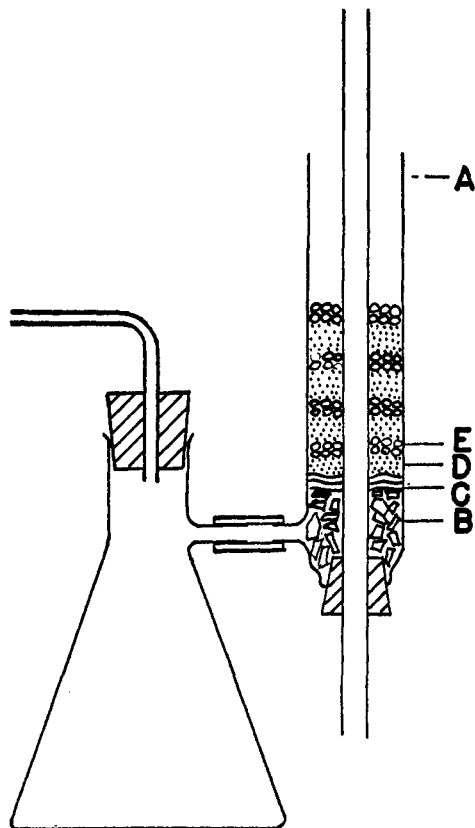


Fig. 1.—Apparatus for preparation of hypophosphates: A, reaction vessel; B, porcelain chips; C, asbestos; D, red phosphorus; E, glass beads.

The red phosphorus was the usual powdered form. The sodium chlorite used was a technical grade obtained from the Mathieson Alkali Works. It was analyzed for its chlorite content by the iodometric method of Jackson and Parsons¹⁰ and found to contain 83.05% sodium chlorite. A purified grade containing 98% sodium chlorite was also tried but it offered no advantage since considerable amounts of impurities were derived from the phosphorus. Furthermore the cost of the purified grade was approximately ten times greater than the cost of the technical grade.

Procedure.—Porcelain chips are placed in the outer chamber of the reaction vessel in sufficient quantity to cover the side-arm opening. A layer of asbestos several cm. in depth is packed into the tube to cover completely the porcelain chips. Alternate layers of red phosphorus and glass beads are placed above the asbestos, using a total weight of approximately 30 g. of phosphorus.

A solution of 54 g. of the technical sodium chlorite in 450 ml. of water is placed in a dropping funnel clamped above the reaction chamber with the tip of the stem just inside the top of the reaction chamber. Cold water is passed through the central tube throughout the course of

the reaction. The chlorite solution is allowed to drop into the chamber containing the phosphorus at a rate of 20 to 35 drops (1 to 2 ml.) per minute. The filter flask, Fig. 1, is connected to a water pump and sufficient suction applied to draw the solution through the column and at the same time keep 5 to 10 ml. of solution above the phosphorus. If the solution is drawn through the phosphorus too fast the heat of reaction is not dissipated, resulting in boiling and spattering and the evolution of chlorine dioxide. After initial adjustment, only occasional attention is required. Four to seven hours are required for the addition of the chlorite solution.

Ten to twelve grams of decolorizing carbon (Norit) is added to the solution of the acids of phosphorus in the filter flask and the mixture allowed to stand overnight. The Norit may be placed in the filter flask before the reaction is carried out, if preferred.

After removing the carbon by filtration, a 15% solution of sodium hydroxide is added to bring the solution to a pH of 5.4 as measured with the glass electrode. At this point many of the cation impurities precipitate as phosphates and, upon standing, disodium dihydrogen hypophosphate starts to deposit. The solution is heated to boiling to complete the precipitation and coagulation of the impurities and to dissolve the disodium dihydrogen hypophosphate. After filtering, the clear solution is allowed to cool and is then placed in the refrigerator overnight. The crystals are filtered, washed several times with ice-cold water and finally air-dried. The disodium dihydrogen hypophosphate hexahydrate obtained in this manner may be recrystallized from water with very small loss. Van Name and Huff¹¹ have shown that recrystallization is necessary to free the compound from small amounts of phosphite.

Some of the compound was purified by recrystallizing it twice from water and finally drying in the air very carefully. This preparation was analyzed for phosphorus by the usual magnesium pyrophosphate method after oxidation to orthophosphate by repeated evaporation on the steam-bath with aqua regia. The water of crystallization was determined by loss in weight at 110°.¹²

Anal. Calcd. for $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$: P, 19.73; H_2O , 34.42. Found: P, 19.60, 19.53; H_2O , 34.36, 34.32.

A yield of 31 to 34 g. of $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ was obtained. This procedure has been repeated many times and by a number of different operators; in each case the yield has fallen within these limits. On the basis of the weight of pure sodium chlorite involved, the yield is 40 to 43%.

The above procedure has never failed to give colorless crystals. However, certain modifications appear to be applicable with some lots of reagents. For example, a preliminary digestion of the phosphorus with hydrochloric acid removes some impurities and may lead to a pure product without the use of the decolorizing carbon. However, two or three recrystallizations may then be necessary.

If the solution is too acid at the time of crystallization, some sodium trihydrogen hypophosphate forms; if neutral or alkaline, the product may contain trisodium hydrogen hypophosphate or even some of the tetrasodium salt. Small amounts of these salts may be eliminated by recrystallization from water.

To prepare a larger quantity of product, more chlorite solution may be passed through the phosphorus remaining in the reaction chamber or more phosphorus and glass beads may be packed in at any time after drawing off the liquid above the phosphorus.

Analysis of Reaction Solution.—After a typical run, some of the solution containing the reaction products was removed before treatment with Norit and analyzed immediately for the various acids of phosphorus.

The hypophosphite and phosphite were determined iodimetrically by the Wolf and Jung¹³ method.

Samples for the determination of hypophosphite¹⁴ were

(11) Van Name and Huff, *Am. J. Sci.*, **45**, 100 (1918).

(12) Salzer, *Ann.*, **187**, 322 (1877).

(13) Wolf and Jung, *Z. anorg. u. allgem. Chem.*, **201**, 337 (1931).

(14) Wolf and Jung, *ibid.*, **201**, 347 (1931).

(10) Jackson and Parsons, *Ind. Eng. Chem., Anal. Ed.*, **9**, 14 (1937).

diluted and adjusted to a pH of 1 to 2 as measured by the glass electrode with the addition of orthophosphoric acid. Silver hypophosphate and silver chloride were precipitated by the addition of an excess of silver nitrate at room temperature and separated by filtration and washing as quickly as possible to prevent the interference of phosphite. The silver hypophosphate was leached out with dilute nitric acid and the hypophosphate oxidized to orthophosphate by repeated evaporation with aqua regia on a steam-bath. The silver ion remaining in solution was removed as silver chloride by the addition of hydrochloric acid. The phosphate was finally precipitated as magnesium ammonium phosphate and ignited to magnesium pyrophosphate.

Orthophosphate was determined essentially by the method of Jones¹⁵ except that the ammonium molybdi-phosphate was weighed rather than titrated.

The total phosphorus was determined by repeated oxidation with aqua regia, precipitation of magnesium ammonium phosphate and ignition to magnesium pyrophosphate.

A summary of the analyses is given below, each value being the average of two or more closely agreeing results.

Phosphorus as orthophosphate	0.0054 g. P per ml.
Phosphorus as hypophosphate	.0122 g. P per ml.
Phosphorus as phosphite	.0102 g. P per ml.
Phosphorus as hypophosphite	.0007 g. P per ml.
Total	0.0285 g. P per ml.

(15) Jones, *Ind. Eng. Chem., Anal. Ed.*, **14**, 538 (1942).

The total phosphorus found by oxidation to orthophosphate was 0.0289 g. of phosphorus per ml. which seems to indicate that little, if any, pyrophosphate or metaphosphates are present.

The above results correspond to the following yields of the various products; 19% orthophosphate, 35% phosphite, 2% hypophosphite and 42% hypophosphate.

Summary

A method is presented for the preparation of disodium dihydrogen hypophosphate hexahydrate based upon the oxidation of red phosphorus by sodium chlorite, NaClO₂. The method possesses marked advantages over previously published methods. The substances used are cheap and readily available, the method is simple and comparatively rapid, and the yield is good.

It has been shown that the oxidation of red phosphorus by sodium chlorite results in the formation of orthophosphate, phosphite and a small amount of hypophosphite in addition to the hypophosphate.

EAST LANSING, MICHIGAN RECEIVED JANUARY 5, 1949

CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE DIVISION OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Electrical Conductivity of Orthophosphoric Acid and of Sodium and Potassium Dihydrogen Phosphates at 25°

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Two recent papers^{2,3} on the thermodynamic properties of orthophosphoric acid and its salts involved calculation of the extent of ionization of that acid on the basis of conductivity data from the literature. Since the range of concentration covered by those data was not adequate as a basis for extensive thermodynamic calculations, the conductivity of orthophosphoric acid and of potassium and sodium dihydrogen phosphates has been studied more extensively. The study covered the concentration range from 0.001 molar to 100% for the acid and up to saturation for the salts.

The limiting equivalent conductance of the dihydrogen phosphate ion, as determined from the conductance of the salts, was surprisingly low and, therefore, was checked by an alternative experimental method. Measurements of e. m. f. were made with suitable concentration cells by means of the lead-lead phosphate electrode, both with and without transference. Although the results by the two techniques were not in as good agreement as might be desirable, the abnormally

low limiting conductance of the dihydrogen phosphate ion was substantiated.

Measurements

Apparatus.—For the conductance measurements, the calibrated bridge was of the Jones and Josephs⁴ type as developed by Dike⁵ and supplied by Leeds and Northrup as type 4666.

The oscillator and amplifier were standard instruments, supplied by the General Radio Company as types 913B and 1231-A. A 4-inch oscillograph served as a null-point indicator, as suggested by Lamson,⁶ and the circuit was that proposed by Jones, Mysels and Juda.⁷

Conductivity cells of the type designed by Jones and Bollinger⁸ were standardized with potassium chloride solutions, using the specific conductance values and the directions given by Jones and Bradshaw.⁹ The cells were platinized according to the directions of Jones and Bollinger¹⁰ and the absence of a significant change of resist-

(4) G. Jones and R. C. Josephs, *ibid.*, **50**, 1049-1092 (1928).

(5) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379-395 (1931).

(6) H. W. Lamson, *ibid.*, **9**, 272-275 (1938).

(7) G. Jones, K. J. Mysels and W. Juda, *THIS JOURNAL*, **62**, 2919-2922 (1940).

(8) G. Jones and G. M. Bollinger, *ibid.*, **53**, 411-451 (1931).

(9) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780-1800 (1933).

(10) G. Jones and D. M. Bollinger, *ibid.*, **57**, 280-284 (1935).

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(2) K. L. Elmore, C. M. Mason and J. H. Christensen, *THIS JOURNAL*, **68**, 2528-2532 (1946).

(3) C. M. Mason and W. M. Blum, *ibid.*, **69**, 1246-1250 (1947).