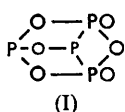## 217. *The Preparation and Methods of Determination of Hypophosphate.*

By W. G. PALMER.

Details are given of an expeditious method of preparing sodium hypophosphate decahydrate from red phosphorus and bleaching powder. Several novel methods for the analytical determination of hypophosphate are described and exemplified: the restriction of its oxidation by aqueous bromine to a narrow range of pH is explained. Evidence is given that the crude product of the oxidation contains the calcium salt of a previously unrecognized dibasic acid of probable formula $H_2P_4O_7$.

ALL known means of obtaining hypophosphates depend on the wet oxidation of elementary phosphorus. Hypochlorites and chlorites [1] afford comparable yields, but with these reagents, as with others, at least 50% of the total phosphorus is converted into orthophosphate. Use of the readily accessible hypochlorite, bleaching powder, to gain maximum yield has not been reported, but a satisfactory procedure is now described. In view of the macromolecular constitution of red phosphorus it seems improbable that the products of its controlled oxidation would be limited to those containing in their molecules two atoms at most of phosphorus. Analysis of the calcium salts obtained as the immediate result of oxidation revealed the probable existence of at least one previously unknown acid, of apparent formula $H_2P_4O_7$, but no means of separation or of increasing its proportion were found. The anhydride of this acid is presumably an isomer of phosphorous anhydride, and might tentatively be assigned the structure (I).

(I)

During the preparation of a series of hypophosphates the hitherto unrecorded ceric salt, CeP_2O_6, was obtained as a yellow hydrated gel; it is probably even more resistant to attack by acids than is thorium hypophosphate.[2]

Determination of Hypophosphate.—There has been a serious lack of reliable methods, adaptable to differing conditions, for the determination of hypophosphate in the presence of other phosphorus oxy-anions. The following have now been tested and proved serviceable: (1) Oxidation by iodic acid at 100° in the presence of 40% sulphuric acid (hypophosphate is stable to iodic acid under the conditions of Andrews's method of titration). (2) Precipitation as $Ag_4P_2O_6$ from a medium that may contain up to 0·5M-nitric acid. (3) Precipitation as $Zn_2P_2O_6$ at pH 4, followed by conversion of this precipitate into $Ag_4P_2O_6$. (4) Oxidation by aqueous bromine in the pH range 6—9 (maximum rate of oxidation at pH 7·7).

Methods (1) and (2) are simple and expeditious but not available in the presence of other reducing oxy-anions of phosphorus. Such oxy-anions may, however, readily be separated by methods (3) and (4). Method (2), in 0·5M-nitric acid, separates hypophosphate completely from ortho-, di-, and tri-phosphate, and from trimetaphosphate: tetra- and poly-metaphosphate interfere. Since hypophosphite and phosphite are oxidized by molecular bromine in freely acid solution,[3] whereas hypophosphoric acid is oxidized only in the range pH 6—9, method (4) offers a means of distinguishing the latter acid.

The interaction of hypophosphate with bromine in aqueous solution merits attention for further reasons. Salzer noticed that, although aqueous bromine had no action upon hypophosphoric acid, yet it readily oxidized the tetrasodium salt.[4] Blaser and Halpern correlated rate of oxidation at 20° with the pH of the solution.[5] Their results, presented as percentage of hypophosphate oxidized in a fixed time by 0·1N-aqueous bromine, are plotted

[1] Leininger and Cholski, *J. Amer. Chem. Soc.*, 1949, **71**, 2385; *Inorg. Synth.*, 1953, **4**, 68.
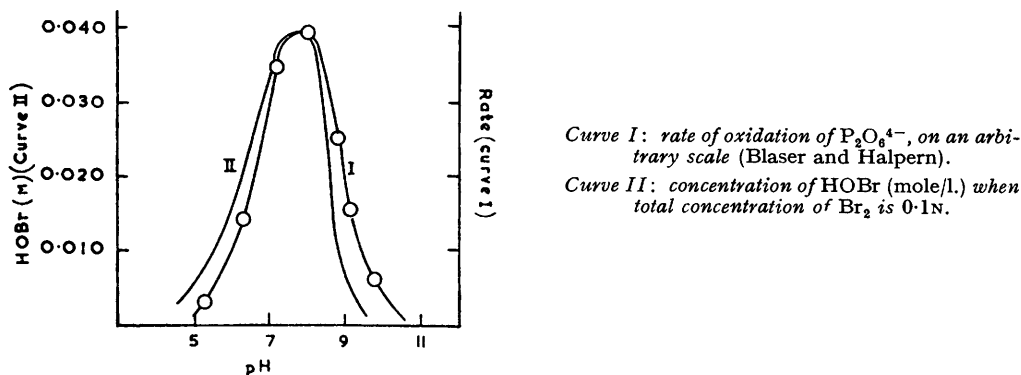[2] Moeller and Quinty, *J. Amer. Chem. Soc.*, 1952, **74**, 6123.
[3] Griffith and McKeown, *Trans. Faraday Soc.*, 1933, **29**, 611; 1934, **30**, 530.
[4] Salzer, *Annalen*, 1886, **232**, 114.
[5] Blaser and Halpern, *Z. anorg. Chem.*, 1933, **215**, 33.

in curve I in the Figure. With the assumptions that at 20° the hydrolysis constant of bromine [6] is $4 \cdot 2 \times 10^{-9}$, the acid dissociation constant of hypobromous acid [7] is $2 \cdot 1 \times 10^{-9}$, and that the concentration of tribromide ion is negligible, the concentration of hypobromous acid in the range of pH studied by Blaser and Halpern has been calculated and plotted as curve II. The identity of the sharp maxima at pH 7·7 and the coincidence in form of the curves leave little doubt that hypobromous acid is the effective oxidant. The product of concentrations [HOBr][BrO⁻], which would be significant for oxidation by bromous acid, has a maximum at pH 8·5 and values appreciably different from zero only in the narrow pH range 7—9. The oxidation of hypophosphate by bromine is thus analogous to the interaction of oxalate with bromine.[8]

Curve I: *rate of oxidation of* $P_2O_6^{4-}$, *on an arbitrary scale* (Blaser and Halpern).

Curve II: *concentration of* HOBr (mole/l.) *when total concentration of* Br_2 *is* 0·1N.

Blaser and Halpern were led to believe that the product of the oxidation is largely, if not exclusively, diphosphate. By a rather more stringent analytical procedure their results have been fully confirmed. $P_2O_6^{4-}$, oxidized by aqueous bromine in the presence of excess of sodium hydrogen carbonate, is converted to the extent of at least 97% into $P_2O_7^{4-}$. This observation need not necessarily imply that $P_2O_6^{4-}$ contains an oxygen bridge between the phosphorus atoms. The hypophosphate species is mainly $HP_2O_6^{3-}$ in the range of pH concerned,[9] and the first reaction is $HP_2O_6^{3-} + HOBr = 2PO_3^- + Br^- + H_2O$; but, the monomeric ion PO_3^- being unstable, this action is followed, before the ions escape from contiguity, by the hydration $2PO_3^- + H_2O = H_2P_2O_7^{2-}$. As it is now known that polythionate ions contain simple chains of sulphur atoms,[10] a similar situation must be assumed to arise when sulphur atoms are removed from these ions by cyanide or sulphite, with the quantitative formation of trithionate (see also following paper).

EXPERIMENTAL

Preparation of Tetrasodium Hypophosphate, $Na_4P_2O_6,10H_2O$.—By means of an adjustable siphon the filtered extract from 100 g. of bleaching powder by 425 ml. of water, cooled to 10°, is run into a stirred mixture of 10 g. of red phosphorus (free from phosphoric acid) with 100 ml. each of water and 3M-acetic acid, cooled in a bath of ice and water. During the oxidation (normally completed in 30 min.) the temperature of the mixture should be 15—25°. The oxidation is very rapid: if addition of hypochlorite is interrupted the liquid ceases to bleach litmus within a few seconds. Test experiments with pure hypophosphate show that it suffers no oxidation under the conditions described.

To the colourless, well-stirred filtrate from excess of phosphorus (5 g.), 20% aqueous sodium hydroxide is slowly added until a permanent turbidity results (24—25 ml.). Addition of 40 g. of hydrated sodium acetate produces a copious white precipitate, which is filtered off. By this means about 85% of the orthophosphate produced in the oxidation remains in the filtrate and all the hypophosphate is recovered in the precipitate as $Ca_2P_2O_6,2H_2O$. The moist cake of solid

[6] Liebhafsky, *J. Amer. Chem. Soc.*, 1934, **56**, 1500.
[7] Kelley and Tartar, *J. Amer. Chem. Soc.*, 1956, **78**, 5752.
[8] Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, 1932, **28**, 107.
[9] Schwarzenbach and Zure, *Monatsh.*, 1950, **81**, 202.
[10] Foss, Furberg, and Zachariasen, *Acta Chem. Scand.*, 1954, **8**, 459, 473.

is introduced in portions into a mixture of 60 ml. each of 4N-sulphuric acid and ethanol, and the whole shaken until in about 15 min. all compact white masses have given place to a uniform crystalline deposit of $CaSO_4,2H_2O$; this is filtered off, and washed with a mixture of 2N-sulphuric acid and ethanol (10 ml. of each), the washings being added to the main filtrate. In the latter 40 g. of hydrated sodium acetate are forthwith dissolved, to produce a crystalline deposit, consisting of $Na_2H_2P_2O_6,6H_2O$ and some hydrated sodium sulphate, all orthophosphate surviving from the earlier stage being retained in the solution as NaH_2PO_4.

In a solution of the solid in 80—90 ml. of hot water, filtered if necessary, and cooled to 40°, 10 g. of sodium hydroxide are dissolved. The salt $Na_4P_2O_6,10H_2O$ crystallizes almost quantitatively during some hours. (Rapid cooling may cause co-deposition of sodium sulphate.) The crystals are washed three times with ice-cold 10% aqueous sodium hydroxide and then thoroughly with ethanol (yield 11·5 g.) [Found: loss at 110°, 41·4; total P, 14·2; P_2O_6 (as $Ag_4P_2O_6$), 35·7; (by HIO_3 oxidation), 35·8; Na_2SO_4, 0·4; phosphate, nil. Calc. for $Na_4P_2O_6,10H_2O$: H_2O, 41·4; P, 14·4; P_2O_6, 36·5%]. From a " model " solution, incorporating pure hypophosphate and imitating that resulting from an actual oxidation, 90·0% of the hypophosphate was recovered as $Na_4P_2O_6,10H_2O$ by the procedure described.

Ceric Hypophosphate, CeP_2O_6,xH_2O.—On mixing equimolecular solutions in N-nitric acid of ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, and sodium hypophosphate, *ceric hypophosphate* is obtained quantitatively as a yellow gel, which is separated and washed on the centrifuge (Found, in air-dried material: Ce, 37·4; P_2O_6, 42·7; H_2O, 19·9%; $P_2O_6/Ce = 1·010$. $CeP_2O_6,4H_2O$ requires Ce, 37·8; P_2O_6, 42·7; H_2O, 19·5%). The gel is unattacked by 1 hour's contact with 3N-nitric acid at 100°, but, like ceric phosphate, readily dissolves to a colourless solution on addition of hydrogen peroxide. At room temperature neither concentrated nitric nor sulphuric acid affects it, but if it is warmed with the latter acid and an equal volume of water is added a solution of ceric sulphate results. Although stable at 100° the gel begins to lose colour slowly at 130° and rapidly becomes colourless at 150° owing to the reaction $6CeP_2O_6 = Ce_4(P_2O_6)_3 + 2Ce(PO_3)_3$.

Determination of Hypophosphate.—(1) *Oxidation with iodic acid.* A sample of the hypophosphate (0·2—0·3 g.) is treated at 100° with a solution of potassium iodate (1 g.) in 40% sulphuric acid (25 ml.). Oxidation is usually complete in 1 hr., and the iodine produced is then distilled into aqueous potassium iodide and titrated. The theoretical equivalence ($I_2O_5 = 5P_2O_6^{4-}$, or 1 ml. of 0·02N-arsenite = 0·00790 g. of $P_2O_6^{4-}$) may be safely assumed.

(2) *Precipitation as $Ag_4P_2O_6$.* To a continuously stirred solution of hypophosphate (0·1—0·15 g.) in 0·5N-nitric acid (10 ml.), 10 ml. of a 10% solution of silver nitrate in 0·5N-nitric acid are added dropwise. After granulation by shaking, the precipitate, collected in a filter crucible, is washed once with a few ml. of the silver nitrate solution and then freely with ethanol. After a short drying at 100° the crucible is gradually heated until the originally cream-coloured content becomes uniformly grey in consequence of the reaction $Ag_4P_2O_6 = 2Ag + 2AgPO_3$, which occurs rapidly at 300° (Found: Ag, 73·4; P, 10·6. Calc. for $Ag_4P_2O_6$: Ag, 73·2; P, 10·5%).

A mixture of 0·1145 g. of KH_2PO_4 with 0·1227 g. of $Na_2H_2P_2O_6,6H_2O$ gave 0·2307 g. of final product (Calc. for the hypophosphate: 0·2306 g.). Similar tests with di-, tri-, trimeta-, tetrameta-, and polymeta-phosphate showed that only the last two interfere.

(3) *Precipitation as silver salt preceded by precipitation as zinc hypophosphate.* In this method the only common interfering phosphorus oxy-acid is diphosphate, which is also precipitated by the zinc reagent. The washed precipitate from 50 g. of pure zinc sulphate and 29 g. of sodium hydrogen carbonate is dissolved in hot aqueous acetic acid containing 31 ml. of glacial acid, and to the solution, diluted to 950 ml. with water, a further 115 ml. of glacial acetic acid are finally added. Of the solution so prepared 25 ml. are equivalent to 0·33 g. of $P_2O_6^{4-}$.

To a solution of hypophosphate (0·1—0·2 g.) in N-nitric acid (5—10 ml.) an equal volume of M-sodium acetate solution is added, followed at once by the zinc acetate reagent (50 ml.). After 30 min. the precipitate is separated in the centrifuge, washed twice with 20 ml. portions of the zinc reagent (not water), and then dissolved in the minimum of dilute nitric acid. From the solution, diluted to 100 ml., silver hypophosphate is precipitated by adding 1 g. of silver nitrate, and finally treated as in method (2). In a test conducted as described 0·1687 g. of $Na_2H_2P_2O_6,6H_2O$ gave 0·3130 g. of $Ag_4P_2O_6$ (Calc.: 0·3163 g.).

(4) *Oxidation by aqueous bromine (acting as HOBr).* Into a glass-stoppered bottle the following are introduced in succession: hypophosphate (0·2—0·25 g.) dissolved in N-hydrochloric acid

(20 ml.); potassium bromate solution (3 g. $KBrO_3$ per l.) (25 ml.); water (55 ml.) containing 5 drops of 2% solution of ammonium molybdate; and potassium bromide (1 g.). Immediately on the last addition the bottle is stoppered and its contents well mixed. A second bottle, similarly charged but without the hypophosphate, serves as control. After 30 min. each bottle is opened for a short time to receive 4·5 g. of pure borax (with precautions against loss of bromine), and when this has been dissolved the bottles are set aside for 1 hr.; finally, iodine released by addition of potassium iodide and sulphuric acid is titrated. A sample (0·2533 g.) of $Na_2H_2P_2O_6,6H_2O$ led to 16·05 ml. of 0·1N-thiosulphate as the difference in titrations of the two mixtures (Calc.: 16·13 ml.).

Product of oxidation of hypophosphate by hypobromous acid. Twice the theoretical amount, *viz.*, 30 ml. of 0·19N-bromine water, was added to a solution of $Na_2H_2P_2O_6,6H_2O$ (0·4110 g.) in water (25 ml.), followed by sufficient sodium hydrogen carbonate (3·5 g.) to saturate the system. After 2 hr. at room temperature the solution was made up to exactly 100 ml. and divided into two equal portions. Excess of bromine was removed by a current of air after addition of acetic acid (8·5 ml.) to each portion, and the precipitates then obtained by adding 30 ml. of zinc acetate reagent were collected and washed separately in the centrifuge. One precipitate was dissolved in 10 ml. of 3N-nitric acid, and the solution diluted to 100 ml. and heated on the water-bath for 1½ hr. From it orthophosphate was precipitated as phosphomolybdate and weighed as $Mg_2P_2O_7$. The zinc content of the second precipitate was then determined by conversion into $ZnNH_4PO_4$.

Calculation from the weights of $Mg_2P_2O_7$ and $ZnNH_4PO_4$ obtained (0·1379 g. and 0·2213 g., respectively) shows (i) that 95% of the phosphorus in the original hypophosphate is recovered in the $Mg_2P_2O_7$ derived from a zinc precipitate that can contain no orthophosphate; and (ii) that the Zn/P atomic ratio in the precipitates formed by zinc acetate reagent is 1·00. If the precipitates had contained $Zn_2P_2O_6$ derived from unchanged hypophosphate then this ratio would be greater than unity. Control experiments with pure diphosphate showed that 98% of $P_2O_7{}^{4-}$ is precipitated as $Zn_2P_2O_7$ from solutions at pH 4. When the results of the oxidation are corrected in the light of this information it appears that not less than 97% of hypophosphate is oxidized to diphosphate.

Composition of the Crude Calcium Salt Mixture resulting from Oxidation of Phosphorus.—The following summary of analytical operations upon this calcium salt mixture suggests that it contains a small proportion of the salt of a previously unknown acid $H_2P_4O_7$, which resembles hypophosphoric acid in that, under the conditions previously specified, the silver and the zinc salts are co-precipitated. The hypophosphate content of the mixture had therefore to be estimated from the known efficiency of the conversion into pure hypophosphate.

(1) Total calcium, 22·05%, estimated after converting all phosphorus compounds into orthophosphate by repeated evaporation to dryness with nitric acid.

(2) The precipitate produced by addition of zinc acetate reagent to a specimen of the mixture dissolved in N-nitric acid contained P, 16·8%, and the filtrate from the precipitate P, 3·04%, of the mixture taken. Total phosphorus, 19·84%. In the precipitate, containing as $Zn_2P_2O_6$ all hypophosphate originally present, the Zn/P ratio was 0·88.

(3) The silver salt precipitate, obtained as before described, contained P, 12·1%, and the ratio Ag/P was 1·70. Calculated total phosphorus as $Ca_2P_2O_6,2H_2O$ and $CaP_4O_7,2H_2O$ (see composition below) 0·0448 g.: recovered from the silver salt precipitate as $Mg_2P_2O_7$, 0·0445 g.

(4) The mixture contained no anions reducing mercuric chloride at room temperature, and therefore no phosphite, since the aqueous solubility of calcium hypophosphite excludes it from the mixture.

(5) Equivalent of the mixture in iodic acid oxidation: Found, 158 (Calc., assuming complete oxidation of $H_2P_4O_7$ to phosphoric acid: 152).

(6) From solutions at pH 0·125 and 0·6, 1 g. of the mixture reacted respectively with 5·9 ml. and 5·3 ml. of 0·1N-bromine during 1 hr.; at pH 3, during 2 hr., 4·6 ml. were taken up. The corresponding uptake by 0·575 g. of pure calcium hypophosphate (see composition below) was 0·2, 0·0, and 0·0 ml. respectively. These results suggest that the new acid is hydrolysed faster than hypophosphoric, to give compounds oxidized by molecular bromine, *e.g.*, phosphite.

The following approximate composition for the calcium salt mixture emerges: $Ca_2P_2O_6,2H_2O$, 57·5; $CaP_4O_7,2H_2O$, 9·4; $CaHPO_4,2H_2O$, 17·0; (gel) hydration lost at 100°, 15·3%.