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A COMPARISON OF METHODS FOR
THE VOLUMETRIC DETERMINATION
OF HYPOPHOSPHITE

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE

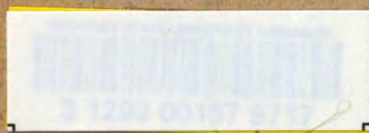
John D. Brooks

1947



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THE COMPARISON OF METHODS FOR
THE VOLUMETRIC DETERMINATION
OF HYPOPHOSPHITE

presented by

John D. Brooks

has been accepted towards fulfillment
of the requirements for

M. S. degree in Chemistry

E. Leiringer
Major professor

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A COMPARISON OF METHODS FOR THE VOLUMETRIC DETERMINATION OF
HYPOPHOSPHITE

by

John D. Brooks

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INTRODUCTION

Theoretically the hypophosphites are powerful reducing agents; however, they are often hard to completely oxidize in short periods with some of our more powerful oxidizing agents. There has been an appreciable amount of work done on the oxidation of these salts. This is especially true of the volumetric methods for determining the hypophosphites. The work as recorded in the literature is often conflicting or misleading. A few examples of this are as follows. A method is given in the literature whereby the investigator used a boiling potassium permanganate solution as an oxidant. A common precaution given students in the laboratory is, not to boil permanganate because it is unstable at high temperatures and especially so in the presence of an acid. Another investigator lists a bromate-bromide method, in which he used either hydrochloric acid or sulfuric acid as a catalyst, with a one hour standing period. The tabulated results show the method to be accurate. Still another investigator claims that a one hour standing period is not a long enough time for complete oxidation, but a three hour standing period is sufficient. Still another worker, following recommended procedures for an iodine oxidation method, finds them to be about 80% efficient. These examples cited are but a few of many discrepancies that occur in the literature.

It became the purpose of this research then to test these methods following the procedures as given in the literature, and at the same time to work on possible new methods of analysis.

HISTORICAL

In 1816 P. L. Dulong (8) isolated the salts of L'acide au phosphoreaux au minimum d'oxygene. He called the acid, acide hypophosphoreaux, hypophosphorous acid. He showed the acids and its salts were prepared by the decomposition of phosphides of the alkaline earths with water.

The hypophosphites are obtained by dissolving the bases in an aqueous solution of the acid, or by boiling phosphorus with the hydroxides of the alkalis or alkaline earths in aqueous solution. The salts are usually stable in air; however when heated, the salts of sodium, thallium, lithium, magnesium, zinc, cadmium, strontium, barium, manganese, and lead give off hydrogen and phosphine, leaving pyro and metaphosphates behind.

The hypophosphites are nearly all soluble in water, and the alkali metal salts are soluble in alcohol. There has not been any work recorded however as to the extent of solubility of the salts.

Boiling out of contact with air causes no change in valence; in air, oxidation to the phosphites and phosphates takes place, C. F. Rammelsberg (28). The hypophosphites are all decomposed by heat to furnish pyrophosphates and metaphosphate. The mole ratio of pyrophosphate to metaphosphate is 1:1 with sodium and thallium salts, 2:1 with magnesium and on

up to 6:1 with the barium salt. H. Rose (30) worked on the gaseous thermal decomposition products of hypophosphites as did Rammelsberg. They found the gaseous products always to be a mixture of hydrogen and phosphine which was spontaneously combustible and which varied according to the circumstance.

Hypophosphites have been, and still are, prescribed in medicines although it is possible to recover the hypophosphite unaltered from the urine twenty-four hours after administering the same. Investigations along this line were made by G. Polke (26), P. Schulz (35), and M. Paqueilin and L. Joly (25).

A good, accurate and rapid method for the determination of hypophosphites has long been sought. The oxidation of hypophosphite to phosphate is surprisingly slow and erratic in spite of the fact that it is a strong reducing agent. The volumetric procedures developed call for closely controlled conditions in order to get fair results and are highly empirical in nature.

Pean de Saint-Giles (34) first attempted to oxidize hypophosphite with permanganate but found that oxidation was incomplete. Amat (1) found that the speed of oxidation by permanganate increases with concentration of hypophosphite, with temperature and with acidity. At high temperatures some permanganate decomposes, while at ordinary temperatures the reaction is incomplete. He recommended adding an excess of permanganate at room temperature, heating to 50 degrees for one-half

hour, adding a measured excess of oxalic acid and back titrating the excess with permanganate.

Marino, and Pelligrini (24) recommend oxidation of the hypophosphites with permanganate in an alkaline solution and at a boiling temperature. The excess permanganate is determined with oxalate. Kolthoff (18, 19) states, that the permanganate method carried out in acid solution and at room temperatures is accurate if allowed to stand twenty-four hours before back titrating the excess permanganate. Zivy (41) adopted the method of Gailhat (9) to determine the hypophosphites, (i.e.) using permanganate in strong sulfuric acid solution in the presence of manganous sulfate and refluxing for twenty-five minutes.

Koszegi (22) recommends the use of permanganate in neutral solution at a boiling temperature, followed by iodometric determination of the manganese dioxide and excess permanganate. Kolthoff (20) pointed out the error in Koszegi's method as well as other methods at elevated temperatures, i.e., the autocatalytic decomposition of some of the permanganate. This was borne out by the fact that Koszegi obtained higher results with his permanganate method than with his gravimetric conversion to magnesium pyrophosphate.

Kolthoff recommends the following changes in Koszegi's method—Allow the flask with the hypophosphite and permanganate to stand for 24 hours at room temperature and then titrate the excess permanganate iodometrically. He recommends further that

blanks should be carried through with the experiment and the necessary correction applied.

A. Schwicker (36) recommends the addition of an excess permanganate solution to the hypophosphite solution. This is followed by a 30 minute heating period, after which the remaining permanganate is titrated either iodometrically or with oxalate. Schwicker states that the rate of oxidation is greatly increased by the addition of four or five drops of a five percent ammonium molybdate solution.

A general method of oxidation in an alkaline solution whereby the permanganate goes to manganate and is then precipitated as barium manganate has been suggested by Stamm (37).

Gall and Ditt (10) use a standard manganate solution in excess and a high temperature to effect the oxidation of the hypophosphites. The excess manganate is reduced by addition of an excess of oxalic acid. This is followed by a back titration of the excess oxalic acid with the original manganate solution.

Pound (27) states, that oxidation of hypophosphite by permanganate in neutral or acid solution is slow and direct titration is impossible. After standing for several days the percentage of hypophosphite determined was no greater than 96%. He found however, that traces of potassium bromide had a catalytic effect, which was possibly due to the formation of free bromine. This effect was great enough to cause complete

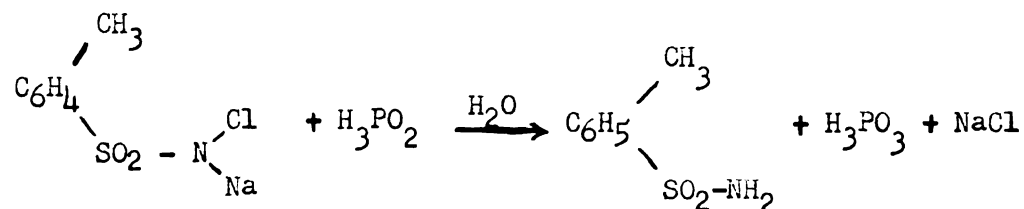
oxidation at room temperature after a few hours.

Dickerson and Snyder (7) were able to obtain satisfactory results when they used mercuric chloride as an oxidant. They found that a one hour heating period followed by a thirty minute cooling period was necessary to obtain quantitative oxidation to phosphate. Ionesco, Matiu, and Popesco (13) and Jean (14) obtained similar results with slight modifications of this method. However Schwicker (36) reported that this method was very slow. The oxidation from hypophosphite to phosphite was fast but from phosphite to phosphate was complete and quantitative only after many hours.

C. A. Wurtz (40) and H. Davey (6) making only qualitative investigations found that hypophosphorous acid was oxidized to phosphorous acid by hypochlorite.

K. A. Hoffman (11) using a water solution of potassium chlorate found the hypophosphites were qualitatively oxidized to phosphate. The oxidation was quite rapid but of no value quantitatively. The speed of the oxidation was increased when osmium tetra oxide was used as a catalyst.

S. Komaroski, V. F. Filonova, and I. M. Korenman (17) recommend the use of the sodium salt of para toluene sulfo chloramine (chloramine T). The results, (they list no data) were satisfactory, although somewhat lower than by the iodometric method of Rupp and Finck (32). The reaction is as follows:



A. Schwicker (36) investigated the use of sodium hypochlorite and found that in the presence of sodium bicarbonate he could oxidize phosphite to phosphate with no interference from any hypophosphite that might be present.

Both Dulong (8), and Kolthoff (20) state that chlorine can be used as a method for the quantitative determination of hypophosphite.

Rupp and Kroll (33) used a bromate-bromide mixture for the oxidation of hypophosphite followed by an iodometric titration after one hour. Kolthoff and Furman (21) state that one hour standing time was not long enough a period, as it gave results that were from 1.5% to 2.% too low. Heating causes a loss of bromine: therefore, they recommend a three hour standing period at room temperature.

W. Manchot and F. Steinhauser (23) stated, that phosphite can be quantitatively oxidized to phosphate by using a fifty percent excess of bromine in potassium bromide solution. The presence of a mineral acid retards oxidation. Oxidation is much more rapid in a neutral solution. It is necessary then to add an excess of either sodium acetate or sodium bicarbonate to the phosphite solution before adding the bromine. Hypophosphite

in the presence of a mineral acid requires three hours before complete oxidation takes place. Oxidation in the presence of an excess of sodium acetate or sodium bicarbonate, and at a sixty degree temperature requires only 30 minutes.

F. Viebock and K. Fuchs (38) recommend the use of a saturated bromine water solution and boiling. The excess bromine is finally boiled off. The solution is cooled, a few drops of phenolphthalein and a few grams of sodium chloride are added; the primary phosphite is titrated to the secondary salt. Excessive heating must be avoided to prevent decomposition of the hypophosphite.

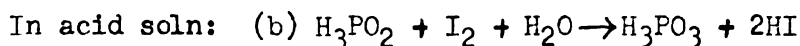
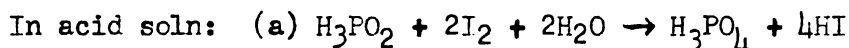
In the national formulary methods, G. L. Jenkins and C. F. Bruning (15) list the potassium permanganate method as unsatisfactory because of its excessive yield and length of time required for oxidation. They recommend a method, good for all hypophosphites, using a bromate-bromide mixture with sulfuric acid as a catalyst.

Rosin (31) recommends the use of an excess of free bromine in presence of sulfuric acid and a three hour standing period.

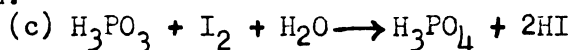
A. Schwicker (36) used a bromate solution in presence of either sulfuric acid or hydrochloric acid. This mixture was heated just below boiling and allowed to stand for forty-five minutes. The hypophosphite is oxidized almost immediately to phosphite. The phosphite in turn is oxidized to phosphate over a longer period.

E. Rupp and A. Pinck (32) used iodine in two different solutions to effect the oxidation of hypophosphite to phosphate. The iodine was used in acid solution for the oxidation of hypophosphite to phosphite. The solution was then neutralized with an excess sodium bicarbonate for the oxidation of phosphite to phosphate. The first oxidation in acid solution is very slow. The second oxidation in neutral solution however is quite rapid.

Boyer and Bauzil (4) gave the following equations from their work on iodometric determinations of hypophosphites.

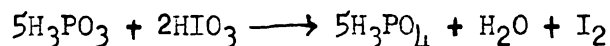
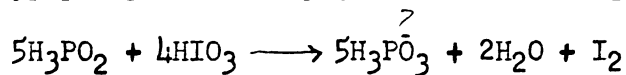


In Neutral soln:



To make the determination quantitative it was necessary to use the equations (b) and (c). They found that the reaction in both (a) and (b) proceeded at a much slower rate using acetic acid, and much faster using hydrochloric or sulfuric acid. Reaction (c) was complete in thirty minutes using sodium bicarbonate and in three hours if sodium carbonate was used.

A. Brukl and M. Behr (5) recommend iodic acid as an oxidant for hypophosphite. They give the following reactions;



Using the iodic acid Brukl and Behr claim gives them a double check method. The solution is boiled and the liberated iodine

is distilled over into a potassium iodide solution where it can be titrated with a standard sodium thiosulfate solution. At the same time potassium iodide can be added to the original solution remaining in the flask, and the liberated iodine titrated with a standard sodium thiosulfate solution.

L. Wolf and W. Jung (39) found that it was impossible in a neutral solution, to oxidize phosphite to phosphate in the presence of hypophosphite. If it was desirable to oxidize both the hypophosphite and phosphite, the iodine solution was first made acid with sulfuric acid and allowed to stand until the hypophosphite was oxidized to phosphite. At this point sodium bicarbonate was added until the solution was made neutral after which oxidation to phosphate takes place.

V. Hovorka (12) recommends the use of potassium iodate and mercuric chloride in an atmosphere of carbon dioxide.

D. Raquet and P. Pinte (29) using iodine, make two separate determinations for a mixture of hypophosphite and phosphite. They determine the hypophosphite with iodine in an acid solution and the phosphite with iodine in a neutral solution. The phosphite is determined first by adding a warm borax solution to the reaction mixture and setting aside for forty-five minutes. The solution is acidified with acetic acid, potassium iodide is added and the liberated iodine is titrated with a standard sodium thiosulfate solution. For the hypophosphite determination hydrochloric acid is added to the reaction mixture and heat

from a steam bath is applied for one hour. At the end of one hour the solution is cooled and a warm borax solution is added and the same procedure prescribed for the phosphite determination is followed.

H. R. Pond (3) made a study of the method of Raquet and Pinte (29) and found the method gave results twenty percent too low. With a longer digestion period 92% of the hypophosphite was oxidized to phosphate.

J. Kamicki (16) found the rate of oxidation of hypophosphite to phosphite by iodine was proportional to the sulfuric acid concentration.

A. Benrath and K. Ruland (2) oxidized hypophosphite to phosphite using ceric sulfate as the oxidant.

PREPARATION OF POTASSIUM HYPOPHOSPHITE

A series of comparisons of analytical methods for the volumetric oxidation of the hypophosphites was run on potassium hypophosphite. A commercial salt (Baker's C.P.) was recrystallized, to insure purity, and made up in .0250 M solutions for the analysis. The potassium salt was chosen in preference to the sodium hypophosphite because it is an anhydrous salt.

It was found by experiment that approximately 200 grams was the maximum amount of potassium hypophosphite that could be put into solution in 100 mls of water heated just to boiling. This proved not to be the best method for the recrystallizing of the salt, however, as the yield after one recrystallization is only 15% by weight of the original 200 grams.

The next method tried, was that of dissolving the potassium hypophosphite in a hot alcohol solution and recrystallizing it in a cold alcohol solution. In this manner it was found, that the maximum weight that could be dissolved was approximately 60 grams in 100 mls of 95 percent alcohol. The yield after one recrystallization was twice that of the first method mentioned, or 30% by weight of the original 60 grams of potassium hypophosphite dissolved.

Procedure for Recrystallization of Potassium Hypophosphite

Heat one hundred milliliters of distilled water in a 250 ml beaker, to a temperature just below boiling. Maintain this

temperature throughout the procedure up to and including the filtration. At the same time weigh on the rough balance, in a beaker, or watch glass, 200 grams of the commercially prepared potassium hypophosphite. When the water has reached the proper temperature, add, with constant stirring, approximately 25 gram portions of the potassium hypophosphite, making sure each time that the salt has all gone into solution before the next portion is added. When the potassium hypophosphite has all been added the solution becomes quite viscous. It is important at this point to continue stirring to prevent any crystals from forming before filtration. The syrupy solution is quickly transferred to a hot water funnel and filtered into 600 mls of redistilled ethyl alcohol. Crystal formation takes place almost immediately. The contents are set aside in the refrigerator for 12 hours to allow for complete precipitation. As was indicated earlier the yield was not good by this method and for this reason it was not repeated.

Procedure for Recrystallization of Potassium Hypophosphite dissolved in hot alcohol

In this method, an all-glass reflux unit was used with a continuous stream of nitrogen blown into the system to keep it free from oxygen.

One hundred milliliters of redistilled ethyl alcohol was placed in a 500 ml flask which was then attached to a condenser by means of ground glass joints. The alcohol was heated

with a glass col mantle, to a boiling temperature. At this time, the previously weighed commercial potassium hypophosphite (60 grams) was quickly introduced into the alcohol and refluxed for 20 minutes. The nitrogen bubbling through the alcohol also served as a stirring effect. After 20 minutes the flask was quickly disconnected and the solution filtered through a hot water filter into 600 ml of ethyl alcohol at room temperature. Crystal formation starts immediately. The solution is set aside in the refrigerator for twelve hours to allow complete precipitation to take place. The crystals are filtered through a buchner funnel and air dried, on porous plates, until they tumble freely. They are then placed in glass stoppered bottles for keeping.

Tests for the presence of phosphite at this time were positive, indicating that some oxidation from hypophosphite to phosphite had taken place during the procedure. Phosphite was found to be present in amounts ranging from 1% to 2%.

A sample of potassium hypophosphite, weighing approximately 2 grams, was placed in a drying oven for a number of hours. The oven temperature was set at 110° for the first few hours and then increased to 130° . To ascertain the loss in weight, the sample was weighed hourly; the maximum loss in weight occurred after 11 hours heating at 130° . There was no further change in weight after heating for 55 more hours at the same temperature. When the temperature was increased above 150° , on another sample, decomposition took place.

Several references list potassium hypophosphite as a deliquescent salt. In order that it might be known what to expect when weighing such a salt, an experiment was performed on a previously dried salt.

The cap was removed from the weighing bottle containing the potassium hypophosphite, leaving a surface of the salt exposed to the air. The weighing bottle was placed on an analytical balance during the exposure period, and weighings were made at one minute, five minute and fifteen minute intervals for a time totaling one hour. During the first half hour the gain in weight due to moisture equaled 0.5 milligrams. At the end of one hour the total gain in weight equaled 11 milligrams. As indicated above there was only a small surface area exposed to the air. When this same experiment was tried with dry crystals placed on a watch glass, the gain in weight after the first few minutes was so rapid, a true weight could not be obtained on the balance.

This indicated that if samples are weighed by difference with a minimum of surface area exposed there should be no error in weighing due to the deliquescence of the potassium hypophosphite.

For the comparisons, a .0250 M solution of potassium hypophosphite was used.

Procedure

A 2.6023 gram sample of potassium hypophosphite was weighed by difference on the analytical balance. This sample was transferred to a one liter volumetric flask and diluted to the mark with distilled water. The solution was shaken thoroughly for five to ten minutes, and was then ready for use. Fresh solutions for analysis were prepared after a maximum of 48 hours inasmuch as test for phosphite showed an increase over the original 1% to 2% present after this time.

PREPARATION OF SODIUM HYPOPHOSPHITE

Several of the comparison methods of analysis for the hypophosphites were run on a commercial preparation (Baker's C.P.) of sodium hypophosphite which, to insure purity, had been recrystallized twice.

Oxidation methods for the determination of hypophosphite should apply equally well to sodium or potassium hypophosphite. There is a difference however in the physical state in which the two salts exist. The potassium hypophosphite can be dried to the anhydrous state, while the sodium hypophosphite exists as a monohydrated salt and cannot be completely dehydrated as shall be indicated later in the report.

It was found by experiment, that approximately 300 grams of the sodium hypophosphite was the maximum amount that could be easily put into solution in 100 ml of water heated just to boiling.

In the first recrystallization 80% by weight of the original material used was recovered. This is compared to the 30% recovery for the best recrystallization method for potassium hypophosphite which could only be recrystallized once due to such poor recovery. The second recrystallization yielded a 58% by weight recovery of the original sodium hypophosphite.

Procedure

Heat one hundred milliliters of distilled water in a 250 ml beaker just below boiling. Maintain this temperature throughout the procedure up to and including the filtration. At the same time weigh out in a beaker or large watch glass, on the rough balance, approximately 300 grams of the commercially prepared sodium hypophosphite. When the water has reached the proper temperature, approximately 25 gram portions of the sodium hypophosphite are added with constant stirring. Making sure each time before adding more that the salt has gone into solution. This should be quite rapid until almost all of the 300 grams have been added. At this time the solution becomes quite viscous and it is important that the stirring be kept up to prevent the crystals from settling out in the beaker. When the last of the salt has been added and the solution is clear it is quickly transferred to a hot water funnel and immediately filtered into 600 ml of redistilled ethyl alcohol which is at room temperature. Crystal formation takes place almost immediately. The alcohol with the filtrate in it is set aside in the refrigerator for 12 hours to allow for complete precipitation. This procedure is repeated for the second recrystallization.

At the completion of the second recrystallization and 12 hours digestion period, the crystals were filtered through a buchner funnel and then air dried on porous plates until they tumbled freely, at which time they were transferred to glass stoppered bottles.

Tests for presence of phosphite were made immediately after completion of the drying and again some months later. The test for phosphite proved to be negative each time.

Mellor states that sodium hypophosphite can be made nearly anhydrous at 200°C. Having previously heated some of the recrystallized salt at 150°C. and detecting the odor of phosphine, which is indicative of decomposition, it was decided to attempt drying at lower temperatures.

Three temperatures, with a total range of 60°, were chosen to work with; they are 75°C, 105°C, and 135°C. The sample dried at 135°C gave the customary evidence of decomposition after 6 hours. The two remaining samples (i.e.) one drying at 75°C. and the one drying at 105°C., were weighed at intervals up to 118 hours. The theoretical amount of water present in the monohydrated sodium hypophosphite is equal to 16.98%. The amount of water lost due to drying for 118 hours was equal to 14.69% for the sample at 75°C and 14.95% for the sample at 105°C. These two samples were again heated at the same temperatures for a total of 200 hours with no significant change in weight. Some oxidation had taken place through over such a long period of exposure to heat and air as is evidenced by the following when phosphite was tested for.

Sample heated at 75°C for 200 hours

Meq of I ₂ used	Meq of I ₂ recovered	% phosphite
2.0968	2.0580	1.85

Sample heated at 105°C for 200 hours

2.0968	2.0590	1.80
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This indicated that at the best there is still 2% water left in the sodium hypophosphite after 200 hours at 105°C, and if this last 2% were to be removed it would require higher temperature or longer heating periods, both conditions under which sodium hypophosphite is unstable.

The preceding evidence indicated that it is not practical to try to obtain anhydrous sodium hypophosphite. For this reason then, the monohydrated sodium hypophosphite was used in a series of comparisons of analytical methods. Six liters of a .0250 M solution of sodium hypophosphite monohydrate were made up and stored in a pyrex bottle under an atmosphere of nitrogen. Periodic test of the solution for the presence of phosphite proved negative.

To insure complete absence of oxygen the storage bottle after filling was tightly stoppered and sealed with wax. The interior was then flushed several times with nitrogen which in turn had been passed through two strong caustic solutions of pyrogallol.

Procedure

An eight liter pyrex bottle was fitted with a three-hole rubber stopper. In one hole was fitted an all glass siphon, in the second hole a short glass stem with a piece of rubber tubing which acted as a safety valve in case the pressure from the nitrogen was too great. The third hole was fitted with glass tubing leading back to two bottles filled with the caustic pyrogallol solution. These bottles were in turn connected with the source of nitrogen.

Three samples of 5.134 grams each are weighed by difference on an analytical balance, and transferred to separate two liter volumetric flasks. The samples are then diluted to the mark on the flask and shaken thoroughly before transfer to the pyrex storage bottle. Again after the three solutions are combined in the large bottle they are shaken very thoroughly from five to ten minutes before the final connections with the nitrogen and siphon are made. When the stopper with the siphon and nitrogen tubes is in place it is secured with copper wire and then melted wax is poured around any possible source of leakage. The system as has been mentioned before is flushed out several times with nitrogen and is then ready for use.

The Wolf and Jung (39) method of testing for phosphite in presence of hypophosphite is carried out periodically. If no phosphite is present the solution is considered to be good.

OXIDATION OF SODIUM HYPOPHOSPHITE WITH IODINE

Rupp and Finck (32), Boyer and Bauzil (4), and Wolf and Jung (39) used iodine in acid solution to oxidize the hypophosphite to phosphite, followed by iodine in sodium bicarbonate solution to complete the oxidation to phosphate. The same procedure recommended by the above investigators was followed here.

Procedure

Twenty ml of .025M solution sodium hypophosphite and a standard solution of iodine approximately 0.1N were pipetted into 250 ml iodine flasks.

5 ml of 4N sulfuric acid was added to each flask which was then tightly stoppered and set aside over night. At the end of approximately 12 hours each flask was opened and enough sodium bicarbonate was added to neutralize the solution. One gram excess of sodium bicarbonate was added to each flask which was stoppered and set aside for one hour. The solution was acidified, at the end of the hour, with 15 ml of 30% acetic acid and the remaining iodine titrated with a standard solution of sodium thiosulfate. Freshly prepared starch was used as an indicator.

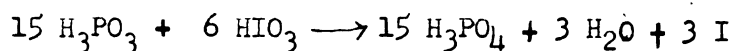
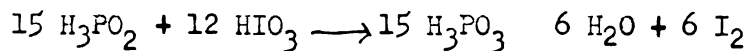
Blanks were carried along with the regular reaction. There was no gain or loss of iodine over the twelve hour period.

The results are as follows:

Meq of H_2PO_2^- used	Meq of H_2PO_2^- oxidized	% H_2PO_2^- oxidized
2.0080	1.9808	98.65
2.0080	1.9859	98.90
2.0080	1.9808	98.65
2.0080	1.9653	97.87
2.0080	1.9550	97.37
2.0080	1.9787	98.56
2.0080	1.9777	98.52
2.0080	1.9705	98.13

OXIDATION OF HYPOPHOSPHITE USING POTASSIUM IODATE
IN SULFURIC ACID SOLUTION

A. Brukl and M. Dehr (5) used iodic acid for the oxidation of hypophosphite to phosphate. The reaction is as follows:



Procedure

Twenty ml of .0249M potassium hypophosphite and 40 ml of 0.1000N potassium iodate solution were pipetted into 250 ml iodine flasks.

Ten ml of 6N sulfuric acid was added to each flask which was stoppered immediately. The flasks were allowed to stand one hour at room temperature. At the end of this period they were heated to drive off all the excess iodine. Potassium iodide was added to the solution and the liberated iodine was titrated with a standard sodium thiosulfate solution. Freshly prepared starch was used as indicator.

Meq H_2PO_2^- used	Meq H_2PO_2^- oxidized	% H_2PO_2^- oxidized
1.9920	1.2339	61.94
1.9920	1.0800	54.21
1.9920	.9921	49.80
1.9920	1.1460	57.49

OXIDATION OF POTASSIUM HYPOPHOSPHITE USING POTASSIUM
BROMATE IN HYDROCHLORIC ACID SOLUTION

Schwicker (36) suggests a method for the determination of hypophosphite whereby enough hydrochloric acid is added to the hypophosphite-bromate mixture to bring it up to 1N.

Procedure:

Twenty ml of a .0251M solution of potassium hypophosphite and 40 ml of 0.1000N potassium bromate were pipetted into 250 ml iodine flasks.

Sixty ml of hydrochloric acid was added to each flask, and the flask was immediately stoppered. A saturated potassium iodide solution was placed in the gutters. The flasks were allowed to stand over periods ranging from one hour to twelve hours at room temperature. The potassium iodide was run into the flask and the amount of potassium bromate remaining determined by titrating the liberated iodine with a standard solution of sodium thiosulfate. Freshly prepared starch solution was used as indicator.

Blanks were run under the same conditions outlined above. There was no loss of bromine at any time.

Meq H_2PO_2^- used	Time	Meq H_2PO_2^- oxidized	% oxidized
2.0880	1 hour	1.5790	75.62
2.0880	1 hour	1.5857	75.94
2.0880	12 hours	1.6208	77.62
2.0880	12 hours	1.7351	83.10
2.0880	12 hours	1.6903	81.00

OXIDATION OF SODIUM HYPOPHOSPHITE WITH POTASSIUM
BROMATE AND SULFURIC ACID

Schwicker (36) states, that sodium hypophosphite can be quantitatively oxidized, in a short period of time, by potassium bromate in a sulfuric or hydrochloric solution.

The procedure recommended by Schwicker was used in this comparison.

Procedure

Twenty ml of .0251M solution of sodium hypophosphite and 40 ml of a 0.1000M solution of potassium bromate were pipetted into 250 ml iodine flasks.

Five ml of 4N sulfuric acid was added to each flask. The flasks were heated just to boiling and the flame was removed. The flasks were set aside for forty-five minutes after which time they were heated again to boiling to drive off all excess bromine. They were cooled, 3 grams of potassium iodide was added to each flask and the remaining bromate titrated iodometrically using a standard sodium thiosulfate solution. Freshly prepared starch solution was used as indicator.

Blanks were carried through the same conditions and no loss of bromate was found.

The results obtained were as follows:

Meq of H_2PO_2^- used	Meq of H_2PO_2^- oxidized	% H_2PO_2^- oxidized
2.0080	2.0857	103.86
2.0080	2.0771	103.44
2.0080	2.0788	103.53
2.0080	2.0728	103.22

OXIDATION OF SODIUM HYPOPHOSPHITE WITH BROMATE-
BROMIDE IN SULFURIC ACID

Schwicker (36), Jenkins and Bruning (15), and Rosin (31) recommend the use of a bromate-bromide mixture catalyzed with sulfuric acid. The procedure as recommended was carried out for this comparison.

Procedure

Twenty ml of .0251M solution of sodium hypophosphite and 40 ml of 0.1000N potassium bromate were pipetted into 250 ml iodine flasks.

One gram of potassium bromide and 5 ml of 4N sulfuric acid was added to each flask. The flask was immediately stoppered. A saturated potassium iodide solution was placed in the gutters. The flasks were set aside, at room temperature, for one hour. At the end of this period they were carefully opened and the potassium iodide solution was allowed to run down into the flask. Here as a precautionary measure against losing any of the escaping gas, the flasks were placed in ice water which reduced the pressure and sucked the potassium iodide from the gutters into the flasks. The remaining bromine was titrated iodometrically using a standard sodium thiosulfate solution.

Results obtained were as follows:

Meq of H_2PO_2^- used	Meq of H_2PO_2^- oxidized	% of H_2PO_2^- oxidized
2.0080	2.0470	101.94
2.0080	2.0521	102.20
2.0080	2.0655	102.86
2.0080	2.0449	101.84

OXIDATION OF SODIUM HYPOPHOSPHITE WITH SODIUM CHLORITE

Sodium chlorite does not react with sodium hypophosphite in either neutral or alkaline solution. The original amount of sodium chlorite used as an oxidant was always recovered in the final titration regardless of time or other conditions. Sodium chlorite is unstable in acid solution so this was not tried.

Procedure

Twenty ml of .0251M sodium hypophosphite and 40 ml of approximately 0.1N sodium chlorite were pipetted into 250 ml iodine flasks. To make the solution alkaline, 5 ml of concentrated sodium hydroxide was added to each flask and the flask tightly stoppered. To make the solution neutral 1 gram of sodium bicarbonate was added to each flask, and the flask tightly stoppered. The flasks were then set aside for times varying from one hour to twelve hours.

OXIDATION OF SODIUM HYPOPHOSPHITE WITH SODIUM HYPOCHLORITE

Schwicker (36) used sodium hypochlorite in a sodium bicarbonate solution to oxidize phosphite in the presence of hypophosphite.

Davey and Wurtz (6) oxidized hypophosphite qualitatively to phosphate using hypochlorite. They did not state the conditions.

Sodium hypophosphite can be quantitatively oxidized to phosphate using sodium hypochlorite in a sulfuric acid solution. As a source of sodium hypochlorite a commercial bleach Chlorox (Chlorox Chemical Company, Oakland, California) was used. One hundred ml was diluted to 1 liter to give an approximately 0.1N solution. The stability of this solution in a brown bottle had previously been worked out in another thesis.

Sodium hypophosphite was allowed to react with sodium hypochlorite under conditions ranging from alkaline to neutral to acid.

Procedure

Forty ml of a phosphate buffer solution (pH 8.5) was introduced into a 250 ml iodine flask. Twenty ml of .025M solution of sodium hypophosphite and 25 ml of a standard sodium hypochlorite solution, approximately 0.1N, were pipetted into the flasks containing the buffer solution and the flasks immediately stoppered.

A saturated potassium iodide solution was placed in the gutters. The flasks were set aside for times varying from one hour to twelve hours at room temperature.

The amount of hypochlorite remaining was determined by allowing the potassium iodide to run into the flask, acidifying with acetic acid and titrating iodometrically with standard sodium thiosulfate solution. In each case the original amount of hypochlorite used was recovered. There was no reaction between hypophosphite and hypochlorite.

Meq H_2PO_2^- used	time	Meq H_2PO_2^- oxidized	% H_2PO_2^- oxidized
2.0080	1 hour	0.0000	0
2.0080	2 hours	0.0000	0
2.0080	12 hours	0.0004	0

The next attempt at oxidation with hypochlorite was tried in a neutral solution.

Procedure

Twenty ml of .0251M solution of sodium hypophosphite and 25 ml of standard sodium hypochlorite solution, approximately 0.1N, were pipetted into 250 ml iodine flasks.

1 gram of sodium bicarbonate was added to each flask which was immediately stoppered and set aside at room temperature for one hour. A saturated solution of potassium iodide was placed in the gutter of each flask. This was allowed to run into the flask upon opening, and the remaining hypochlorite was determined. This was titrated iodometrically using a standard sodium thiosulfate solution.

The results obtained were as follows:

Meq of H_2PO_2^- used	Meq H_2PO_2^- oxidized	% H_2PO_2^- oxidized
2.0080	.5608	27.92
2.0080	.4893	24.31
2.0080	.6122	30.44

These results indicate that phosphite may be present, (36), however when the original hypophosphite solution was tested for phosphite using the method of Wolf and Jung (39) no phosphite was found.

Before trying hypochlorite in acid solution it was necessary to check it's stability in acid solution.

Procedure

Twenty ml of water and 20 ml of sodium hypochlorite solution were pipetted into iodine flasks. Ten ml of 6N sulfuric acid was added to each flask which was immediately stoppered and set aside at room temperature for 12 hours. This gave a solution approximately 1.5N with respect to sulfuric acid.

The results were as follows:

Meq of NaClO used	Meq of NaClO recovered
3.2979	3.2979
3.2979	3.2979
3.2979	3.2979

This particular acidity was chosen because in all previous experiments where a halogen oxidant has been used the acidity has been 1N.

Procedure

Twenty ml of .0251M solution of sodium hypophosphite and 25.00 ml of a standard solution of sodium hypochlorite, approximately 0.1N were pipetted into 250 ml iodine flasks.

10 ml of 6N sulfuric acid was added to each flask which in turn was immediately tightly stoppered and set aside at room temperature for one hour. A saturated potassium iodide solution was placed in the gutters. At the end of the hour standing time, the flasks were carefully opened.** The potassium iodide solution was allowed to run into the reaction solution and the remaining hypochlorite was determined iodometrically using a standard sodium thiosulfate solution.

Meq of H_2PO_2^- used	Meq of H_2PO_2^- oxidized	% H_2PO_2^- oxidized
2.0080	2.0139	100.29
2.0080	2.0100	100.09
2.0080	2.0102	100.10
2.0080	2.0165	100.31

**Note: There is considerable pressure built up inside the iodine flask during the reaction. To avoid loss, due to the sudden release of pressure upon opening, the flasks were placed in ice water. A ten percent potassium iodide solution placed in the gutter before opening will be sucked down into the flask by the reduced pressure.

The same procedure outlined on the preceding page was followed with the exception of the time factor. This was varied over periods from 15 minutes to 12 hours. Oxidation is incomplete prior to 45 minutes, but from 45 minutes up to 12 hours, the time of standing has no effect on the oxidation. This is indicated in the following results:

Meq H_2PO_2^- used	Time	Meq H_2PO_2^- oxidized	% H_2PO_2^- oxidized
2.0080	15 Min	1.7540	87.35
2.0080	15 Min	1.7841	88.84
2.0080	30 Min	1.9045	94.84
2.0080	30 Min	1.9546	97.34
2.0080	45 Min	2.0100	100.09
2.0080	45 Min	2.0102	100.10
2.0080	12 Hrs	2.0086	100.00
2.0080	12 Hrs	2.0076	99.98

It was found by experiment, that in all cases where the excess of hypochlorite solution present was less than 50% of the total amount necessary for oxidation of hypophosphite to phosphate the oxidation was incomplete. Hypochlorite present in amounts in excess up to 100% of the total amount necessary for oxidation had no harmful effect.

SUMMARY

Potassium hypophosphite and sodium hypophosphite are inexpensive and readily obtainable on the commercial market. It is for this reason the commercial salts were used in the preceding work in place of laboratory preparations.

Under similar conditions pertaining to the dissolving of sodium hypophosphite and potassium hypophosphite, and to the recrystallization of the two salts, experiment proved that potassium hypophosphite was less soluble and gave a smaller percent yield than the sodium hypophosphite.

Test for oxidation to phosphite during the above procedures showed the potassium salt to have been oxidized while the sodium hypophosphite was not. The sodium hypophosphite did however show a positive test for phosphite upon heating in an attempt to dehydrate it.

To run analyses on potassium hypophosphite whereby it was oxidized all the way to phosphate, it would first be necessary to determine accurately each time the amount of phosphite present. In view of this fact, only those analyses of the potassium hypophosphite which were definitely incomplete as far as oxidation to the phosphate is concerned, are presented. To avoid making a primary analysis for phosphite it was necessary to obtain a phosphite-free salt. From the above it can be seen that the only salt of this type is the monohydrated sodium hypophosphite. In all analyses where sodium hypophosphite

was used, unless otherwise stated, it can be assumed to be the monohydrated salt.

Seven types of volumetric oxidations were tried during the course of the work. The first five of these had previously been worked out and reported in the literature as reliable methods.

- (1) Oxidation with iodine in first and acid solution and then neutral solution. The best results obtained were approximately 98% oxidation from hypophosphite to phosphate.
- (2) Oxidation with potassium iodate in sulfuric acid solution. The best results obtained ranged from 49% to 61% oxidation from hypophosphite to phosphate.
- (3) Oxidation with potassium bromate in hydrochloric acid solution. The best results obtained were approximately 77% oxidation from hypophosphite to phosphate.
- (4) Oxidation with potassium bromate in sulfuric acid solution. The best results obtained were approximately 103% oxidation from hypophosphite to phosphate.
- (5) Oxidation with a bromate-bromide mixture in sulfuric acid solution. The best results obtained were 102% oxidation from hypophosphite to phosphate.

- (6) Oxidation with sodium chlorite in either a neutral or an acid solution. The results were negative. There was no reaction.
- (7) Oxidation with sodium hypochlorite in sulfuric acid solution. The results, when certain minimum requirements were satisfied as indicated in the outline of the method, always gave a 100% oxidation from hypophosphite to phosphate.

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