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Qualitative Tests for Periodate and Iodate in the Presence of Each Other[1]

BY HOBART H. WILLARD AND J. J. THOMPSON

In the course of an investigation of the action of a soluble periodate on the salts of various metals (to be described in a later paper), a few metals were found which formed periodates insoluble even in solutions which were quite strongly acid. Since the corresponding iodates were soluble it was found possible by this means to precipitate a very small amount of periodate in the presence of a large amount of iodate. Bismuth was chosen because its periodate is least soluble and can be obtained in a fairly dense and easily filterable form.

Experimental

One gram of bismuth nitrate and 50 mg. of sodium iodate were dissolved in 30 cc. of water containing sufficient perchloric acid to maintain a clear solution. This was added to 5 cc. of water containing 0.1 mg. of periodate ion. Immediately the solution became opalescent due to the precipitation of the very insoluble bismuth periodate. If more than 50 mg. of iodate ion was present, too much acid was required to keep the bismuth iodate from precipitating, thereby diminishing the sensitivity of the test because of the increased solubility of the bismuth periodate. To detect smaller proportions of periodate, 5 g. of sodium iodate and various amounts of sodium periodate were dissolved in 100 cc. of water, which was acidified with 1 cc. of nitric acid, sp. gr. 1.42 Then 12 g. of barium nitrate was added to precipitate most of the iodate. This was filtered off and the filtrate tested for periodate by adding bismuth nitrate. It was found that 0.6 mg. of periodate ion could be detected in 5 g. of iodate ion in a volume of 100 cc.

It was not possible to detect the presence of small amounts of iodate in periodate by precipitating the periodate with bismuth and testing the filtrate for iodate, because small quantities are completely adsorbed by the bismuth periodate. However, it was found that 1.5 mg. of iodate ion could be detected in the presence of 5 g. of periodate in a volume of 25 cc., if most of the periodate was first precipitated as potassium metaperiodate, KIO_4, by adding an excess of potassium nitrate. This was shown by dissolving 5 g. of sodium periodate and 1.5 g. of sodium iodate in 100 cc. of water and adding 10 g. of potassium nitrate to the boiling solution, which was then allowed to evaporate at 80° to 25 cc. The solution was cooled in ice, filtered and washed with ice water. The cold filtrate was slightly acidified with nitric acid and tested for iodate by adding 5 cc. of 0.5 M silver nitrate. An opalescence appeared due to the formation of silver iodate. This was the limit of sensitivity.

All ions which are precipitated by silver interfere in the detection of iodate. Reducing ions react with periodate while chloride, bromide and

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[1] From a dissertation submitted by J. J. Thompson to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

phosphate ions interfere with its detection because they precipitate bismuth salts. The procedures given above are suitable for testing reagent iodate and periodate.

Summary

Six tenths of a milligram of periodate ion in the presence of 5 g. of iodate ion can be detected in 100 cc. of solution by first removing most of the iodate with barium nitrate, and then precipitating the periodate with bismuth nitrate.

One and five-tenths milligram of iodate ion can be detected in the presence of 5 g. of periodate ion in 25 cc. of solution by first removing most of the periodate as the insoluble potassium periodate, KIO_4, and then precipitating the iodate with silver nitrate.

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Periodates of Lead

BY HOBART H. WILLARD AND J. J. THOMPSON[1]

The literature of the periodates of lead is confusing. Not less than seven salts are described. An investigation of this subject resulted in the identification of only two salts, namely, triplumbous paraperiodate, $Pb_3H_4(IO_6)_2$, and the mesoperiodate, $Pb_3(IO_5)_2$. The former might also be considered as the mesoperiodate dihydrate, $Pb_3(IO_5)_2 \cdot 2H_2O$, but this is improbable for reasons given later.

A study of the periodates of lead involved: (a) the preparation of a few soluble periodates, (b) methods of analysis of the lead periodates.

Preparation of Soluble Periodates.—Sodium metaperiodate, $NaIO_4$, was prepared by dissolving trisodium paraperiodate, $Na_3H_2IO_6$, in a 15% nitric acid solution and evaporating until crystals of sodium metaperiodate formed. The trisodium paraperiodate was obtained by first oxidizing iodine to iodate by means of sodium chlorate and subsequently oxidizing the iodate to periodate in an alkaline solution with chlorine gas. The potassium salt, KIO_4, was obtained directly by the latter process. Periodic acid, H_5IO_6 or $HIO_4 \cdot 2H_2O$, was obtained by treating barium periodate, $Ba_3H_4(IO_6)_2$, with concentrated nitric acid, filtering off the barium nitrate and removing the excess of nitric acid by vacuum distillation. The barium salt was prepared by treating trisodium paraperiodate with barium nitrate. The details of these processes will be published in a later paper. Periodic acid can also be prepared electrolytically.[2]

Analysis of the Periodates of Lead.—Two methods for analyzing the precipitated lead periodates were employed. The procedures were as follows.

(1) The lead periodate was treated with 10 cc. of sulfuric acid (sp. gr. 1.84) and heated until it was converted completely to lead sulfate and periodic acid. It was then diluted to 300 cc. and cooled. The lead sulfate was filtered onto a Gooch crucible, washed with dilute sulfuric acid and ignited in an electric muffle at 500° for two hours. The filtrate was neutralized with sodium hydroxide, then a solution containing 9 g. of borax and 9 g. of boric acid was added, and finally 5 g. of potassium iodide. The iodine liberated was titrated with 0.1 *N* arsenite.[3]

(2) The periodate was treated in the same manner as described in (1) except that after filtering off and washing the lead sulfate, the periodic acid in the filtrate was reduced with sulfur dioxide and the iodine determined gravimetrically as silver iodide.

Experimental

A study was made of the salts obtained by varying the concentration of lead, the acidity and temperature. Experiments were made by precipitating the periodate from: (A) hot and cold concentrated neutral solutions of a lead salt; (B) hot and cold dilute neutral solutions of a lead salt; (C) acid solutions.

Lead Periodate (A) from Concentrated Neutral Solutions.—To study the type of salt formed from a concentrated solution, 25 g. of C. P. lead nitrate was dissolved in 100 cc. of water and the lead periodate precipitated at

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[1] From a dissertation submitted by J. J. Thompson to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Willard and Ralston, *Trans. Am. Electrochem. Soc.*, **62**, 249 (1932).

[3] E. Müller and O. Friedberger, *Ber.*, **35**, 2655 (1902).