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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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

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).

25° by the slow addition of 100 cc. of water containing 17 g. of sodium metaperiodate, $NaIO_4$, with continuous mechanical stirring. A white granular precipitate was formed which, after filtering, was twice suspended in fresh water and washed thoroughly by decantation, using ice water, then filtered on a fritted glass filter, washed and dried over phosphorus pentoxide. The dry salt remained white and was crystalline, as shown by the microphotograph in Fig. 1.

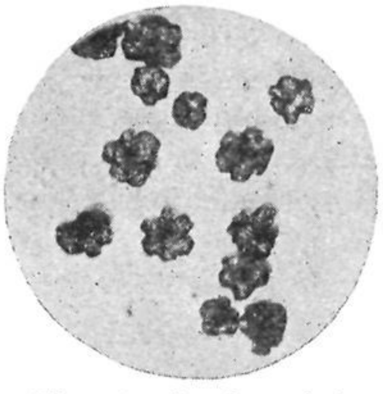

Fig. 1.—Lead periodate from cold, concentrated neutral solutions.

When the solution was maintained at 100° instead of 25°, a yellow-orange crystalline precipitate of impure triplumbous paraperiodate, $Pb_3H_4(IO_6)_2$, was formed. The analyses of the salts precipitated at the different temperatures are given in Table I.

Lead Periodate (B) from Dilute Neutral Solutions.—A study of the precipitates from dilute solutions of a lead salt was made by dissolving 25 g. of lead nitrate in 500 cc. of water and precipitating the lead at 25° by the slow addition of 17 g. of sodium metaperiodate in 200 cc. of water. A white crystalline precipitate was formed. This was filtered, washed and dried over phosphorus pentoxide. The crystals which consist of thin plates are shown in Fig. 2.

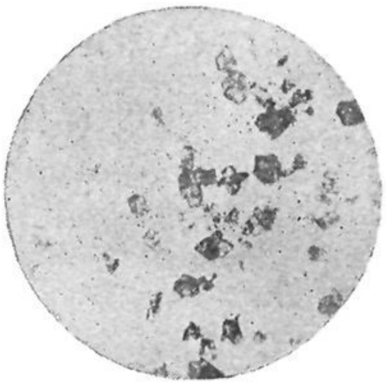

Fig. 2.—Lead periodate from cold, dilute neutral solution.

When precipitated at 100°, the crystals were light orange in color. Analyses of the salts dried over phosphorus pentoxide are shown in Table I. In both cases triplumbous paraperiodate was formed.

Lead Periodate (C) from Acid Solutions.—When 25 g. of lead nitrate was dissolved in 100 cc. of 0.8 *N* nitric acid and the lead precipitated at 100° by the slow addition of 17 g. of sodium metaperiodate in 100 cc. of water, the first 10 cc. of the periodate solution did not give a permanent precipitate, but as more was added a white flocculent precipitate formed which gradually changed to a very light cream-colored, fine, crystalline salt that settled rapidly. The salt was filtered, washed with 150 cc. of hot 1% nitric acid, transferred to a beaker, and washed by decantation, using cold 1% nitric acid, filtered on a fritted glass filter, finally washed with 100 cc. of ice water, and dried over phosphorus pentoxide. Results of analyses in Table I show that impure $Pb_3H_4(IO_6)_2$ was formed.

In the mother liquor white crystals formed upon cooling. These were filtered, washed, dried over phosphorus pentoxide and analyzed. The analyses showed that the salt was impure $Pb_3H_4(IO_6)_2$.

Further study in hot and cold acidified solutions resulted in the preparation of pure triplumbous paraperiodate. It was found that when the acidity was approximately 0.006 to 0.1 *N* with nitric acid, or 0.9 *N* with acetic acid, the pure salt was obtained. Results are shown in Table I.

TABLE I

ANALYSES OF LEAD PERIODATE (A), (B) AND (C)

Sample	% PbO Found		% I_2O_7 Found		Temp. of soln., °C.	Normality of acid	Method of analysis
(A)	61.81	61.82	34.17	34.24	25	....	1
	61.88	61.77	33.86	34.04	25	....	2
(A)	62.03	62.29	33.63	33.38	100	....	1
	62.15	62.31	33.68	33.62	100	....	2
(B)	61.87	61.86	33.80	33.82	25	....	1
	61.98	61.93	33.91	34.09	25	....	2
(B)	62.01	62.02	33.73	33.69	100	....	1
	62.41	62.38	33.87	33.69	100	....	2
(C)	61.93	62.11	33.87	33.90	100	0.8 *N* Nitric acid	1
	62.30	62.21	33.85	33.89	25	0.8 *N* Nitric acid	1
(C)	62.35	62.32	34.13	34.09	100	0.16 *N* Nitric acid	2
	62.47	62.42	33.90	33.97	25		2
(C)	62.46	62.38	34.10	34.07	100	0.047 *N* Nitric acid	2
(C)	62.05	62.23	34.12	34.13	100	0.88 *N* Acetic acid	2
	62.47	62.56	34.14	34.16	25		2

The theoretical for $Pb_3H_4(IO_6)_2$ is 62.49% PbO and 34.13% I_2O_7.

Microphotographs of the different crystal structures are shown in Fig. 3.

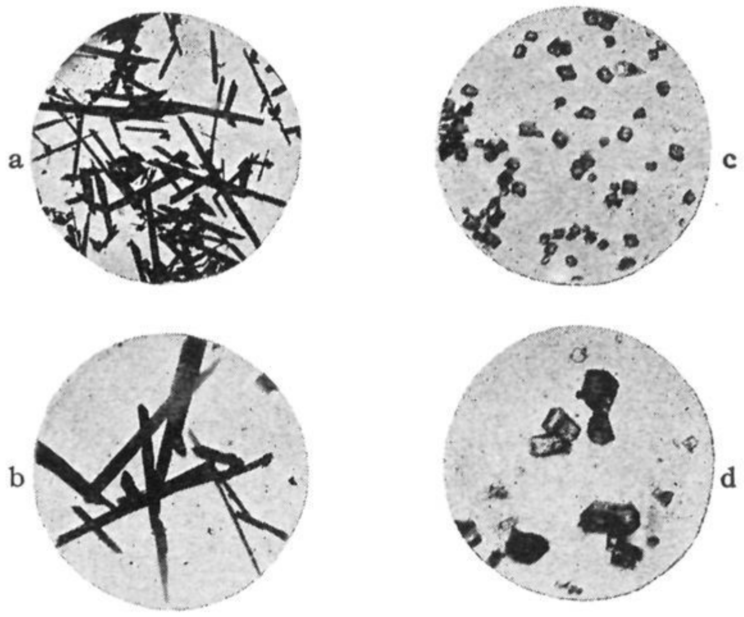

Fig. 3.—Lead periodate from acid solutions: a, 0.8 *N* nitric acid, 100°, no precipitate formed until cooled; b, 0.8 *N* nitric acid, 100°, no precipitate formed until cooled; c, 0.047 *N* nitric acid, 100°; d, 0.047 *N* nitric acid, 100°.

The Behavior of Triplumbous Paraperiodate on Heating.—Kimmins stated that the para salt was converted into the meso form, $Pb_3(IO_5)_2$, when it was heated for four hours at 275°. In an effort to prepare the meso salt, pure $Pb_3H_4(IO_6)_2$ was heated at 275° for four hours and then analyzed by Method 2. The results indicate that the para salt was converted essentially into the meso form, but qualitative tests showed that in its conversion a portion had undergone decomposition with the formation of some lead iodate.

PbO found, 64.44, 64.46, 64.55, calcd. for $Pb_3(IO_5)_2$, 64.68%. I_2O_7 found, 35.39, 35.39, 35.35, calcd., 35.34%.

When pure or impure triplumbous paraperiodate was heated above 130°, the formation of anhydrous meso salt caused a change in color to a dark brick red. The intensity of the color change and the amount of water lost were dependent upon the temperature and the time of heating. If the brick red salt was pulverized very finely, it became orange colored.

When the pure paraperiodate was converted into the anhydrous meso salt, the loss in weight corresponding to water was always too great, varying from 3.49 to 3.61% compared to the theoretical value of 3.38%; therefore the temperature of heating was varied from 130 to 275°, and the time from three minutes to six hours. Volumetric analyses of the heated samples showed that when the temperature was high enough to remove all the water there was a loss of oxygen with consequent formation of iodate.

It is believed that the salt before heating is the paraperiodate and not the mesoperiodate dihydrate for two reasons: (1) the water is retained up to 130°; (2) the anhydrous meso salt when kept under water for fifteen hours and again dried at 110° is found to have absorbed only 5% of the water lost.

Summary

1. Lead periodate was precipitated under varying conditions of acidity, temperature and concentration, only triplumbous paraperiodate, $Pb_3H_4(IO_6)_2$, being formed, although crystals of very different types and colors were obtained. It was pure only when precipitated from 0.006 to 0.1 *N* nitric acid or 0.9 *N* acetic acid solutions. This salt might also have the formula $Pb_3(IO_5)_2 \cdot 2H_2O$ but the para formula is more probable because the water is retained up to 130° and is not taken up by the anhydrous salt.

2. When the para salt was heated to 275° for fifteen minutes it was converted into triplumbous mesoperiodate, $Pb_3(IO_5)_2$, with slight reduction to iodate.

3. None of the other periodates of lead described in the literature could be prepared.

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The Activity Coefficients of the Alkali Chlorides and of Lithium Iodide in Aqueous Solution from Vapor Pressure Measurements

BY ROBERT A. ROBINSON AND DONALD A. SINCLAIR

Vapor pressure measurements should, in theory, provide a very accurate means of evaluating the activity coefficient of a salt in solution, but so far this method has hardly been used, mainly because of the elaborate and time-consuming technique required. The object of this paper is to show that after some improvements have been made in an isopiestic method previously described,[1] vapor pressure measurements will yield activity data with an accuracy comparable with that achieved in the e. m. f. and the freezing point methods.

Experimental Procedure

The apparatus consists of four silver dishes, gold-plated internally, 3.8 cm. square and 2 cm. deep, each dish weighing about 35 g. Into two of these dishes 2 cc. of potassium chloride solution is introduced while the other two contain a solution of another salt of approximately the same composition. The dishes are placed on a copper block, 2.5 cm. thick, in a desiccator which is evacuated at the beginning of an experiment and then rocked in a thermostat at 25°. Distillation occurs until the two solutions have the same vapor pressure, equilibrium being attained in twenty-four hours except with solutions 0.5 *M* and less in concentration, when periods up to three days may be required. The dishes are fitted with flap-lids, held open during an experiment by a wire bridge attached to the exit tube of the desiccator, so arranged that at the conclusion of an experiment the lids can be allowed to fall by rotating the exit tube through a small angle without opening the desiccator. This prevents contamination of the solutions by grease, dust or particles of mist on admitting air to the desiccator. From the changes in weight of the solution it is easy to find the concentrations of the isopiestic solutions, the error being not greater than 0.3%, which corresponds to 0.0005 mm. pressure in a 0.2 *M* solution. Several experiments in succession can be made with the same solutions.

To illustrate the accuracy attainable, two runs were made with potassium chloride solutions in each dish. The initial and final concentrations are given in Table I, from which it can be seen that although in the first experiment the initial concentrations differed widely, the final concentrations did not differ by more than one part in 2000, while in the second experiment the over-all variation was less than one part in 700. Our practice was, naturally, to commence with solutions having vapor pressures as nearly equal to one another as possible, so that the case illustrated by the first experiment is an extreme one designed to test the capability of the method.

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[1] *J. Phys. Chem.*, **37**, 395 (1933).