229. *Periodic Acid and Periodates. Part I. Analytical Determination of Periodic Acid.*

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In the course of a series of researches on the oxygen compounds of iodine now in progress in this laboratory, attention was first directed to periodic acid, since the existence of hydrates of iodine heptoxide containing less water than the ordinary periodic acid (paraperiodic acid), $H_5IO_6(I_2O_7,5H_2O)$, is doubtful, metaperiodic acid, $HIO_4(I_2O_7,H_2O)$, having been only once described (Lamb, *Amer. Chem. J.*, 1902, **27**, 134). It has now been shown that metaperiodic acid is a definite compound, and a new hydrate, $H_4I_2O_9$, dimesoperiodic acid, has been obtained. No evidence could be found of the existence of mesoperiodic acid, H_3IO_5, or of the anhydride, I_2O_7.

Before commencing a study of the dehydration of paraperiodic acid it was necessary to have available proved analytical methods for the determination of iodine heptoxide in any of its forms of hydration, and of the periodates. The existing methods have therefore been critically tested, and two new and satisfactory methods have been introduced.

Preparation of Paraperiodic Acid, H_5IO_6.—Wells's method (*Amer. Chem. J.*, 1901, **26**, 278) was slightly modified. A rapid stream of chlorine is passed through a boiling 10% solution of 60 g. of sodium hydroxide containing 12·7 g. of iodine. A white precipitate of disodium paraperiodate, $Na_2H_3IO_6$, is formed and causes bumping. The flame is removed and chlorine is passed till the effervescence, which begins after precipitation, ceases. The sodium periodate is filtered off, washed, and boiled with a dilute silver nitrate solution containing the equivalent of 3 mols. of silver nitrate to 1 atom of iodine. The resulting black precipitate of silver mesoperiodate, Ag_3IO_5, is suspended in water, and chlorine is passed with agitation till the precipitate is nearly white but some of the silver salt still remains. The filtrate is concentrated on a water-bath and kept in a vacuum desiccator over calcium chloride. Monoclinic crystals (Rammelsberg, *Ann. Physik*, 1868, **134**, 531) of paraperiodic acid are thus obtained. Crystals could not be obtained by keeping the concentrated solution at atmospheric pressure over concentrated sulphuric acid or phosphoric oxide for 7 days.

The crystals give off ozone on standing, as mentioned by Rammelsberg (*Ber.*, 1868, **1**, 73). Both starch–iodide paper and tetramethyl-base solution gave a distinct positive test for ozone, but benzidine solution gave only a faint brown colour. The crystals when heated at 100° gave all three reactions for ozone distinctly. If, during the preparation of the acid, passage of chlorine through the silver mesoperiodate suspension is too prolonged, chlorine peroxide is evolved from the crystals of the acid on standing in a desiccator. The crystals were finally dried over phosphoric oxide or sulphuric acid. They cannot be dried at 100° in air, although Rammelsberg (*Ann. Physik*, 1868, **134**, 531) found them to be stable at this temperature. We find that slow decomposition occurs, and the ultimate solid product on prolonged heating in an open weighing bottle is iodine pentoxide. The following table shows the effect of heating 2·2357 g. of acid at 100° in air (calc. for conversion into I_2O_5 : loss, 26·75%).

Time of heating.	Loss of wt., g.	Loss, %.	Time of heating.	Loss of wt., g.	Loss, %.	Time of heating.	Loss of wt., g.	Loss, %.
15 hours	0·4761	21·29	3 days	0·5203	23·27	10 days	0·5789	25·90
1 day	0·4773	21·39	5·66 ,,	0·5425	24·26	14 ,,	0·5915	26·45
2 days	0·4951	22·14	7 ,,	0·5549	24·82			

Further heating caused sublimation, and thus the loss for complete dehydration could not be determined. The iodine found in the residue was 75·85% (calc. for I_2O_5 : 76·05%).

Determination of Periodic Acid.—(1) In the method given by Scott (" Standard Methods of Chemical Analysis," 1926, **1**, 244) and used by Malaprade (*Bull. Soc. chim.*, 1926, **39**, 330), the acid is treated with a concentrated solution of potassium iodide in the presence of hydrochloric or sulphuric acid, and the iodine liberated is titrated with thiosulphate. One eighth of the total iodine is that present in the acid : $I_2O_7 + 14HI = 8I_2 + 7H_2O$.

This method was found to give low values for iodine in all the samples of paraperiodic acid examined (Found, in different samples A—E, as below : I, 53·33, 53·77, 53·69, 54·17, 53·81. Calc. for H_5IO_6 : I, 55·70%).

(2) Kimmins's method (J., 1887, **51**, 356) was found satisfactory after slight modification. In the original method the mixture of periodic acid, potassium iodide solution, and hydrochloric or sulphuric acid is heated in a stoppered bottle for 6 hours in boiling water. It was found unnecessary to heat for such a long time and satisfactory results were obtained at a lower temperature, 60°. The iodine was titrated as in method (1) [Found, for first three samples in (1) : I, 54·97, 55·34, 55·11%]. It is necessary to heat the mixture of the acid, potassium iodide solution and hydrochloric (or sulphuric) acid, otherwise the reaction is not quite complete. This is shown by the following experiment.

1·2839 G. of paraperiodic acid were dissolved in water and made up to 250 c.c.; 10 c.c. of this solution were mixed with potassium iodide and hydrochloric acid. In one set of experiments the mixture was heated for about 15 minutes at 60°, but in the second set the iodine was liberated without heating.

Vol. (c.c.) of $N/10$-$Na_2S_2O_3$ used when mixture is heated	17·80	17·90	17·85
,, ,, ,, ,, ,, not heated	17·45	17·40	17·40
,, ,, ,, calculated for H_5IO_6		18·01	

(3) The acid was dissolved in water and reduced to hydriodic acid by passing in sulphur dioxide. The iodine was then precipitated as silver iodide in the presence of nitric acid, and the silver iodide weighed.

Sample.	H_5IO_6, g.	AgI formed, g.	I found, %. (Calc. for H_5IO_6, 55·70%.)
A	0·1204	0·1248	56·02
B	0·1738	0·1804	56·09
C	0·1212	0·1254	55·95
D	0·2336	0·2424	56·07

(4) The use of Bunsen's method (*Annalen*, 1853, **86**, 265) showed that only three oxygen atoms of $HIO_4,2H_2O(H_5IO_6)$ were active. A known amount of the acid was boiled with concentrated hydrochloric acid in a small flask with a ground-glass joint, and the chlorine produced was passed through potassium iodide solution in U-tubes immersed in cold water. The iodine liberated was titrated against thiosulphate.

Sample.	H_5IO_6, g.	N/10-$Na_2S_2O_3$ used, c.c.	Weight of acid calculated if all the four O atoms are active.	Weight of acid calculated if only three O atoms are active.
A	0·0878	22·50	0·0641	0·0855
B	0·0298	7·70	0·0219	0·0293
C	0·0700	18·35	0·0523	0·0697
D	0·0521	13·80	0·0393	0·0524

The results show that the reaction probably proceeds in two stages :

(i) $HIO_4 + 6HCl = HOI + 3H_2O + 3Cl_2$.

(ii) $HOI + HCl = H_2O + ICl$.

The solution in the flask turns yellow, which is the colour of iodine monochloride solution in hydrochloric acid, in which it is stable and does not decompose on boiling (Bunsen, *Annalen*, 1852, **84**, 1; Schützenberger, *Compt. rend.*, 1877, **84**, 389). Lamb (*Amer. Chem. J.*, 1902, **27**, 134) probably used the above reaction equation when determining periodic acid by this method, although he gives no details.

(5) Periodic acid could be titrated with standard sodium hydroxide, and methyl-orange as indicator (H_5IO_6 taken, g. : 1·2478, 1·2839. Found, g. : 1·2472, 1·2882 respectively). With methyl-orange, periodic acid is monobasic (Giolotti, *Gazzetta*, 1902, **32**, 340), but with phenolphthalein it behaved as a dibasic acid. Samples A, B, and C showed basicities towards methyl-orange of 1·04, 0·95, 0·98, and towards phenolphthalein of 2·01, 2·08, —, respectively. The neutralisation thus proceeds in two stages :

(i) $H_5IO_6 + NaOH = NaH_4IO_6$ (methyl-orange).

(ii) $NaH_4IO_6 + NaOH = Na_2H_3IO_6$ (phenolphthalein).

In the particular solution used, no precipitation of sodium periodate occurred. When a solution of potassium hydroxide was used, a precipitate was formed. Titration with sodium carbonate and methyl-orange also showed that the acid was monobasic.

(6) *Determination of Oxygen Value.*—A very successful method of determining the oxygen content of paraperiodic acid is to heat the solid in a combustion tube in an atmosphere of carbon dioxide (prepared by heating pure sodium hydrogen carbonate). The oxygen evolved is collected in a Schiff's nitrometer containing 40% potassium hydroxide solution.

Sample.	H_5IO_6, g.	Vol. of O collected at S.T.P., c.c.	Wt. of O, g.	O, %.
A	0·0667	11·59	0·01655	24·81
B	0·0667	11·45	0·01635	24·51
C	0·0520	8·78	0·01254	24·11
D	0·1247	21·40	0·03057	24·51
E	0·0599	9·84	0·01405	23·47

Decomposition according to the equation $4H_5IO_6 = 10H_2O + 2I_2 + 7O_2$ requires O, 24·51%.

SUMMARY.

Kimmins's method for the determination of periodic acid is slightly modified in that the mixture of periodic acid, potassium iodide solution, and hydrochloric acid is heated only for 15 minutes at about 60°. Bunsen's method shows that only three oxygen atoms are active, so that iodine chloride is probably produced during the reaction. The oxygen content has been found by heating the acid in a combustion tube in an atmosphere of carbon dioxide and collecting the oxygen in a Schiff's nitrometer. Iodine has also been estimated by reducing the acid by sulphur dioxide and precipitating as silver iodide in the presence of nitric acid.

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