231. *Periodic Acid and Periodates. Part III. Sodium and Silver Periodates.*

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Ammermüller and Magnus (*Ann. Physik*, 1833, **28**, 514) prepared disodium paraperiodate, $Na_2H_3IO_6$, by passing chlorine into a solution of equal parts of sodium hydroxide and iodate, and silver metaperiodate, $AgIO_4$, by evaporating a solution of silver dimesoperiodate in warm nitric acid. Rammelsberg (*Ann. Physik*, 1868, **134**, 368) and Kimmins (J., 1887, **51**, 356; 1889, **55**, 146) studied these salts in greater detail. As the disodium and diargentous paraperiodates were produced during the preparation of periodic acid (Part I), we thought it desirable to examine their properties again. Some differences from recorded results were found. Work is in progress on the calcium, barium, and strontium salts, and the results will be communicated.

Disodium paraperiodate, $Na_2H_3IO_6$, prepared as described in Part I, was dried at 100°. It has a smell of iodoform and is only slightly soluble in water. Sodium was determined as sulphate by heating in a crucible with sulphuric acid (Found : Na, 16·43, 16·89, 16·57. Calc. : Na, 16·91%); iodine was estimated by method (2) of Part I (Found : I, 46·12, 45·98, 46·00. Calc. : I, 46·69%), and also by method (3) (Found : I, 46·38, 46·31, 46·03%). Bunsen's method [see (4), Part I] gave no definite results. It seems that a mixture of oxygen and chlorine is evolved when the sodium salt is boiled with concentrated hydrochloric acid, but attempts to determine the nature of the reaction led to no definite results, although the results with the free acid indicate that three atoms of oxygen are active.

		Weight of sodium periodate calculated		
$Na_2H_3IO_6$, g.	$N/10$-$Na_2S_2O_3$ used, c.c.	if four O atoms are active.	if three O atoms are active.	by multiplying titre by 0·0049.
0·1262	26·00	0·0884	0·1177	0·1274
0·0204	4·25	0·0144	0·0192	0·0208
0·0578	11·80	0·0401	0·0534	0·0578
0·0406	8·10	0·0275	0·0367	0·0397
0·0315	6·25	0·0212	0·0283	0·0306

The figures in cols. 3 and 4 are lower than the corresponding figures in col. 1, whilst the values in col. 5, obtained by multiplying the titre by the arbitrary factor 0·0049, are almost the same as those in col. 1; no explanation can be given for this agreement.

Hohnel (*Arch. Pharm.*, 1894, **232**, 222) claims to have obtained disodium paraperiodate by the action of sodium peroxide on iodine suspended in water, but we have been unable to confirm this reaction.

Effect of Heat on Disodium Paraperiodate.—On heating, the sodium salt turns yellow and gives off water. On further heating, sublimation of iodine pentoxide occurs until the salt decomposes with the evolution of iodine and oxygen, leaving sodium monoxide. This mode of decomposition was confirmed by quantitative estimation of the oxygen evolved when the salt was heated in a boat in a combustion-tube under the conditions of method (6) in Part I (Calc. for $4Na_2H_3IO_6 = 4Na_2O + 2I_2 + 3H_2O + 7O_2$: 20·58%).

$Na_2H_3IO_6$, g.	Vol. of O evolved at S.T.P., c.c.	Wt. of O, g.	O, %.
0·0410	5·68	0·008114	19·79
0·0248	3·42	0·004871	19·70
0·0332	4·64	0·006628	19·96

This result was further supported by the fact that the residue in the boat consists entirely of sodium carbonate and no iodide is present.

On prolonged heating of the salt in a crucible, sodium monoxide remains (Found: Na_2O, 23·00, 21·59, 21·88. Calc.: Na_2O, 22·7%).

Effect of Heating Disodium Paraperiodate, $Na_2H_3IO_6$, *in a Vacuum.*—The salt was heated for 24 hours in the vacuum desiccator by an electrical arrangement at 100° and at 125°. There was no loss of water or change in weight. This indicates that the salt cannot be represented as $Na_4I_2O_9,3H_2O$, as suggested by Ostwald and Walden (*J. pr. Chem.*, 1885, **32**, 311; Walden, *Z. physikal. Chem.*, 1888, **2**, 65) and Cornec (*Ann. Chim. Phys.*, 1913, **30**, 157). According to the Ostwald–Walden rule, the simplest formula for 1 : 2 periodates should be $M_4I_2O_9$, and therefore the three known solid 1 : 2 alkali periodates should not be formulated as $M_2H_3IO_6$ but as $M_4I_2O_9,3H_2O$ ($M = Na$, K, or NH_4). The experiments do not support this, but there is one point in favour of the above formulæ. On being heated, the disodium salt $Na_2H_3IO_6$ gives at first a sublimate of iodine pentoxide, which can be more easily explained by the formula $Na_4I_2O_9,3H_2O$, giving $2Na_2O + I_2O_5 + O_2$. Iodine pentoxide on further heating is decomposed into its elements: $2I_2O_5 = 2I_2 + 5O_2$.

The corresponding yellow silver salt, $Ag_2H_3IO_6$, has probably the constitution $Ag_4I_2O_9,3H_2O$, since, as described later, it loses water at 100° in a vacuum desiccator: $Ag_4I_2O_9,3H_2O = Ag_4I_2O_9 + 3H_2O$.

By passing chlorine through a concentrated solution of sodium hydroxide (about 65 g. per 600 c.c.), a mixture of equal quantities of disodium and trisodium paraperiodates, $Na_2H_3IO_6$ and $Na_3H_2IO_6$, was obtained (Found, in two specimens: Na, 20·55, 20·42. Calc. for $Na_2H_3IO_6$, 16·91; for $Na_3H_2IO_6$, 23·47; mean, 20·19%). Similarly, the iodine determined by method (2) (Part I), *viz.*, 44·79, 44·63, corresponded with the mean of that for the two salts, 46·69 and 43·19, respectively. The mixture did not appear to be homogeneous, as some of the particles had a more shining appearance than the others. It had the smell of iodoform. Under the microscope only crystalline plates of irregular shape could be seen.

Silver Periodates.—Diargentous paraperiodate, $Ag_2H_3IO_6$ or $Ag_4I_2O_9,3H_2O$, was obtained as a by-product in the preparation of periodic acid (Part I). When disodium paraperiodate is boiled with silver nitrate solution, a black precipitate of silver mesoperiodate, Ag_3IO_5, is obtained, which is filtered off hot. The filtrate on cooling gives a crop of yellow crystals of $Ag_2H_3IO_6$ (Found, as AgCl in HNO_3 solution: Ag, 48·94, 48·98. Calc. for $Ag_2H_3IO_6$: Ag, 48·86%). These should not be boiled with water, as they are then changed into the black mesoperiodate.

The oxygen value of the silver salt, unlike that of the analogous sodium salt, $Na_2H_3IO_6$, corresponds with the evolution of the whole of the oxygen and the production of a residue of silver and silver iodide. The oxygen value corresponding with the decomposition $4Ag_2H_3IO_6 = 4AgI + 4Ag + 6H_2O + 9O_2$ is 16·28%.

$Ag_2H_3IO_6$, g.	Vol. of O collected at S.T.P., c.c.	Wt. of O, g.	O, %.
0·0578	6·62	0·009457	16·36
0·0389	4·38	0·006257	16·08
0·0554	6·24	0·008914	16·06

This mode of decomposition was confirmed by heating the salt in a crucible, and examining the residue. The quantitative results were slightly low, since some of the silver iodide began to sublime.

Kimmins (J., 1887, **51**, 356) regards the silver salt, $Ag_2H_3IO_6$, as $Ag_4I_2O_9,3H_2O$. He claims to have dehydrated the compound at 100° to $Ag_4I_2O_9,H_2O$, and at 130° to $Ag_4I_2O_9$. We carried out similar experiments, but failed to obtain any intermediate hydrate. On heating the compound at 85°, the loss of weight indicates decomposition after the whole of water has been lost. Rammelsberg (*Ann. Physik*, 1868, **134**, 368) reported 5·53% loss at 100°, and also that a higher temperature, 150°, is required to remove all the water, but neither Kimmins nor Rammelsberg seems to have heated the compound for a sufficiently long time. The decomposition is rather slow, but proceeds until the loss is 7·75%. The rate of decomposition at 85° is shown below :

Time of heating, hours	15	21	48
Loss, %	7·30	7·45	7·75

There was no further loss on heating at this temperature or at 135°. The loss due to water would have been 6·20%, and the additional loss must be due to evolution of oxygen, a mixture of silver mesoperiodate and silver iodate probably being left (Found : Ag, 53·85, 53·15. Calc. : Ag, 53·06%) : $2Ag_4I_2O_9,3H_2O$ or $4Ag_2H_3IO_6 = 2Ag_3IO_5 + 2AgIO_3 + 6H_2O + O_2$.

Both $AgIO_3$ (Hill and Simmons, *J. Amer. Chem. Soc.*, 1909, **31**, 821; Millon, *Ann. Chim.*, 1843, **9**, 400) and Ag_3IO_5 are found to be quite stable at 135°.

The silver salt $Ag_4I_2O_9,3H_2O$ was heated at 90° in a vacuum desiccator. The rate of dehydration was much slower than when the salt was heated in air, as is seen from the following results :

Time of heating, hours	16	26	31	47
Loss, %	0·90	1·81	2·42	5·90

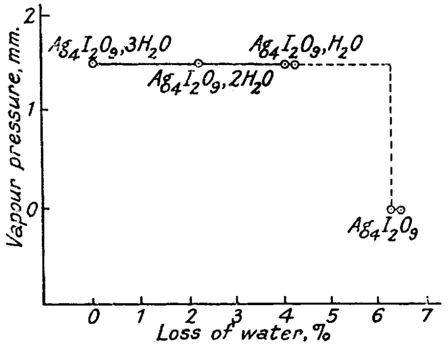
Complete dehydration was attained after about 48 hours.

This slow rate of dehydration or decomposition led us to believe that atmospheric oxygen at ordinary pressure plays some part in the change. In order to confirm this view, the salt was heated in an atmosphere of nitrogen at 85°; the rate of dehydration was found to be much slower than in air at ordinary pressure.

We were thus able to dehydrate the silver salt $Ag_4I_2O_9,3H_2O$ completely in a very high vacuum at 90° (Found, in two specimens : Ag, 51·68, 52·25. Calc. for $Ag_4I_2O_9$: Ag, 52·05%), but were unable to obtain evidence of intermediate hydrates. The oxygen values, obtained as in Part I (6), also correspond with $Ag_4I_2O_9$. Two specimens gave 17·12, 16·95% (Calc. for $2Ag_4I_2O_9 = 4AgI + 4Ag + 9O_2$, 17·34%).

Vapour-pressure Determination.—In the dehydration of the trihydrate, $Ag_4I_2O_9,3H_2O$, we stopped heating at the points corresponding with the di- and the mono-hydrate, and determined the vapour pressures of the solids at 90° in the way described in Part II. The anhydrous salt gave no vapour pressure at 90°, but the other so-called hydrates gave the same small vapour pressure as the dimesoperiodate, $Ag_4I_2O_9,3H_2O$, *viz.*, 1·5 mm. (Fig. 1). At 100° the vapour pressures of the trihydrate and of the two supposed hydrates were all 2·5 mm. These results show that the intermediate hydrates do not exist.

FIG. 1.



Vapour pressures of silver salts at 90°.

Silver Mesoperiodate, Ag_3IO_5.—This salt is obtained by boiling disodium paraperiodate, $Na_2H_3IO_6$, with silver nitrate solution (Wells, *Amer. Chem. J.*, 1901, **26**, 278), whereupon it forms a black precipitate. It was also obtained by boiling the silver salt $Ag_2H_3IO_6$ in water, the crystals becoming black (Rosenheim and Liebknecht, *Annalen*, 1899, **308**, 55). The product was washed thoroughly and dried at 85° (Found, in three specimens, as AgCl : Ag, 62·41, 60·35, 62·10. Calc. for Ag_3IO_5 : Ag, 61·00%). The oxygen values of the first two specimens were 15·12, 14·93 (Calc. for $2Ag_3IO_5 = 2AgI + 4Ag + 5O_2$: 14·87%).

Diargentous Mesoperiodate, Ag_2HIO_5.—By dissolving the yellow crystals of $Ag_2H_3IO_6$ in water containing a few drops of nitric acid and keeping the solution, Kimmins (J., 1887, **51**, 356) obtained reddish-brown crystals of the mesoperiodate. This result was confirmed (Found : Ag, 50·00, 50·17. Calc. : Ag, 50·94%).

SUMMARY.

Disodium paraperiodate, $Na_2H_3IO_6$, does not show any loss of water at 100° in a vacuum, but on strong heating it decomposes : $4Na_2H_3IO_6 = 4Na_2O + 2I_2 + 6H_2O + 7O_2$.

Diargentous paraperiodate, $Ag_2H_3IO_6$, behaves as $Ag_4I_2O_9,3H_2O$ and loses the whole of the water on heating at 90° in a vacuum, anhydrous silver dimesoperiodate $Ag_4I_2O_9$ being obtained. It cannot be dehydrated at ordinary pressure in air as it decomposes. No intermediate hydrate can be obtained by dehydration in vacuum.

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