

XXXIV—CONTRIBUTIONS FROM THE LABORATORY OF  
GONVILLE AND CAIUS COLLEGE, CAMBRIDGE. No. IX.

*Periodates.*

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Cambridge.

AT the suggestion of Mr. Pattison Muir, I undertook the preparation and examination of certain periodates of sodium, potassium, and silver, as the results obtained by previous observers are discordant, and the methods of analysis employed by them appear to be faulty. In most cases, the periodates have been analysed by heating them so as to

convert them into iodides (in some cases there being also a residue of oxide as in Rammelsberg's analysis of  $K_4I_2O_9$ ), and estimating the metal and iodine in the residue. In this investigation, however, the iodine and metal in the periodates have been estimated directly, thereby obviating any error which might arise from a mistaken view as to the exact nature of the residue obtained on heating (for methods of analysis, see Appendix, p. 361).

*Periodates of Sodium.*

Langlois (*Ann. Chim. Phys.*, **34**, 257), by passing chlorine through a boiling solution of equal weights of caustic soda and sodium iodate, obtained the salt  $Na_2H_3IO_6$ ; although this salt is undoubtedly formed in considerable quantities if the solution is saturated in the cold, I found that when it is concentrated at the boiling point of the mixture, a large quantity of another sodium salt is obtained having the composition  $Na_3H_2IO_6$ ; the latter is a white granular precipitate, less soluble than the di-sodium salt, from which it may be separated by washing with small quantities of water for about 30 hours.

Calculated for $Na_2H_3IO_6$ .		Calculated for $Na_3H_2IO_6$ .		Found.
Na..	16·9 p. c.	Na..	23·46 p. c.	Na.. 23·66 p.c.
I...	46·68 ,,	I...	43·19 ,,	I... 42·47 ,,

With a less concentrated solution, I obtained a mixture of about equal quantities of the salts  $Na_2H_3IO_6$  and  $Na_3H_2IO_6$ .

C. Rammelsberg (*Pogg. Ann.*, **134**, 368, 499) does not mention either of these salts, but states that he obtained the salt  $NaIO_4$  on neutralising periodic acid with sodium hydrate. This would point to different thermal relations between the acid and sodium hydrate on neutralisation to those obtained by Thomsen for potassium hydrate.

*Periodates of Potassium.*

*a.*  $KIO_4$ .—This salt is obtained by a method similar to that used for the sodium salts; but as it is more difficult to obtain in consequence of its greater solubility, it is necessary to concentrate the solution of potassium hydrate and potassium iodate before passing chlorine through it. The salt must be recrystallised repeatedly. My analyses of this salt confirm the results of Magnus and Ammermüller, and of Langlois, who, however, did not estimate the potassium and iodine from the periodate but from the iodide obtained on heating.

*b.*  $K_3HI_2O_9$ .—Magnus and Ammermüller say that on concentrating the solution obtained above after removal of  $KIO_4$ , a second salt is obtained in small quantity having the composition  $K_4I_2O_9$ . Langlois

does not mention this salt, but Rammelsberg obtained crystals having the composition  $K_4I_2O_9, 3H_2O$ . I have not investigated this salt, although I observed on concentrating the solution that a further crystallisation took place. I found, however, that on adding a very small quantity of nitric acid to a dilute solution of the washings from the precipitate of  $KIO_4$ , and to the solution left after crystallising out  $KIO_4$ , a well-defined white crystalline precipitate was at once formed, which on analysis was found to have the composition  $K_3HI_2O_9$ . This salt is much less soluble than  $KIO_4$ , and contains no water of crystallisation.

Calculated for $K_3HI_2O_9$ .		Found.	
K....	22·61 per cent.	K....	22·67 per cent.
I....	49·2       ,,	I....	48·23       ,,

#### *Periodates of Silver.*

These are best obtained by dissolving the sodium salts in water containing nitric acid, and precipitating with silver nitrate; different salts being formed according to the strength of nitric acid used: I have found it possible in many cases to change the silver salt by decreasing or increasing the strength of acid. The order in which they are formed is as follows:—

- (1.)  $Ag_2HIO_5$ ,
- (2.)  $Ag_2H_3IO_6$ ,
- (3.)  $Ag_3H_2IO_6$ ,
- (4.)  $AgIO_4 \cdot H_2O$ .

*a.*  $Ag_2HIO_5$ .—If the amount of nitric acid used be just sufficient to effect the dissolution of the sodium salt, a dark-brown precipitate will be formed on adding silver nitrate; this has the formula  $Ag_2HIO_5$ .

Calculated for $Ag_2HIO_5$ .		Found.	
Ag....	50·94 per cent.	Ag....	50·82 per cent.
I.....	29·99       ,,	I.....	28·34       ,,

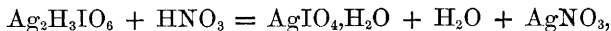
It is generally stated that the silver salt prepared in this way has the composition  $Ag_5IO_6$ ; I have been unable to obtain this salt, however, either by this method or by that given by Rammelsberg, viz., treating  $Ag_4I_2O_9, 3H_2O$  with silver nitrate in the cold.

*b.*  $Ag_2H_3IO_6$ .—This salt is obtained when a slight excess of nitric acid is used in dissolving the sodium salt. It is thrown down as a dark-red precipitate on addition of silver nitrate.

Calculated for $\text{Ag}_2\text{H}_3\text{IO}_6$ .		Found.	
Ag. . . .	48·87 per cent.	Ag. . . .	48·85 per cent.
I . . . .	28·73 „	I . . . .	28·24 „

*c.*  $\text{Ag}_3\text{H}_2\text{IO}_6$ .—With a further excess of nitric acid, a slate-coloured precipitate is formed which on analysis appears to have the composition expressed by the formula  $\text{Ag}_3\text{H}_2\text{IO}_6$ , but the determinations of silver and iodine do not yield satisfactory results owing to the formation of a small quantity of silver iodide which can scarcely be separated from the periodate. In consequence of this, the determination of silver was too low, and that of the iodine too high. I propose to make further experiments on this point.

*d.*  $\text{AgIO}_4, \text{H}_2\text{O}$ .—If the sodium salts be dissolved in concentrated nitric acid and treated with silver nitrate, or if the silver salts mentioned above be dissolved in strong nitric acid and evaporated on a water-bath, orange crystals are formed of the formula  $\text{AgIO}_4, \text{H}_2\text{O}$ . This salt is stated by Rammelsberg and others to be without water of crystallisation. It is very difficult to estimate the water in this salt, as part of the water is given off at the temperature necessary to free the crystals from the last traces of nitric acid, but the whole of the water is not removed until the salt has been kept for some hours in the air-bath at  $130^\circ$ . The results obtained, however, leave no doubt as to the composition of the salt. The change may probably be expressed by the equation



the silver nitrate crystallises out on evaporating the nitric acid solution after the separation of the orange crystals.

*e.*  $\text{AgIO}_4$ .—On keeping the orange crystals for six hours at  $130^\circ$ , a bright yellow powder is formed which has the formula  $\text{AgIO}_4$ .

Calculated for $\text{AgIO}_4$ .		Found.	
Ag. . . .	36·12 per cent.	Ag. . . .	36·6 per cent.
I . . . .	42·4 „	I . . . .	41·45 „

*f.*  $\text{Ag}_4\text{I}_2\text{O}_9, 3\text{H}_2\text{O}$ .—On treating the orange crystals,  $\text{AgIO}_4, \text{H}_2\text{O}$ , with water, periodic acid is formed, and light-yellow crystals which have the composition  $\text{Ag}_4\text{I}_2\text{O}_9, 3\text{H}_2\text{O}$ . This was proved by direct estimation of the silver and iodine, and also by driving off the water, and estimating the silver and iodine in the dehydrated salt (see below).

*g.*  $\text{Ag}_4\text{I}_2\text{O}_9, \text{H}_2\text{O}$ .—On keeping the light-yellow crystals at  $100^\circ$  for 12 hours, a claret-coloured salt is obtained, which has the formula

$\text{Ag}_4\text{I}_2\text{O}_9, \text{H}_2\text{O}$ , proved by direct estimation of the silver and iodine, and also by analysis of the dehydrated salt.

Loss of water calculated = 4.08 per cent.  
 „ „ found = 4.15 „

Rammelsberg obtained a loss of 5.53 per cent. at  $100^\circ$ ; he says that a portion of the third molecule is given off, but I found the weighings to be quite constant after 12 hours, and that no more water was given off until the temperature reached  $130^\circ$ , at which temperature the whole of the water was removed. Rammelsberg also states (*Pogg. Ann.*, **134**, 368) that if the salt with 3 mols.  $\text{H}_2\text{O}$  be first converted into  $\text{Ag}_4\text{I}_2\text{O}_9, \text{H}_2\text{O}$ , it then requires a higher temperature— $150^\circ$ —to drive off the last molecule of water.

*h.*  $\text{Ag}_4\text{I}_2\text{O}_9$ .—This salt is formed as a chocolate-coloured powder on keeping the claret-coloured salt at  $130^\circ$  for 12 hours.

Loss of water calculated = 2.12 per cent.  
 „ „ found = 2.49 „

Estimation of silver and iodine in the dehydrated salt—

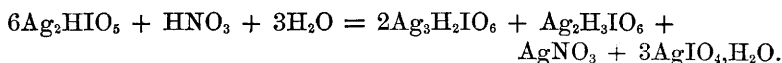
Calculated for $\text{Ag}_4\text{I}_2\text{O}_9$ .		Found.	
Ag. . . .	52.04 per cent.	Ag. . . .	52.01 per cent.
I . . . .	30.6 „	I . . . .	31.16 „

I have, therefore, prepared and analysed the following silver periodates:—

- (1.)  $\text{Ag}_2\text{HIO}_5$  (dark-brown),
- (2.)  $\text{Ag}_2\text{H}_3\text{IO}_6$  (dark-red),
- (3.)  $\text{Ag}_3\text{H}_2\text{IO}_6$  (slate-coloured),
- (4.)  $\text{AgIO}_4, \text{H}_2\text{O}$  (orange crystals),
- (5.)  $\text{AgIO}_4$  (bright-yellow powder),
- (6.)  $\text{Ag}_4\text{I}_2\text{O}_9, 3\text{H}_2\text{O}$  (light-yellow),
- (7.)  $\text{Ag}_4\text{I}_2\text{O}_9, \text{H}_2\text{O}$  (claret-coloured),
- (8.)  $\text{Ag}_4\text{I}_2\text{O}_9$  (chocolate-coloured).

The effect of nitric acid in bringing about a change in the silver salts is well shown by its action on  $\text{Ag}_2\text{HIO}_5$ . If this salt is treated with acid not strong enough to completely dissolve it, it is converted into the dark-red and slate-coloured salts which can easily be separated, and on filtering from the precipitated salts, and evaporating the filtrate on a water-bath, orange-coloured crystals of  $\text{AgIO}_4, \text{H}_2\text{O}$  are deposited; whilst on further evaporation a small quantity of silver nitrate separates out.

This reaction is probably represented by the following equation :—



On treating the potassium salts with strong nitric acid and silver nitrate, the same silver periodate,  $\text{AgIO}_4, \text{H}_2\text{O}$ , is produced on evaporation as that formed from the sodium salts. I am at present investigating the nature of the intermediate compounds, and also the effect of heat on the periodates, to see whether it is possible by this means to pass from a member of one series to a member of another, as from  $\text{H}_3\text{IO}_6$  to  $\text{H}_3\text{IO}_5$ . These results, together with analyses of periodates of other metals, I hope to communicate in another paper, when it may be possible to criticise the existing scheme of classification of these compounds.

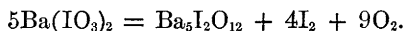
I must express my thanks to Mr. Pattison Muir for continued help and suggestions during the course of these experiments.

#### *Appendix.*

*Methods of Analysis.*—The sodium and potassium were estimated in the usual way as sulphates, and the silver as chloride.

The iodine was estimated by a method similar to that used for determining this element in iodates. A weighed quantity of periodate was treated with a concentrated solution of potassium iodide and excess of strong hydrochloric acid in a bottle with a well-fitting stopper, which was immersed in boiling water for six hours; the iodine was then titrated with sodium thiosulphate. One-eighth the quantity so found represents the amount present in the given weight of the periodate.

In order to test this method, I prepared some pure barium periodate by passing air over heated barium iodate, the amount obtained being within 0.1 per cent. of that required by equation :—



This salt, and a silver salt of known composition, gave results agreeing within 0.2 per cent. of the amount required by calculation.

The best results are obtained with about 0.3 gram of the sodium or potassium salt and 0.5 gram of the silver salts, in a bottle of about 250 c.c. capacity. The action is quite complete after keeping the mixture at  $100^\circ$  for six hours.