230. *Periodic Acid and Periodates. Part II. The Dehydration of Paraperiodic Acid.*

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Lamb (*Amer. Chem. J.*, 1902, **27**, 134) states that metaperiodic acid, HIO_4, is obtained by heating paraperiodic acid at 100° under a pressure of 12 mm. for about 22 hours. This experiment was repeated in a vacuum desiccator containing an electrical heating arrange-

ment. The acid lost two molecules of water, leaving metaperiodic acid, but during the process of heating, sublimation occurred and the loss of water could not be determined accurately by weighing the residue. At a lower temperature, *viz.*, 87°, a longer time, about 48 hours, was required for the dehydration and some sublimation took place. By heating at 80° in vacuum for 15—45 hours, no sublimation occurred, and the loss of weight corresponded with the formation of *dimesoperiodic acid*, $H_4I_2O_9$. The formation of these two acids was demonstrated both by analyses of the residues and by measurements of vapour pressure during the course of dehydration.

The iodine in the residue was determined by method (3) and the oxygen values by method (6), in Part I.

Experimental.

The following are the results of the dehydration in a vacuum at 100°.

Sample.	HIO_4, g.	AgI obtained, g.	I found, %.	Sample.	HIO_4, g.	AgI obtained, g.	I found, %.
A	0·0500	0·0618	66·79	C	0·0380	0·0469	66·69
B	0·0696	0·0868	67·39	D	0·1940	0·2396	66·74

Mean: I, 66·90 (Calc. for HIO_4: I, 66·14%).

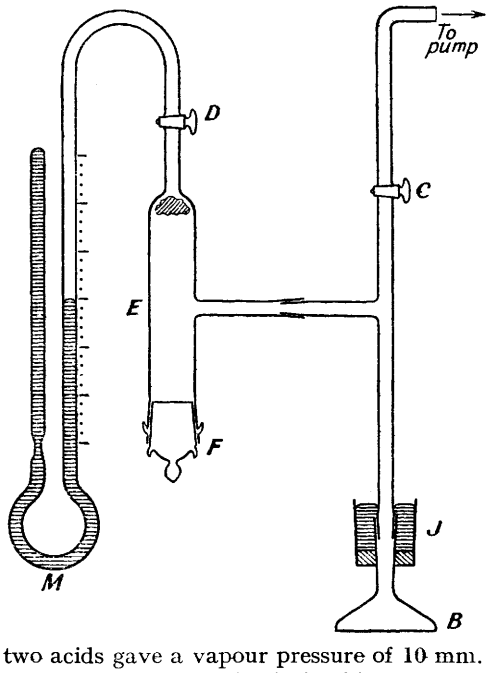
Sample.	HIO_4, g.	Vol. of O collected at S.T.P., c.c.	Wt. of O, g.	O, %.
A	0·0301	6·05	0·008642	28·71
B	0·0783	15·44	0·022050	28·14
C	0·1390	27·60	0·039430	28·40
D	0·0646	12·67	0·018100	28·01
			Mean	28·31

Decomposition according to the equation $4HIO_4 = 2H_2O + 2I_2 + 7O_2$ requires O, 29·16%.

The percentage of iodine is somewhat high and that of oxygen somewhat low, so a small amount of decomposition of periodic acid had occurred. On the assumption that this took place with the formation of iodic acid, the composition of the residue would be HIO_4, 87·00; HIO_3, 13·00%. If iodine pentoxide is formed, the residue would be HIO_4, 92·33; I_2O_5, 7·67%.

Vapour Pressure of Para- and Meta-periodic Acids at 100°.—In these experiments the acid was contained in a small bottle, *B* (Fig. 1), which was connected on one side with a manometer, *M*, through a tube *E* having a stopper *F* and a stop-cock *D*. Some washed and dried glass wool was placed in *E* in order to protect the mercury of the manometer from attack by the product of sublimation. The bottle, *B*, was also connected with a double-fall automatic Sprengel pump, a stop-cock *C* being interposed.

Fig. 1.



At room temperature a high vacuum was recorded by the manometer. The stop-cock *C* was then closed, and the bottle *B* heated in a water-bath at 100°. The vapour pressure on the manometer was read. In order to avoid leakage through the ground joint caused by expansion on heating, the neck of the bottle was fitted into a rubber stopper surrounded with a wide tube *J* containing mercury, as shown.

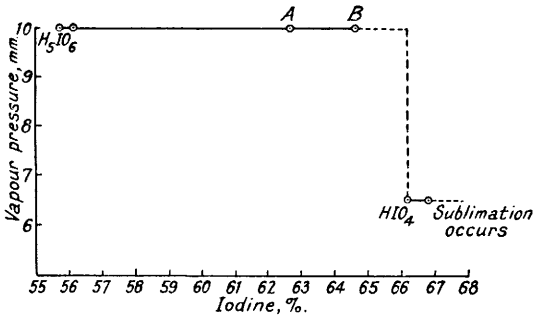
The vapour pressure of the paraperiodic acid at 100° was thus found to be 10 mm., and that of metaperiodic acid, 7·5 mm. A mixture of the two acids gave a vapour pressure of 10 mm.

It was not found possible to dehydrate the paraperiodic acid completely in this apparatus at 100° since copious sublimation occurred, leading to attack of the mercury in the pump and the manometer. Slight decomposition of the acid also took place, a few bubbles of gas being collected from the pump. The difference between the two vapour pressures at 100° is small and we were thus not able to find if there was any other intermediate hydrate between

$I_2O_7,2H_2O$ and $I_2O_7,5H_2O$, although we have been able to prepare dimesoperiodic acid, $H_4I_2O_9$, as described later, by dehydrating paraperiodic acid at 80° in a vacuum desiccator. Moreover, by reason of the slight decomposition, we were unable to find a point between the vapour pressures of the para- and the meta-acid. The graph (Fig. 2) shows the vapour pressures of these two acids, and also the points obtained with two products made by partially dehydrating the para-acid at 100° in a vacuum desiccator. The composition of the residue in the bottle *B* was determined by an estimation of iodine by method (3) of Part I.

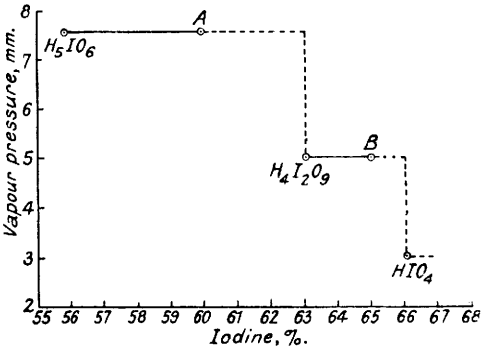
Dimesoperiodic Acid, $H_4I_2O_9$.—Lamb (*loc. cit.*) attempted to prepare mesoperiodic acid, H_3IO_5, by dehydrating paraperiodic acid at different temperatures and pressures. In all experiments, he found that the point corresponding to the hydrate H_3IO_5 was passed without the least indication of the formation of a definite compound. His observations have been confirmed in so far as the meso-acid is concerned, but we have found that a definite point is reached which corresponds to the formation of another hydrate, *dimesoperiodic acid,* $H_4I_2O_9$.

FIG. 2.



Vapour-pressure curve of paraperiodic acid and metaperiodic acid at 100°.

FIG. 3.



Curve showing vapour pressure by dehydrating paraperiodic acid at 85°. *Points A and B were obtained from samples prepared at* 85° *in a vacuum desiccator.*

Paraperiodic acid was heated in the vacuum desiccator at 80° for 15—45 hours and the loss of water determined, since no sublimation occurred at this temperature.

Time of heating, hours.	Wt. of H_5IO_6, g.	Wt. of $H_4I_2O_9$ formed, g.	Loss of wt. due to H_2O, g.	H_2O, %.
15	1·0768	0·9589	0·1179	10·93
19	0·9962	0·8848	0·1114	11·18
29	0·4522	0·4002	0·0520	11·50
45	0·6813	0·6022	0·0791	11·75

The loss calculated for the reaction $2H_5IO_6=H_4I_2O_9 + 3H_2O$ is 11·84%. No further loss was obtained in 48 hours.

Iodine was determined in the dimesoperiodic acid $H_4I_2O_9$ by method (3) (Found : I, 62·68, 62·05, 62·90, 62·70, 62·70 in five separate preparations A—E, as below. $H_4I_2O_9$ requires I, 63·02%). The oxygen value was determined by method (6). The calculated value for $H_4I_2O_9$ is 27·87% ($2H_4I_2O_9 = 4H_2O + 2I_2 + 7O_2$).

Sample.	$H_4I_2O_9$, g.	Vol. of O collected at S.T.P., c.c.	Wt. of O, g.	O, %.
A	0·0600	11·20	0·0160	26·66
B	0·0610	11·20	0·0160	26·22
C	0·0267	4·84	0·0068	25·90
D	0·0694	13·10	0·0187	26·90
E	0·0454	8·50	0·0121	26·74

The formation of $H_4I_2O_9$ was confirmed by determining the vapour pressures of para-, dimeso-, and meta-periodic acids and their mixture at 85°; these were 7·5, 5, and 3 mm. respectively. A mixture of the last two gave a vapour pressure of 5 mm., and one of the first two 7·5 mm. The curve (Fig. 3) shows the relationship between the percentage of iodine and vapour pressure at 85°. The points A and B were obtained from samples prepared by dehydration at 85° in a vacuum desiccator.

Attempts to prepare iodine heptoxide by heating paraperiodic acid at a higher temperature

in the vacuum desiccator resulted in the formation of iodic acid; the residue after heating at 125° was analysed for iodine by method (3) (Found in three separate preparations: I, 70·01, 70·36, 73·11. Calc. for HIO_3: 72·15%).

The oxygen values were obtained by method (6): that of HIO_3 is 22·72% ($4HIO_3 = 2H_2O + 2I_2 + 5O_2$).

Sample.	Residue taken, g.	Vol. of O collected at S.T.P., c.c.	Wt. of O, g.	O, %.
A	0·0430	6·80	0·009714	22·87
B	0·0418	6·57	0·009385	22·45

It was thought that the sublimate formed during the preparation of metaperiodic acid by the dehydration of paraperiodic acid in a vacuum desiccator might be iodine heptoxide. The para-acid was heated in an open weighing bottle at 100° in the vacuum desiccator, and the heating continued for a long time in order to obtain enough sublimate on the sides of the weighing bottle. The meta-acid was removed from the bottle, the sublimate weighed, and the iodine value found by method (3) (Found in two separate preparations: 66·61, 68·04, mean 67·32%). The sublimate does not consist of iodine heptoxide (Calc.: I, 69·39%) but of metaperiodic acid (Calc.: I, 66·14%). The slightly higher value is due to formation of iodic acid, since the sublimate gave the reaction for this.

SUMMARY.

Paraperiodic acid, $HIO_4,2H_2O$, at 100° in a vacuum loses two molecules of water, and metaperiodic acid, HIO_4, is formed. On heating at 80°, in a vacuum, two molecules of paraperiodic acid lose three molecules of water and dimesoperiodic acid, $H_4I_2O_9$, is formed. Mesoperiodic acid, H_3IO_5, and the anhydride, I_2O_7, were not obtained.

The vapour pressures of paraperiodic acid at 100° and 85° are 10 and 7·5 mm., respectively; those of dimeso- and meta-periodic acid at 85° were 5 and 3 mm., respectively.

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