XXVI.—*Mercury and Bismuth Hypophosphites.*

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It is probable that Rose's well-known observation in 1827 that mercuric chloride is reduced by a solution of hypophosphorous acid, first to mercurous chloride and then to metallic mercury, is the cause of no attempts having been made to prepare a mercury hypophosphite, as there seemed to be but little chance of success. At the suggestion of Dr. Divers, to whom I am much indebted for advice, I have tried the effect of using the nitrates of mercury, and in the course of my experiments have obtained the salt which is described below.

Mercurous Nitrate Hypophosphite.

This double salt is the only mercury-derivative of hypophosphorous acid I have been able to prepare ; it is precipitated on adding a solution of potassium or barium hypophosphite to a solution of mercuric or mercurous nitrate, but the mercury solution must not be too dilute, and as free from acid as possible ; care must also be taken to avoid using excess of the hypophosphite. The compound is not obtained when the mercury nitrate solution is added to the hypophosphite, or if too much of the latter is added to the mercury nitrate, as in either case the double salt is at once decomposed.

Since the formation of the salt from mercuric nitrate necessarily involves the oxidation and waste of much of the hypophosphite, and also yields a mother liquor which acts strongly on the precipitate, mercurous nitrate should be used ; moreover potassium hypophosphite is preferable to the barium salt, as with the latter the precipitate is liable to contain barium, apparently as nitrate.

The solution of mercurous nitrate, free from nitrous acid, is best prepared by dissolving mercuric oxide to saturation in nitric acid, and then shaking the solution violently with metallic mercury for a few minutes ; in this way, the mercuric salt is quickly and completely changed to mercurous salt.

As the white precipitate obtained on adding potassium hypophosphite to an excess of mercurous nitrate is slowly decomposed when left in contact with the mother liquor, it must be quickly collected and drained on a tile, without previous washing. The *mercurous nitrate hypophosphite* thus obtained is unstable when moist, although when dry it decomposes but slowly, becoming grey in the course of time. It is a white, micaceous powder, slightly soluble in water, by which it is soon decomposed with separation of mercury. Its composition is expressed by the formula $\text{HgH}_2\text{PO}_2, \text{HgNO}_3, \text{H}_2\text{O}$; it loses its water of crystallisation in a vacuum desiccator, but undergoes scarcely any decomposition, even when kept for some time. When heated, it turns grey above 90° , and explodes a little above 100° , yielding mercury and nitrous vapours; it also explodes if touched with a hot wire.

With hydrochloric acid, it first gives mercurous chloride and then metallic mercury, whilst hot, strong, nitric acid dissolves it completely with escape of nitrous fumes. Sodium chloride converts it into mercurous chloride and sodium hypophosphite, which only very slowly react, yielding metallic mercury. Potassium hydroxide blackens it probably from formation of mercurous oxide.

The mercury and phosphorus in the salt were determined by dissolving it in nitric acid, evaporating to dryness, dissolving in hydrochloric acid, and precipitating the mercury by hydrogen sulphide, and the phosphoric acid by magnesia mixture. The mercuric sulphide was freed from any sulphur precipitated along with it, and dried at 105 – 110° . The nitric acid was estimated by treating the salt with strong sulphuric acid in Lunge's nitrometer. Loss of weight in the desiccator served for the water determination. The analytical results which follow refer to three separate preparations of the salt.

	Calculated.	Found.		
		I.	II.	III.
Mercury	73.39	73.35	73.01	73.04
Nitrogen	2.59	2.78	2.76	2.82
Phosphorus	5.68	5.56	5.25	5.50
Water	3.30	3.01	2.45	—

This salt is of interest as a double salt of univalent or quasi-univalent mercury, since it points to the mercurous salts being salts of the radicle $(\text{Hg}_2)''$ rather than of Hg' .

A salt has been described by H. Rose (*Ann. Phys. Chem.*, 1837, **40**, 75) as produced by the action between mercuric nitrate and phosphine, and to which he assigned the formula

This explosive substance* would seem to be related to the salt I have described, for it is not remote in composition from

and is more probably a mercurous than a mercuric salt.

Bismuth Hypophosphite.

This salt has not hitherto been described. It may be prepared by mixing a solution of bismuth nitrate, free from any unnecessary excess of nitric acid, with barium or potassium hypophosphite, avoiding excess of bismuth nitrate, as the salt is soluble in it. The bismuth hypophosphite, which is precipitated as a white crystalline powder, slowly decomposes in contact with the mother liquor, but, if collected at once and dried on a porous tile, it can be preserved for days unchanged.

The analysis of this salt was carried out much in the same way as that of the mercury salt, except that the bismuth sulphide was dissolved in nitric acid and the solution precipitated by ammonium carbonate as usual. Water was determined as loss in the vacuum desiccator. In the following table the calculation is for

which therefore expresses the composition of the salt.

	Calculated.	Found.		
		I.	II.	III.
Bismuth	49.41	49.49	49.49	48.77
Phosphorus	22.09	21.67	21.34	21.19
Water	4.29	3.11	3.26	3.39

Bismuth hypophosphite decomposes very readily when heated, becoming black and giving off phosphine at temperatures only a little above 100°. At a stronger heat, metallic globules and bismuth phosphate are obtained. The globules consist of metallic bismuth free from phosphorus. As about two-thirds of the bismuth is obtained as metal, the decomposition of the bismuth hypophosphite by heat may be expressed by the equation—

This hypophosphite is noticeable for yielding metal instead of phosphide, but this fact is in accordance with the observation of Berzelius, that bismuth phosphide completely decomposes when heated.

* It was again examined by Aschan in 1885 (*Chem. Zeit.*), but not quantitatively.