Mercury and Bismuth Hypophosphites.

by

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Probably because of H. Rose's well-known observation in 1827 of the reduction of mercuric chloride to mercurous chloride and of this to metallic mercury by a solution of hypophosphorous acid, no expectation of success has led to any attempts to prepare a mercury hypophosphite. At the suggestion of Dr. Divers, F.R.S., to whom I am much indebted for advice, I have tried the use of the nitrates of mercury, and have thereby obtained the salt which I shall now describe.

Mercurous nitrate hypophosphite.

This double salt is the only mercury derivative of hypophosphorous acid I have been able to produce. It is precipitated from a solution not too dilute, and almost as free from acid as possible, of either mercuric or mercurous nitrate by a solution of potassium or barium hypophosphite used in quantity small enough to leave some of the mercury nitrate in solution. It can not be got by adding the mercury nitrate to the hypophosphite, or when too much of the latter salt is added to the mercury nitrate, because, in either case, it is at once decomposed.

Since the formation of the salt from mercuric nitrate necessarily involves the oxidation and waste of much of the hypophosphite added, and also yields a mother-liquor very active on the precipitate, mercurous nitrate is the proper substance to select in preparing it.

Potassium hypophosphite is also preferable to the barium salt, for when the latter is used the precipitate is liable to contain barium, apparently as nitrate.

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

As the white precipitate obtained by adding the potassium hypophosphite to the excess of mercurous nitrate is slowly decomposed by its mother-liquor, it must be quickly removed and drained on a tile without previous washing.

Mercurous nitrate hypophosphite is unstable, but when dry it only slowly decomposes, becoming grey in the course of some days. 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—

$$HgH_2PO_2,HgNO_3,H_2O$$

It loses its water in a vacuum desiccator with scarcely any further decomposition for some time. Heated, it turns slightly grey above 90° and explodes a little above 100° yielding mercury and nitrous vapours. Any quantity of it can be exploded at the common temperature by touching it with a hot wire.

With hydrochloric acid, it first gives mercurous chloride and then metallic mercury. With cold dilute nitric acid it yields metallic mercury, while 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 to give metallic mercury. Potassium hydroxide blackens it by formation probably of mercurous oxide at first.

The mercury and phosphorus in the salt were determined by dissolving it in nitric acid, evaporating to dryness, dissolving in hydrochloric acid, precipitating mercury by hydrogen sulphide, and phosphoric acid by magnesia mixture. The mercuric sulphide was freed from any co-precipitated sulphur, 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.

	Calc.	Found.		
		I.	II.	III.
Mercury	73·39	73·35	73·01	73·04
Nitrogen	2·57	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 mercurous salts being salts of the radical $(Hg_2)''$ rather than of $(Hg)'$.

A salt has been described by H. Rose (*Pogg. Ann.*, **40**, 76.), as produced by reaction between mercuric nitrate and phosphine and to which he has given the formula—

$$P_2Hg_3'',3[Hg''(NO_3)_2,Hg''O]$$

This explosive body* would seem to be related to the salt I have described, for it is not remote in composition from $3Hg'NO_3,Hg'H_2PO_2$, and is more probably a mercurous than a mercuric salt.

Bismuth Hypophosphite.

How it comes that this salt has hitherto escaped notice it is not

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

easy to understand. It is prepared by mixing a solution of bismuth nitrate, free from any unnecessary excess of nitric acid, with barium or potassium hypophosphite, avoiding excess of the bismuth nitrate, in which it is soluble. The bismuth hypophosphite precipitates as a white crystalline powder, slowly decomposed by its mother-liquor, and soluble in bismuth nitrate solution. Filtered off 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 $Bi(H_2PO_2)_3,H_2O$, which therefore expresses the composition of the salt :—

	Calc.	Found.		
		I.	II.	III.
Bismuth	49·41	49·49	49·40	48·77
Phosphorus	22·09	21·67	21·34	21·19
Water	4·27	3·11	3·26	3·39

Bismuth hypophosphite decomposes very readily by heat, 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 washed with dilute hydrogen chloride to cleanse them from adhering phosphate and then dissolved in nitric acid prove to be 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—

$$3Bi(H_2PO_2)_3=2Bi+Bi(PO_3)_3+6P+9OH_2$$

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