

XXXV.—*Mercury Hyponitrites.*

By P. C. RAY, D.Sc. (Edin.).

PRELIMINARY NOTICE.

IT has been shown elsewhere* that mercurous nitrite, on prolonged contact with a large bulk of water, partially dissociates into mercury and mercuric nitrite, but that nearly 22 per cent. of the salt dissolves *as such*. We have thus a neutral solution containing both mercurous and mercuric nitrite. It occurred to me that, if this solution were treated according to the method of Divers,† the discoverer of hyponitrites, it might be possible to obtain the corresponding mercury compounds.

Mercurous Hyponitrite.

Divers reduced sodium nitrite by means of sodium amalgam, neutralised the solution with acetic acid, and finally added silver nitrate to it. This method, however, proved to be a failure in the present case. Instead of mercurous hyponitrite, as was expected, there was an almost immediate grey, and even blackish, deposit of metallic mercury.

The explanation of the reduction in this case is probably to be looked for in the formation of hydroxylamine simultaneously with the hyponitrite. It thus became necessary to find a method of preparing sodium hyponitrite to the exclusion of this reducing agent.

On consulting the literature on this subject, I came across Zorn's method as improved by Dunstan and Dymond (Trans., 1887, 51, 646). I found that the sodium hyponitrite prepared by their method is quite free from hydroxylamine; and, although a trace of ferric hydroxide, probably in a colloidal form, passes through the filter paper, imparting to the liquid a slight brown colour, it is completely precipitated and the solution becomes perfectly clear on allowing it to stand overnight.

Preparation.—To the solution containing mercurous and mercuric nitrite, sodium hyponitrite solution in a highly diluted form is cautiously added drop by drop; a copious, flocculent, yellow precipitate

* This vol., p. 340; also *Zeit. anorg. Chem.*, 1896, 12, 365.

† *Proc. Roy. Soc.*, vol. xix. (1870—71).

is at once obtained, which is apt to turn slightly greenish afterwards. A good deal depends on the way in which the two solutions are mixed ; for instance, if the order be reversed, or if too much of the hyponitrite solution be used at once, the precipitate turns grey and even black. Although it is possible to remove the whole of the mercurous mercury by the addition of the hyponitrite solution in successive portions, a considerable quantity of mercuric mercury is carried down along with the mercurous. If more hyponitrite is now added to the filtrate containing only mercuric nitrite, a voluminous, gelatinous, white precipitate, exactly resembling aluminium hydrate, is thrown down.

There are substantial grounds for believing that the yellow substance obtained above by fractional precipitation is a mixture of mercurous and mercuric hyponitrites. It thus became necessary to study the properties and composition of the latter before those of the former could be ascertained.

Mercuric Hyponitrite.

The solution containing the mercurous and mercuric nitrites was treated with sodium chloride to get rid of the mercurous mercury, and to the filtrate, which now contained only mercuric nitrite, sodium hyponitrite solution was added ; the gelatinous, flocculent precipitate thus produced was thoroughly washed on a filter, and dried over sulphuric acid. The impalpable, dirty white powder thus obtained is only sparingly soluble even in boiling dilute nitric acid, whilst strong nitric acid, strange to say, has scarcely any action on it ; it is, however, readily soluble in warm, dilute hydrochloric acid. Two separate preparations were analysed.

- I. 0.2558 salt gave 0.2516 HgS. Hg = 84.83.*
- II. 0.2238 „ „ 0.2180 HgS. Hg = 83.96.
- II. 0.2328 „ „ 6.6 c.c. moist nitrogen at 33° and 757.5 mm. N = 2.97.

The formula $\text{Hg}(\text{NO})_2 + 3\text{HgO} + 3\text{H}_2\text{O}$, or $\text{Hg}(\text{NO})_2 + 3\text{Hg}(\text{OH})_2$ requires Hg = 83.16 ; N = 2.91 per cent.

The presence of water was proved qualitatively ; it is easily given off when the substance is gently heated in a test-tube.

Analyses of two separate preparations of the light yellow powder, a mixture of mercurous and mercuric hyponitrites, gave the following results after being dried over sulphuric acid.

- I. 0.371 gave 0.367 HgS. Hg = 85.28.
- II. 0.1565 „ 0.1532 HgS. Hg = 84.37.

The nitrogen in I amounted to 4 per cent.

$\text{Hg}_2(\text{NO})_2$ requires Hg = 86.95 ; N = 6.09 per cent.

* As the sodium hyponitrite solution was alkaline, it is very likely traces of mercuric oxide were carried down ; hence the percentage of mercury is rather too high.

The low percentage of nitrogen and of mercury in the mixture is now easily accounted for, as it contained a considerable proportion of mercuric hyponitrite.

Apart from the results of the analysis, the reasons for believing that in the above mixture we really have a mercurous hyponitrite are (1) That when gently warmed with dilute hydrochloric acid a part of the mercury is thrown down as calomel and bubbles of a gas are slowly given off, consisting apparently of a mixture of nitrogen and nitrogen monoxide; (2) That the pale yellow, amorphous substance resembles in physical properties the analogous silver compound. If the silver compounds be compared with the corresponding mercury salts, it is found that the colour is deeper in the case of the metal of high atomic weight; silver nitrite, for example, is pale yellow, whereas mercurous nitrite is distinctly yellow; silver bromide is pale yellow, and mercurous bromide has been obtained as yellow spangles; again, silver iodide is distinctly yellow, and the colour of mercurous iodide is, perhaps, a shade deeper.*

The hyponitrites of mercury have been found to be far more stable towards heat than the nitrites and nitrates of this metal. I am continuing this work in the hope of discovering a method of obtaining *pure* mercurous hyponitrite, and I also intend to take up a systematic examination of the gases evolved by the action of heat and of dilute acids on these compounds, on the lines of Divers and of Berthelot and Ogier.†

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE,
CALCUTTA.
