

CXXXII.—*The Decomposition of Mercurous and Silver Hyponitrites by Heat.*

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IN order to investigate the action of heat on mercurous and silver hyponitrites, the salts were heated in a short length of combustion tube, as previously described (Trans., 1905, **87**, 180), a tube filled with glass beads moistened with aqueous potassium hydroxide being interposed between the heating tube and the Sprengel pump to absorb any nitrous fumes.

I. *Mercurous Hyponitrite*.*

The salt began to decompose, although very slowly, at 80°, and, on further raising the temperature, assumed a black colour, eventually changing at 150° to reddish-yellow, at which point decomposition ceased. No further evolution of gas was observed on raising the temperature to 200°, and no nitrous fumes were at any time visible.

A. *Analysis of the Gases Evolved.*

The nitric oxide in the gaseous product was estimated by absorption in alkaline sodium sulphite (Divers, Trans., 1899, **75**, 82), in which nitrous oxide is practically insoluble (see p. 1402). The nitrous oxide in the residual gas, which was found to support combustion without appreciable diminution of volume, was estimated by absorption in cold water. A small residue of nitrogen always remained. The nitrogen absorbed as nitrite by the alkali hydroxide was also estimated.

* Divers states (Trans., 1899, **75**, 120, 121) that "mercuric hyponitrite is decomposed by heat largely into mercuric oxide and nitrous oxide, but partly into metal and nitric oxide . . . the decomposition of mercurous hyponitrite by heat resembles that of the mercuric salt, except that much more metal is produced, as is natural."

B. Analysis of the Solid Residue.

The residue consisted of mercury, part of which was deposited in the cooler parts as a mirror, and mercuric oxide; the latter, however, was always associated with distinct traces of mercurous nitrate, and considerable difficulty was experienced in determining its amount. When the residue was treated with dilute nitric acid in the cold, the mercuric oxide and mercurous nitrate were at once dissolved, leaving globules of mercury behind, but no concordant results could be obtained, the amount of mercurous mercury being disproportionately high. Treatment with dilute hydrochloric acid was equally unsatisfactory.

Hada has already shown (Trans., 1896, 69, 1667) that in presence of finely-divided mercury, a considerable proportion of mercuric nitrate or chloride is reduced to the mercurous state. The best method of determining the amount of mercurous nitrate seemed to be to estimate the nitrogen by Dumas' method. In some cases, therefore, the decomposition tube was once more exhausted and heated to dull redness; the nitrous fumes evolved were absorbed in the alkali, and the gas which was collected was found to be pure oxygen.* The nitrogen which was absorbed by the alkali hydroxide, in the form of nitrate and nitrite, which represented the nitrogen of mercurous nitrate, was estimated. That the residue really contained mercurous and not mercuric nitrate was proved by subjecting it to repeated levigation. In this manner the minute globules of mercury were removed, and, on treatment with dilute hydrochloric acid, calomel was still obtained, whilst the filtrate gave mercuric mercury.

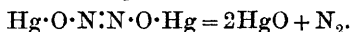
In one experiment, 0.399 gram of salt gave 1.7 c.c. of nitrogen, 8 c.c. of nitrous oxide, and 19.1 c.c. of nitric oxide; the nitrogen absorbed in the potassium hydroxide in the circulation tube as nitrite in the first stage was 0.79 c.c., and that absorbed in the second stage in the form of nitrate and nitrite, due to mercurous nitrate, was 1.7 c.c., the total moist nitrogen being 21.74 c.c., measured at 27° and 760 mm.; the percentage of nitrogen therefore amounts to 6.03, that required by theory being 6.09.

The results of the above and two more experiments in which 0.329 gram and 0.4335 gram of salt respectively were heated are given in the following table, the nitrogen in the different forms being given in percentages :

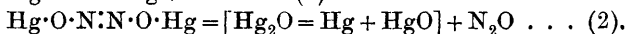
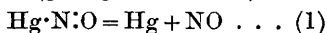
* The amount of oxygen was found to correspond with the mercuric oxide formed in the several reactions given below.

No. of expt.	N ₂ as such.	N ₂ as N ₂ O.	N ₂ as NO.	N ₂ absorbed in KOH in both stages.	Total N ₂ .
I.	0.47	2.22	2.65	0.69	6.03
II.	0.54	2.59	2.44	0.61	6.18
III.	0.61	2.16	2.50	0.85	6.12

From the results recorded above, it is established that the main products of decomposition of mercurous hyponitrite are mercury and mercuric oxide, with nitric oxide and nitrous oxide; mercurous nitrate and nitrogen are formed in small quantities only, and are probably due to secondary actions. If the "oxylic" formula of the salt be accepted with the diazo-grouping (Divers, *loc. cit.*, 123), then, according to the usual decomposition of diazo-compounds, nitrogen should have formed the main product; in fact, Zorn's observation that ethyl hyponitrite breaks up into nitrogen and alcohol (and aldehyde) would lend support to this view. We should thus have expected the decomposition to proceed according to the following equation, the more so as mercuric oxide is a stable compound at 150—200°:

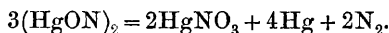


But as the amount of nitrogen actually obtained was very small, the "oxylic" structure alone does not seem satisfactorily to explain the experimental results. As, however, nearly half the amount of nitrogen of the salt appears as nitric oxide, a sort of tautomeric change seems to take place under the action of heat, and, roughly speaking, half the number of molecules retains the "oxylic" (yielding nitrous oxide) and the other half assumes the "imidic" structure (giving nitric oxide), thus:

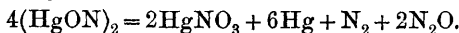


This would bring the hyponitrite into close relationship with the corresponding nitrites (compare Rây and Gañguli, *Proc.*, 1905, 21, 278).*

We have now to account for the formation of the small, but by no means negligible, quantity of mercurous nitrate. The reaction which readily suggests itself is



But this equation is hardly admissible, as the amount of free nitrogen actually formed is equal to that existing in the mercurous nitrate (see Expt. I). Possibly the nitrate is the product of a more complex reaction, for example,



* The "imidic" constitution of mercury hyponitrites has already been hinted at (*Trans.*, 1897, 71, 1104).

II. *Silver Hyponitrite.*

In view of the interesting results with mercurous hyponitrite, it seemed desirable to study further the action of heat on the silver analogue, although Divers has already described it (Trans., 1899, 75, 108).

The substance, which was pale yellow, was washed and dried exactly as the corresponding mercury compound. The analyses of several distinct preparations are given below :

	I.	II.	III.	IV.	Theory.
Ag.....	77·81	78·50	77·37	77·23	78·26
N	10·78	—	—	—	10·15

It will be seen that the percentage of silver is slightly lower, whilst that of nitrogen is correspondingly higher, than the theoretical amounts. This appears to be due to the fact that traces of alkali, including sodium nitrite and hyponitrite, are carried down with the precipitate. The method of heating was precisely the same as in the preceding instance.* We shall therefore confine ourselves to giving only the results of a few typical experiments. The gases evolved were as in the case of the preceding compound nitrogen, nitrous oxide, and nitric oxide, but nitrous fumes were also distinctly perceptible. The solid residue consisted of a white mass of metallic silver with a small amount of silver nitrate. The following table shows the percentage yield of each of these compounds :

Exp.	N as NO.	N as N ₂ O.	N as such.	N absorbed in the KHO.	N in AgNO ₃ .	Total.
I.	6·38	1·02	1·11	1·44	0·35	10·30
II.	6·77	1·28	1·01	1·08	0·35	10·49

The percentage of silver obtained in the metallic state and also as nitrate was :

	As free silver.	As nitrate.	Total.
I.	74·49	2·74	77·23
II.	74·55	2·68	77·23

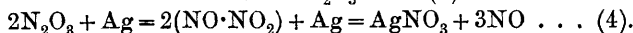
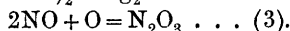
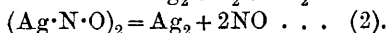
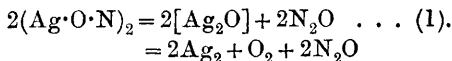
It will be seen that the decomposition products of silver and mercurous hyponitrites are similar in many respects. The only difference is that in the former case nitrogen monoxide is formed in much smaller quantity ; indeed, after the absorption of nitric oxide by alkaline sodium sulphite solution,† the residual gas, which is made up

* The salt began to decompose very slowly at 100°, and at 140° the evolution of the gas was brisk.

† About 1·5 to 2 c.c. of a solution of sodium sulphite was used for this purpose, and it was proved that it was almost without appreciable solvent action on nitrogen monoxide.

MERCUROUS AND SILVER HYPONITRITES BY HEAT. 1403

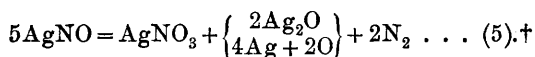
of almost equal volumes of nitrogen monoxide and nitrogen, did not support the combustion of phosphorus. A comparative study of the effect of heat on the two compounds helps us to understand the mechanism of the reactions. What actually happens seems to be as follows :



In the case of mercurous hyponitrite the proportion of "oxylic" to "imidic" molecules was nearly equal, whereas in the present instance by far the larger number of molecules is "imidic"; moreover, as silver oxide is unstable towards heat, its existence is only hypothetical. What we really get is silver and oxygen. The formation of nitrous fumes is thus easily accounted for.* A part of the nitrogen trioxide or, if its existence at a high temperature be denied, the nitrogen peroxide which it yields (and which may be looked upon as nitrosyl nitrate) acts on silver and yields silver nitrate.

The nitrous fumes, however, would be absorbed by the potassium hydroxide (Rây and Gañguli, Proc., 1905, 21, 279).

The production of nitrogen has yet to be explained. It is quite possible that a portion of the salt decomposes in the following way :



Silver nitrate is formed, according to our view, in conformity with equations (4) and (5); in the table given above, the ratio of nitrogen in the total silver nitrate and that in the free state is nearly as 1 : 3; if the silver nitrate according to equation (4) be left out of account, the above ratio will probably come out as 1 : 4, as demanded by equation (5).

The formation of nitrogen according to the equation : $3(\text{AgON})_2 = 4\text{Ag} + 2\text{AgNO}_3 + 2\text{N}_2$ is not borne out by the analytical data given above.

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* The occurrence of nitrous fumes, according to our view, is due only to a secondary reaction, whilst Divers (*loc. cit.*, p. 110) and Kirschner (*Zeitsch. anorg. Chem.*, 1898, 16, 424) regard it as a direct product of heating the salt. Divers also looks on the nitric oxide as the result of a series of complex reactions. It should be noted that these chemists conducted their experiments in quite a different manner, which introduced complications.

† In our next paper we hope to prove that hyponitrous acid breaks up mainly according to the equation : $5\text{HNO} = \text{HNO}_3 + 2\text{H}_2\text{O} + 2\text{N}_2$.