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LII.—*Mercuric Nitrite and its Decomposition by Heat.*

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IT has been shown (Trans., 1897, 71, 340) that when mercurous nitrite is treated with water, it undergoes the following dissociation, $Hg_2(NO_2)_2 = Hg + Hg(NO_2)_2$, but only to the extent of about 78 per cent., the rest going into solution along with the mercuric nitrite to form a mercuroso-mercuric nitrite having the formula

$$2HgNO_2,4Hg(NO_2)_2.$$

When the mercurous mercury is removed from solution by sodium chloride, a sodium mercuric nitrite is formed, from which dimercur ammonium nitrite has been obtained (Trans., 1902, 81, 644). But all attempts to isolate mercuric nitrite itself in the solid state have hitherto been unsuccessful.

Lang tried to prepare mercuric nitrite by means of the double decomposition occurring between mercuric chloride and silver nitrite, but obtained, on evaporating, a basic salt to which he assigned the improbable formula $3HgO,N_2O_3,H_2O$ (*Kongl. Svenska Vet. Akad. Handl.*, 1860; *J. pr. Ch.*, 1862, 86, 295). A repetition of Lang's experiment, with certain modifications, has now not only yielded the normal salt, $Hg(NO_2)_2$, but has also shown that the cause of Lang's failure was the interesting decomposition which mercuric nitrite undergoes when gently heated.

Silver nitrite being very sparingly soluble in the cold, and heat acting prejudicially on a solution of mercuric nitrite, the following method was found, after repeated trials, to be the best for preparing mercuric nitrite.

Silver nitrite, purified by recrystallisation, and pure mercuric chloride are weighed out in molecular proportions and rubbed together in a mortar to a fine paste with water, a little more water being gradually added with continued stirring. The mass is then washed into a stoppered bottle and violently agitated. It is well known that silver nitrate does not remove the whole of the chlorine from a solution of mercuric chloride; silver nitrite behaves in a like manner, and, therefore, the solution thus prepared contains unavoidably a very little silver nitrite, but not enough to be troublesome.

The pale yellow solution of mercuric nitrite, thus obtained, cannot be evaporated on a water-bath without the salt decomposing to a considerable extent, but on concentrating the solution *in vacuo* over sulphuric acid, the salt crystallises in tufts of fine needles. The salt thus obtained is contaminated only with traces of silver nitrite. By

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the analysis of two distinct preparations, its composition was found to conform with the formula $Hg(NO_2)_2$.

	Found.		Calculated.
Mercury	67·81	69·13	68·49 per cent.
Nitrogen	9·35	9·46	9·59 ,,

Mercuric nitrite has a light yellow colour ; it dissolves only partially even in boiling water, the larger proportion decomposing into mercuric oxide and nitrous acid. When kept exposed in the air, it slowly liquefies, and gives off nitrous fumes. When treated with a solution of caustic alkali, the solid salt yields mercuric oxide, whilst the whole of its nitrogen is obtained in solution as nitrite. This is proved by the fact that the nitrogen in the filtrate, when estimated by the Crum-Frankland method, is the same in amount as when measured by the "urea" process. Mercuric nitrite is not stable in presence of air, even when preserved in a stoppered bottle inside a desiccator ; it slowly evolves nitrous fumes, and if the stopper is loosened so as to allow the fumes to pass out and be absorbed by the sulphuric acid, the salt is transformed, in course of time, into a white powder of basic mercuric nitrate. In this respect, mercuric nitrite affords a striking contrast with mercurous nitrite, since the latter keeps well for years in a dry atmosphere. When exposed in a vacuum over sulphuric acid, before it has begun to change, the salt shows, however, no tendency to decompose if left undisturbed, but decomposition, when once begun, cannot be arrested.

If the original solution of mercuric nitrite is kept for some time in a stoppered bottle which is opened from time to time, the salt undergoes, but only to a very limited extent, much the same change as that presently described, which happens to it when heated in the solid state. Thus, a solution of sp. gr. 1·065 in the course of three weeks gave the proportion of mercuric to mercurous mercury as 13·7 : 1. If, however, the solution is preserved in a tube which has been exhausted of air and then sealed up, the salt remains absolutely undecomposed.

In its original solution, mercuric nitrite does not give any precipitate of oxymercuric sulphate with sodium sulphate, a fact which points to the "nitronic" constitution of the salt.

Decomposition by Heat.—A solution of mercuric nitrite, when evaporated on the water-bath, decomposes in two ways. The residue near the edge of the deposit consists almost wholly of crystalline, red mercuric oxide, whilst that in the middle of the deposit is a mixture of mercurous nitrate and undecomposed mercuric nitrite, with only traces of the oxide. It is probably this mixture which Lang took to be the basic nitrite he describes. For purposes of comparison, a solution of mercuric nitrate was similarly evaporated to dryness on the water-

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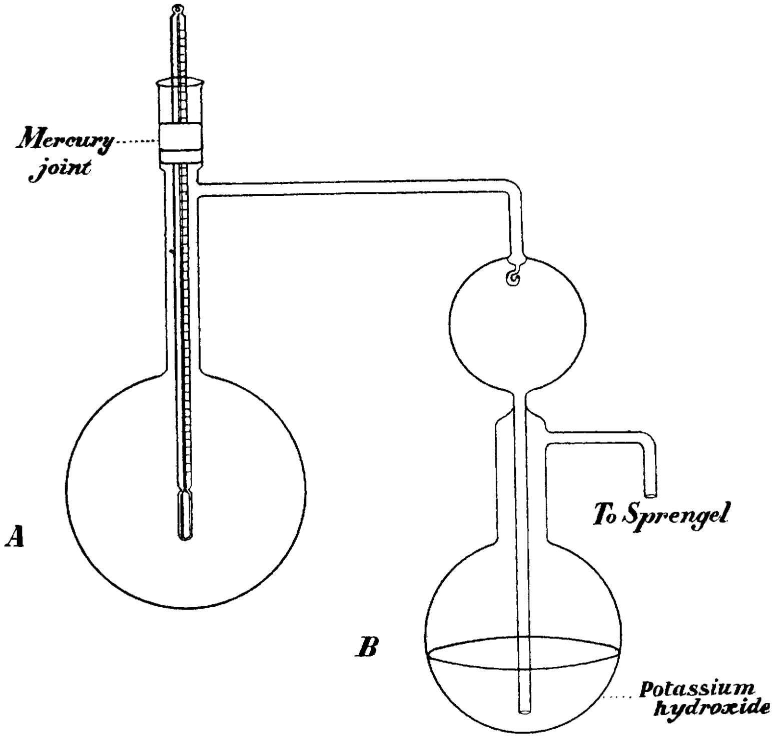
bath; this time the residue consisted of colourless crystals of mercuric nitrate interspersed with yellow streaks, indicating the partial formation of a basic salt. It will thus be seen that mercuric nitrite behaves in quite a different manner from the nitrate.

In order to study this decomposition more carefully, the following method and apparatus were devised.

The bulb, *A* (see fig.), contained from 5 to 10 c.c. of the solution of mercuric nitrite, whilst a dilute solution of potassium hydroxide was placed in the bulb, *B*. The use of this alkali was necessary in order to protect the mercury in the pump from the action of the mixed gases, but it also served as a means of ascertaining whether any nitric oxide was being evolved other than that liberated by the decomposition of the nitrous anhydride produced. After the apparatus had been exhausted, the bulb, *A*, was gently heated, taking care that the temperature did not rise above 60°. Until the evaporation of the liquid was completed, very little gas was given off, in fact not more than 0·5 c.c. But the solid salt began to decompose rapidly, giving off



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gas which was almost entirely absorbed by ferrous sulphate solution. The residue was found to consist of a mixture of mercurous nitrate and mercuric nitrite with only a small proportion of mercuric oxide, and no mercury whatever in the free state.

A similar result was obtained when solid mercuric nitrite was put into the apparatus and heated by keeping the bulb *A* immersed in water, the temperature of which was gradually raised to the boiling point. When the temperature had risen to 95°, the salt fused and intumesced; then nitric oxide was for some time regularly evolved, but ultimately the gas in the bulb became reddish-brown. The gas, which was treated and collected as before, was found to be almost entirely soluble in ferrous sulphate solution, whilst the solid residue consisted mainly of mercurous nitrate. The ratio of the nitrogen as nitrate to that as nitrite was as 4·33 : 1.

It will thus be seen that when the solid salt is heated it decomposes chiefly into mercurous nitrate and nitric oxide, thus: $2Hg(NO_2)_2 = 2HgNO_3 + 2NO$, only a small quantity decomposing into mercuric oxide and nitrous anhydride.

It might be supposed, firstly, that mercuric nitrite in the solid state really decomposes at first into mercurous nitrite and nitric peroxide, thus: $2Hg(NO_2)_2 = Hg_2(NO_2)_2 + 2NO_2$, just as auric chloride breaks up into aurous chloride and chlorine; secondly, that the mercurous nitrite thus formed decomposes into free mercury and nitric peroxide; and, lastly, that these, by their interaction, give rise to the mercurous nitrate and nitric oxide actually obtained (Trans., 1903, **83**, 491).

In order to settle this point satisfactorily, the earlier experiment with mercurous nitrite (*loc. cit.*) was repeated in the new apparatus. At 100° there was no appreciable amount of gas evolved. It was only when the bulb was directly heated by the flame and the temperature exceeded 200° that the decomposition took place. In this case the resulting mercurous nitrate was deposited in thin needles, interspersed with minute globules of mercury, on the bulb and stem of the thermometer, whilst, when the reaction is carried on in a short horizontal tube, the crystals of mercurous nitrate shoot forth from the upper side of the tube. In this case, as formerly pointed out, a portion of the vapour of the mercury acting on the nitrous fumes gives rise to mercurous nitrate, the remainder being deposited in globules. Heat thus acts on mercurous and mercuric nitrites in entirely different ways, the mercurous nitrate being produced as a pseudo-sublimate in the case of the former salt, whereas it is produced in the mass of the decomposing salt in the case of the latter compound.

The present investigation shows that when a solution of mercuric nitrite, obtained by double decomposition between mercuric chloride

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and silver nitrite, is concentrated *in vacuo* over sulphuric acid, it yields the normal salt, mercuric nitrite; and that when this salt is heated at 100°, it breaks up in two ways as indicated by the equations,

$$(1)\ Hg(NO_2)_2 = HgO + N_2O_3.$$
$$(2)\ Hg(NO_2)_2 = HgNO_3 + NO.$$

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