LV.—Decomposition of Mercurous Nitrite by Heat.

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WHEN describing mercurous nitrite in 1896, one of us ventured to express the hope that this salt would prove to be the analogue of silver nitrite in all essential properties (*Zeit. anorg. Chem.*, 1896, 12, 365), and has since shown that, by interaction with ethyl iodide, the substance yields both ethyl nitrite and nitroethane, and that in this production of nitroethane much nitric oxide is evolved (*Annalen*, 1901, **316**, 250). A study of the action of heat on mercurous nitrite has emphasised the likeness between this compound and the silver salt.

The mercurous nitrite, in a thin layer, was heated *in vacuo* in a tube connected with a Sprengel pump. In the first experiment, a portion of the tube was blown into a bulb, which was kept immersed in a freezing mixture in order to liquefy, if possible, the nitric oxide evolved; but as none of the gas could be thus condensed, the bulb was discarded in subsequent experiments. The tube was generally heated by means of a Bunsen burner, but sometimes by a spirit lamp, keeping the flame rather low. Care was taken to localise the heating to the lower side of the tube and to just that part of it on which

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the nitrite rested, but no attempt was made to carry out the decomposition at a fixed temperature throughout. Heating for nearly two hours at 195° failed to decompose the salt completely. The temperature of decomposition in our experiments was probably about 250° .

The decomposition was complete in about two minutes. Almost from the outset it was noticed that colourless needles of mercurous nitrate began to shoot out from the upper wall of the tube somewhat away from its heated part, and also that a thin layer of yellow basic nitrate,* intermixed with minute globules of mercury, was deposited The residue, consisting of mercuric oxide, was dull red at the sides. whilst hot, but on cooling became orange-coloured. It is generally stated that mercuric oxide prepared by dry methods, either by direct oxidation of the metal or by heating mercurous nitrate, is red and crystalline, but the variety here obtained was an orange-coloured, amorphous, impalpable powder, resembling more the precipitated oxide, and therefore containing possibly a trace of basic nitrate. Scarcely any nitrous fumes were noticed until the later stages of the heating, when a faint reddish-brown colour could be seen; the indisputable proof of the evolution of some nitrogen peroxide lay, however, in the soiling of the mercury in the pump. The gas, which was collected and measured, consisted of pure nitric oxide almost completely absorbed by a concentrated solution of ferrous sulphate.

Mercurous nitrite contains 5.70 per cent. of nitrogen, of which, in different experiments, 3.65, 3.20, 3.70, 3.05, 2.93, and 4.21 per cent. were obtained as nitric oxide. In the experiment which gave the last quantity, the tube had been more strongly heated, and most of the nitrate was thereby decomposed. Omitting this one, the mean of the other numbers is 3.31. In the omitted experiment and in the one which gave 2.93 per cent. of nitrogen as nitric oxide, the nitrogen as nitrate in the residue was determined by the Dumas method. In the former case, it was 0.77 per cent., and in the latter 2.23 per cent. The production of nitric oxide equivalent to 3.26 per cent. as nitric oxide and 2.44 per cent. as nitrate-values sufficiently near to 3.31 and 2.23, the numbers found-requires the following equation : $7(HgNO_2)_2 = 8NO +$ $3(\text{HgNO}_3)_2 + 2\text{HgO} + 6\text{Hg}.$ Allowance for the small quantities of mercuric nitrate and of nitrogen peroxide also produced could, if they were known, be made in this equation without affecting its general character. As for the former compound, its ascertained proportion, together with its equivalent of mercury, would then take the place of the corresponding quantity of mercurous nitrate. The escaping nitrogen peroxide gives rise to mercurous nitrate, which is lost in the

* The composition of this basic mercurous nitrate will be discussed in a forthcoming paper on mercuroso-mercuric nitrates. pump, and to nitric oxide, which passes through with the rest of this gas directly produced in the decomposition. For example, the difference between 5.7, the total nitrogen, and the sum of 3.31 and 2.23, found as nitric oxide and nitrate, is 0.16, which is nearly 0.4 in $7(\text{HgNO}_2)_2$. Taking this to have been lost as NO₃ in the mercury of the pump, the above equation becomes $7(\text{HgNO}_2)_2 = 7.6 \text{NO} + 0.4 \text{N}_2 \text{O}_4 + 2.8(\text{HgNO}_3)_2 + 2 \text{HgO} + 6.4 \text{Hg}.$

Repeated attempts were made to determine directly the proportions of the components of the heterogeneous residue in the tube, but without success in obtaining results consistent either with the compounds which could be seen on inspection or with the amount of nitric oxide measured. The method consisted in gently shaking the contents of the tube with cold dilute nitric acid (sp. gr. 1·100). A clear solution was quickly obtained, some globules of mercury only being left. The mercurous and mercuric radicles in the solution were estimated in the usual way, whilst the undissolved mercury was not weighed, but its quantity calculated by difference. The method evidently failed in consequence of much of the mercuric oxide and mercury going together into solution as mercurous salt, in spite of the efforts made to prevent this happening.

It will be seen that the results of heating mercurous nitrite serve to confirm those obtained by Divers and Shimidzu with silver nitrite (Trans., 1885, 47, 634). These chemists have shown that silver nitrite is not directly converted into nitrate through oxidation by the nitrogen peroxide, but indirectly from the reduced metal acting on the gas. Silver, however, being non-volatile, they had to perform other experiments in order to prove the point. In our case, such control experiments have been unnecessary, because of the volatility of mercury. Its vapour, acting upon that of the peroxide when both are set free from the nitrite, forms mercurous nitrate, which is deposited on the tube in the manner described, only a small fraction of the mercury remaining in the free state. The decomposition of the salt would seem, then, to proceed in the following manner: $(HgNO_2)_2 = 2Hg + (NO_2)_2$, being followed by a secondary reaction * $2(NO)NO_3 + 2Hg = (HgNO_3)_2 + 2NO$, almost simultaneously set up, as already shown by Divers and Shimidzu.

When the non-oxylic constitution of mercurous nitrite is adopted, the formation of the mercuric oxide has to be explained as being

^{*} Ramsay and Cundall found that when a mixture of nitric oxide and nitrogen peroxide is kept over mercury, the volume of the gases remains constant, and that the metal is not apparently attacked (Trans., 1885, 47, 191), and think it probable that the care which was taken in drying the product was the cause of the mercury remaining unattacked. We are also of opinion that it is the presence of traces of moisture which brings about the reaction.

due either to the oxidation of the metal by the nitrogen peroxide $Hg + NO_2 = HgO + NO$, or to the decomposition of the nitrate, $HgNO_3 = HgO + NO_2$. The oxide was, however, formed in the tube just where the nitrite lay at the beginning of the experiment, and care was always taken during the heating not to disturb the nitrate on the upper side of the tube. Hence, another explanation seems to The one that occurs to us is that, under the influence of be required. heat, the atoms in some of the molecules of the nitrite arrange them selves as Hg'NO₂, the non-oxylic form, and in others assume the oxylic form, HgO·NO, scission taking place in each case at the indi-The decomposition of the salt seems, then, to proceed cated point. simultaneously in both directions, * unless conditions favourable to one mode of decomposition causes this to predominate over the other. Thus the thinness of the layer of the salt, and the degree of suddenness in imparting heat are both operative in modifying the result.

This view of the constitution of mercurous nitrite is also quite in keeping with the fact that it gives rise to both nitroethane and ethyl nitrite. In the case of silver nitrite, we have no means of either proving or disproving this view. The silver oxide, supposing it to be formed, would at once break up into metallic silver and free oxygen, and the latter would then combine with the nitric oxide to form the peroxide. Thus, as far as silver nitrite is concerned, it would make no difference whether we accept the oxylic or non-oxylic constitution of the salt, or both. Fortunately, owing to the stability of mercuric oxide at the temperatures at which we conducted the experiments,† the heating of mercurous nitrite affords evidence that both views are correct.