DECOMPOSITION OF DIMERCURAMMONIUM NITRITE BY HEAT. 323

## XXXIV.—Decomposition of Dimercuranmonium Nitrite by Heat.

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THE preparation of dimercurammonium nitrite has been already described at some length (Trans., 1902, 81, 644), and evidence has been adduced in support of the view that it is a derivative of ammonium nitrite.

The solution of sodium mercuric nitrite, from which it is obtained by the action of ammonia, does not contain mercury as cation, but as part of a complex anion; it does not, therefore, undergo the hydrolysis so characteristic of oxylic mercuric salts, and has presumably a non-oxylic constitution. Two samples of the salt were prepared, and dried at  $95^{\circ}$  for analysis:

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Found : Hg = (I) 84.74; (II) 84.61. N = (I) 6.33; (II) 6.16. NHg<sub>2</sub>NO<sub>2</sub>,  $\frac{1}{2}H_2O$  requires Hg = 85.29. N = 5.97 per cent.

Method of Experiment.-From 0.2 to 0.6 gram of salt was placed in a small bulb, the drawn-out stem of which was connected with a Sprengel pump. A preliminary trial proved that the salt commenced to decompose, although very slowly, at about 140°, and that even at 210° a portion of it remained undecomposed. The bulb was therefore cautiously and gradually immersed in a bath of molten sodium and potassium nitrates, mixed in about equal proportions (m. p. 218°). The temperature was slowly raised to 250°, when no more gas was evolved, the "click" in the fall-tube remaining persistent. Raising the temperature to 280° made no difference in this respect. The gas which was evolved was found to consist of a mixture of nitrous oxide, nitrogen, and oxygen; nitrous fumes were not noticed; in fact, the mercury in the fall-tube was not in the least tarnished, nor could even a trace of nitric oxide be detected. If, however, the bulb was suddenly plunged in a bath previously heated to 225°, the mode of decomposition was slightly different. Mercury in the shape of fine dust was at once deposited on the glass, and in the gaseous mixture nitric oxide could be recognised.

The nitrous oxide was removed by alcohol, and sometimes by repeated shaking with cold water, until no more absorption took place. The oxygen was in some instances removed by alkaline pyrogallate, but generally by means of phosphorus. The residue in the bulb was of a greyish-yellow colour; it consisted mainly of mercuric oxide with a small proportion of mercuric nitrate. This was proved by boiling the mixture with a solution of sodium hydroxide. The filtrate indicated the presence of nitrogen in the form of nitrate. Metallic mercury, both as a mirror and in fine globules, was deposited in the stem of the bulb. More than a dozen experiments were performed, the results of some of which are tabulated below :

				Total O			
" Free "	N as	N as		in the	Hg as	Hg as	" Free
N.	$N_2O$ .	Hg(NO <sub>3</sub> ) <sub>2</sub> .	Oxygen.	salt.	$Hg(MO_3)_2$ .	HgO.	$_{ m Hg.}$
I. 3·21	1.55	1.21	0.21	6.82	8.64	57.20	19.45
II. 3·17	1.48	1.32	0.17		9.43	55.31	20.55
III. 3·43	1.44	1.10	0.22				
IV. 3·53	1.60	0.84	0.34		6.00	62.65	16.68
V. 3·73	1.52	0.72	0.25		5.14	63.31	16.84

In those experiments in which nitric oxide was obtained, the nitrogen was distributed as follows:

	" Free " N.	N as $N_2O_{\bullet}$	N as $Hg(NO_3)_2$ .	N as NO.
I.	2.54	1.03	2.31	0.09
п.	3.22	2.24	0.29	0.55
III.	2.69	1.95	0.92	0.38

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Discussion of Results.—It has already been pointed out that the halogen derivatives of the mercurammonium group  $(NHg_2^{-})$  may be regarded as non-oxylic in constitution, since they decompose under the action of heat according to the equation :

$$2NHg_2X = N_2 + 2Hg + 2HgX,*$$

where X = Cl or Br.

From analogy, one would naturally expect that the nitrite of the series should decompose as follows :

 $2NHg_2NO_2 = N_2 + 2Hg + 2HgNO_2$ ,

and that the mercurous nitrite thus formed, being unstable at this temperature, would yield its own products of decomposition (compare Rây and Sen, Trans., 1903, 83, 491). We have repeated the experiment on the decomposition of mercurous nitrite. The initial temperature of decomposition has been found to be almost the same as that of dimercurammonium nitrite, namely, 140°, and it is completed at 247°. In order to protect the mercury in the Sprengel pump from being soiled, a glass spiral, packed with glass beads and moistened with sodium hydroxide solution, was interposed, as in some of the previous experiments (compare Trans., 1905, 87, 180). The gaseous product which was collected was found to be nitric oxide. Moreover, had dimercurammonium nitrite decomposed according to the equation given above, exactly half the nitrogen would have been given off as "free" nitrogen, but it varies from 3.2 to 3.7 per cent. The formation of nitrous oxide is rather remarkable. The reaction evidently seems to proceed in three or four directions simultaneously, which may be expressed by the following equations:

$\mathrm{NHg}_2\mathrm{NO}_2 = \mathrm{N}_2 + 2\mathrm{HgO}$ .	•	•	•	•	•	•	(1)
$(\text{compare NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2$	0)						
$NHg_2NO_2 = N_2O + HgO + Hg$							(2)
$\mathbf{N}\mathbf{H}\mathbf{g}_{2}\mathbf{N}\mathbf{O}_{2} = \mathbf{N}_{2} + 2\mathbf{H}\mathbf{g} + \mathbf{O}_{2}$		•					(3)
$3 \mathrm{NHg}_{2} \mathrm{NO}_{2} = \mathrm{Hg} (\mathrm{NO}_{3})_{2} + 2 \mathrm{N}_{2}$	+5	H	ς.				(4).

We are at present engaged in studying the decomposition of dimercuranmonium nitrate, in the hope that further light may be thrown on these points.

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\* Rây, "Studien über die Konstitution der Dimerkurammonium Salze" (Zeitsch. anorg. Chem., 1902, 33, 193; also, Sen, ibid., 197).