XXXIII.—The Nitrites of Mercury and the Varying Conditions under which they are formed.

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

Mercurous Nitrite,* Hg₂(NO₂)₂.

In an earlier paper \dagger on the preparation of the above salt, I said that "yellow nitric acid of sp. gr. 1.410 is diluted with water in the proportion of 1 to 3; a large excess of mercury is at once poured into the liquid, the heat of solution of the acid in water helps to start the reaction." This has since been repeated several times, and I have found that colourless nitric acid acts just as well, and that it is better to dilute it in the proportion of 1 to 4; in other words, dilute nitric acid containing 13 to 14 per cent. N₂O₅ seems to be most favourable for the growth of the yellow, thin needles and prisms. For the results of analyses, see A I, II, Table, p. 345.

Method of Analysis.

Estimation of Mercury.—The mercury which separates out on gently heating the salt with water has been termed "free" mercury; that contained in the clear solution in the mercurous state was thrown down as chloride by means of sodium chloride, and that existing in the filtrate in the mercuric form was estimated as sulphide. For details, see *loc. cit.*, p. 267. Sometimes the free mercury comes out too low; this is due chiefly to imperfect coagulation of the grey powder and loss by volatilisation.

As a further check, some of the salt was dissolved in the minimum amount of strong nitric acid, sodium chloride was added to the solution, and the precipitated calomel was redissolved in aqua regia, and the total mercury precipitated as sulphide. For result of this analysis and the formula, &c., see A III, Table, p. 345.

In the memoir referred to above, the mercury in the mercuric salt was generally thrown down as calomel by the addition of phosphorous acid; this method invariably gave too low results, in fact 30.7 was

^{*} Compare Divers and Haga, Trans., 1887, 41, p. 49.

⁺ Zeit. anorg. Chem., 1896, 12, 365, (from Journal Asiatic Society Bengal, 1896, lxv., ii, No. 1).

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taken as the mean percentage of mercury both in the "free" state as also in the mercuric salt; in only one instance was the mercuric mercury estimated as sulphide, and this gave 31.33 as the percentage (*loc. cit.*). I naturally gave preference to the number 30.7, and was thus misled into assigning the formula $Hg_2(NO_2)_2 + H_2O$ to the salt. I have, however, since then succeeded in preparing a hydrated salt of this formula, which will be described later on.

Estimation of the Nitrogen.—As stated in the first paper, the nitrogen was estimated by the Crum-Frankland method.

Determinations of nitrogen by the direct method, however, seemed highly desirable, especially as the various basic nitrites and nitrates to be subsequently described are but sparingly soluble in water, and are only partially decomposed on treatment with an alkali; consequently, the total nitrogen cannot be obtained in the soluble form. The method employed was that of Dumas, somewhat simplified. The salt was placed in a porcelain boat in a combustion tube and the whole length of the tube between the boat and the delivery tube was closely packed with bright copper foil, well-dried magnesite being used for the supply of carbonic anhydride. This method had the additional advantage that the various stages of decomposition of the salts could be watched, and also that it was easy to see whether water was given off from them.* For analytical data, see A II, Table, p. 345.

Formation of the Nitrite as Dependent on the Strength of the Acid.

A. Nitric acid (1:4).—It has already been pointed out that the acid (sp. gr. 1.41) diluted in the proportion of 1 to 4 of water favours the growth of the yellow needles and prisms. It was, however, thought desirable to systematically study the conditions under which the nitrites are formed.

With this $\operatorname{acid}(1:4)$, the needles begin to appear in the course of about half an hour, and at the end of 24 hours a considerable crop is obtained. As, however, the crop thus formed on the surface of the mercury acts as a protective layer, thereby hindering the action of the liquid on the metal, the salt ceases to grow; the deposit of the nitrite, therefore, should be removed, and the mercury and liquid carefully decanted off into another beaker, when a second crop will be obtained the next day. By repeating the process, successive crops can be collected from day to day.

B. Nitric acid (1:6).—The first crop of crystals of mercurous nitrite was collected next day, and two others at intervals of 5 days, but a

^{*} I avail myself of this opportunity to express my sincere thanks to Mr. N. Chandra Nâg, M.A., Junior Assistant, Chemical Department, for his assiduous and ungrudging help in making the nitrogen estimations.

small quantity of the crystals of nitrite from the last crop was left with the mother liquor and the excess of mercury; 12 days afterwards a single, colourless, bright crystal was observed, and 2 days after this a large crop of the same kind of crystals was collected. This salt, on analysis, was found to be that described below as "Marignac's salt."

C. Nitric acid (1:1).—The action was immediate and very energetic, torrents of red fumes being evolved, and the liquid turning bluish to greenish; after about half an hour, the action seemed almost to cease. At the end of about 20 hours, a crust of long, colourless needles was formed; the lower part of the crust, however, consisted of the yellow nitrite mixed with the former.

D. Nitric acid (1:2).—The action was somewhat less energetic, the product consisting practically of yellow salt, a small portion only being transformed into colourless needles.

Behaviour of Nitric Acid towards Mercurous Nitrite.

Strong nitric acid, in the cold, has no immediate action on the salt; but, after a few minutes, energetic action sets in. If the mixture is heated immediately after adding the strong nitric acid, a violent action begins, copious red fumes are given off, and a clear solution of mercuric salt is obtained. If, after adding strong nitric acid, a small quantity of water is poured in, action at once commences, nitrous fumes are evolved, and the liquid becomes bluish; at the same time, a few globules of mercury separate, but disappear on warming the liquid, which contains both mercurous and mercuric salts. If, however, the salt be treated with *cold*, dilute nitric acid, the action is very slow, bubbles of gas being given off at intervals; it is only after the action has continued 3 to 4 days that the salt dissolves, and colourless crystals of mercurous nitrate ("Marignac's salt") crystallise out.

Influence of the presence of Nitrous Acid in promoting the formation of the Nitrite.

Russell,* Divers,[†] and, lately, Veley [‡] have come to the conclusion that it is the nitrous acid present in the nitric acid that plays the prominent part in the dissolution of metals like silver, mercury, and copper, &c. In order to decide what advantage, if any, would be gained if nitrous acid were initially present, three parallel experiments were started simultaneously.

I.—50 c.c. of colourless nitric acid, sp. gr. 1.410, diluted with 150 c.c. of water, to which was added an excess of mercury.

- * C. S. J., 1874, 27, 3.
- + Ibid., Trans., 1883, 43, 443; Trans., 1885, 47, 231.
- ‡ Proc. Roy. Soc., 1890, 48, p. 458.

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11.—The same as above, with a few drops of red fuming nitric acid. III.—The same as in I, with 5 c.c. of red fuming nitric acid.

In I, after the lapse of about 15 minutes, there was scarcely any deposit of yellow needles, in II the deposit was distinctly visible, in III more so; after the lapse of another hour, a deposit was formed in I; in fact, the amounts in I and II were much the same; whilst in III it was somewhat larger. Next day, the yield was found to be practically the same in all three. It is evident, therefore, that nitrous acid over and above that present even in colourless nitric acid, gives a slight advantage at first, but this disappears in the long run.

I. Monhydrated Mercurous Nitrite. II. Basic Mercuroso-mercuric Nitrites; and III. Mercuric Nitrite.

Mercurous nitrite, $Hg_2(NO_2)_2$, has been shown to undergo partial decomposition when treated with water, thus: $Hg_2(NO_2)_2 = Hg(NO_2)_2 + Hg$. Nearly 22 per cent. of the salt, however, remains in solution as such. When the solution was hot and concentrated, it was noticed that a yellow, powdery mass separated on cooling, and, on analysis, this was found to be the unaltered nitrite, $Hg_2(NO_2)_2$. On allowing a somewhat dilute solution to evaporate spontaneously in a shallow dish, the salts mentioned above were obtained in succession. A detailed description of each is given below.

I. Monhydrated Mercurous Nitrite : $Hg_2(NO_2)_2 + H_2O$.—In the course of 2 to 3 days a crop was obtained consisting of glistening, pale, lemonyellow prisms. The action of water on this salt is precisely similar to that on mercurous nitrite. When kept in contact with water for some time, metallic mercury, in a fine state of division, begins to separate. The method of analysis was the same as that employed for mercurous nitrite. For results, see Table.

On comparing the result with that of mercurous nitrite, it would appear that the rate of dissociation of this hydrated salt is different, although in its general behaviour it resembles the former. (*Vide* B I, II, III, Table, p. 345.)

That the present salt contains water of crystallisation is proved by the fact that, when kept in the desiccator over strong sulphuric acid, it effloresces somewhat; but the former salt, $Hg_2(NO_2)_2$, neither loses in weight nor in brilliancy under similar conditions.

As the analyses given represent different preparations, it is evident that a salt of constant composition is always formed.

Of the several salts described in the present paper, this is the only one which yielded crystals big enough for measurement. Mr. T. H. Holland, of the Geological Survey of India, kindly undertook to examine the crystals (see the next paper).

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II. Basic Mercuroso-mercuric Nitrites.—Of these there are two, namely, the a-salt, having the formula $9 \text{Hg}_2\text{O},4 \text{HgO},5 \text{N}_2\text{O}_3,8 \text{H}_2\text{O}$, and the β -salt, $\text{Hg}_2\text{O},2 \text{HgO},\text{N}_2\text{O}_3,2 \text{H}_2\text{O}$. When the triclinic prisms of the above monhydrated salt had ceased to grow, small, orangecoloured nodules began to appear along with them, and then deep yellow clusters of needles or feathery tufts starting from a nucleus. These two basic salts have been named a and β respectively. The analyses (see Table, p. 345) belong to two distinct preparations.

The behaviour of the present class of salts was entirely different from that of the previous normal nitrites. When kept in contact with water, scarcely any change was noticed, and no separation of mercury took place, but on agitating with a few drops of dilute nitric acid, they dissolved completely. Dilute nitric acid, therefore, can be used in the diagnosis of the two classes of salts—normal and basic.

If dilute nitric acid is poured on the normal salt and the mixture warmed, copious red fumes are at once evolved and an energetic action begins; a small portion of mercury separates, dissolving slowly in the acid, with gentle effervescence. Nitric acid, in fact, seems to act in a two-fold manner. First, it displaces the nitrous acid, and then dissolves the mercury set free. Mercurous nitrate, for the most part, with only a small proportion of mercuric nitrate, remain in solution.

When the salts are *basic*, nitric acid seems first to enter into combination with the base, and if the acid be very cautiously added drop by drop, not the least trace of nitrous fumes is evolved. Dilute nitric acid does not appear to exercise any oxidising action on these salts.

In analysing these salts, they were dissolved, as explained above, and the mercurous and mercuric mercury estimated as calomel and sulphide respectively. (*Vide* C I—IV, D I—III, and E I—IX, Table, p. 345).

The water in this and the following salts is easily given off when they are gently heated in a test-tube, but it is not given off in the desiccator, even when they are finely powdered; it seems preferable, therefore, to regard it as "water of constitution" (vide "Marignac's salt," below).

On referring to the table of results of analyses, it would appear that the mercurous mercury is sometimes too high by 0.6 to 0.8 per cent., whilst the mercuric mercury is too low on an average by about the same amount. The explanation appears to be that none of these salts could be washed or crystallised, and that, during the process of drying on a porous tile, some portion of the thick mother liquor was absorbed by the salts.

III. Mercuric Nitrite, $12 \text{HgO}, 5 \text{N}_2 \text{O}_3, 24 \text{H}_2 \text{O}$.—After the yellow, feathery crystalline tufts of the β -salt had ceased to be deposited, the mother liquor was still found to contain distinct traces of the mercurous salt, and the salt which now began to appear consisted of thin

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scales, almost white with a faint yellowish tint; these were, however, slightly contaminated with the mercurous salt. When the mother liquor had evaporated to dryness, very thin scales were formed, adhering to the bottom of the basin, and consisting purely of the mercuric salt; these were easily detached from the dry, granular residue, composed mainly of mercuric nitrite with a slight admixture of the mercurous salt. These scales, which were almost white with a yellowish tint, were kept over sulphuric acid before being analysed. The presence of water was proved qualitatively.

Transformation of the Nitrite into Nitrate.

(a) Monhydrated Mercurous Nitrate, $Hg_2(NO_3)_2 + 2H_2O$.—The circumstances under which the nitrite is transformed into the nitrate have already been alluded to (see ante, p. 341). At first, I came to the conclusion that the nitrate formed is invariably "Marignac's salt," a description of which will be found below. It has lately been observed, however, that this is not the case. When the nitrite is prepared from an acid diluted in the proportion of 1:3, the conversion of this salt into a nitrate takes place more rapidly than when dilute acid 1:4 or 1:6 has been used. Sometimes in the course of two days, or even one day, colourless, soft crystals make their appearance side by side with the nitrite, but they soon disappear to reappear again in another form; they are highly efflorescent, falling to powder when exposed to dry air. In fact, whenever the transformation of the nitrite into nitrate takes place slowly, the more stable "Marignac's salt" is formed, and this explains why this nitrate has been so long overlooked by workers in this field. The new mercurous nitrate is sometimes deposited in isolated crystals, and sometimes as a thick crust; in the latter case, some of the mother liquor always remains enclosed.

Prep. I.-For analysis, small individual crystals were picked out.

1.0388 of the salt lost, in the desiccator, 0.0660; loss = 6.35 per cent. 0.1300 of this dehydrated salt gave 6.2 c.c. moist nitrogen at 31° and 759 mm.

Prep. II.—0.4406, keptover H_2SO_4 , lost 0.0275 (loss = 6.24 per cent.), and gave 0.3665 of HgS.

	Theory for	Theory for	Found.						
	$HgNO_3 + H_2O$.	HgNO ₃ .	as hydr. salt.	as dehydr. salt.					
Hg	71.43	76.33		76.49					
N		5.34		5.13					
H ₂ O	., 6.43	_	6.30 (mean) —						

(b) Marignac's salts $5Hg_2O_3N_2O_5 + 2H_2O$ or $3Hg_2(NO_3)_2 + 2Hg_2(OH)_2$ or $Hg_2(NO_3)_2, 4Hg_2(OH)NO_3$.—This is the form into which the normal

nitrite, described above, is ultimately converted. Regarding this compound, the information in Watts' *Dictionary of Chemistry*, edited by Morley and Muir (vol. iii., p. 514) and in Roscoe and Schorlemmer's well-known treatise, is very vague and meagre. The account given of it in Fremy's *Encycl.* (tome iii., 14° Cahier, p. 243), based on Marignac's original memoirs,* is more complete, but the method of preparation, or rather formation, of this salt is different from that described below; and this probably explains the want of uniformity in the formulæ proposed by Gerhardt and by Marignac respectively.

The formation of the nitrite and its ultimate conversion into the nitrate is fully explained in my first paper (*loc. cit.*).

In confirmation of the views there put forward, the following proof may be adduced. The residues from several preparations of the nitrite, consisting of mercury mixed up with some nitrite, together with the mother liquor, were in one case stored up in a tall, well-stoppered bottle, but the vessel did not burst, nor was the stopper thrown out. The fact is, there was no pressure of gas inside; the bubbles of nitric oxide during their ascent through the long column of liquid were completely absorbed. At first, mercurous nitrite gradually formed and accumulated, but afterwards slowly dissolved, and in the course of about two months a hard crust of "Marignac's salt" was deposited on the surface of the mercury, from which large, well-formed crystals with sharp edges projected.

I am able fully to confirm Marignac's statements as to the general properties of this salt. The crystals are very hard, and colourless; retain their lustre unimpaired when exposed to the air, and do not lose water over sulphuric acid in a vacuum; they give up water, however, easily enough when gently heated in a test-tube. It is necessary to bear in mind that the mercurous nitrite is not directly changed into this nitrate, but passes through the transitional form of the monhydrated nitrate $Hg_2(NO_3)_2 + 2H_2O$, although this latter stage oftentimes appears to be omitted.

Analysis.

This salt is a definite and stable compound, the analytical results fully confirming Marignac's formula; nearly a dozen analyses of different preparations were made. This affords independent testimony from a high authority as to the trustworthiness of the methods of

* Ann. Chim. Phys., 1849, [3], 27, 515.

estimating mercury and nitrogen employed throughout the present investigation.

In a future communication, I hope to throw further light on the formation as well as on the constitution of the nitrites described above.

Summary.

From the foregoing investigation, it seems to be established-

1.—That by the action of dilute nitric acid in the cold,* the strength varying from 10 to 23 per cent. or so, mercurous nitrite is *always* formed.

2.—That the mercurous nitrite thus formed slowly dissolves in the mother liquor, resulting in the production of mercurous nitrate of two kinds (a), monhydrated mercurous nitrate, $Hg_2(NO_3)_2 + 2H_2O$, and (b), the basic nitrate, termed "Marignac's salt."

3.—That when a neutral dilute solution of mercurous and mercuric nitrites (the products of dissociation) is allowed to evaporate spontaneously, monhydrated mercurous nitrite, $Hg_2(NO_2)_2 + H_2O$, two mercurosomercuric nitrites, and a basic *mercuric* nitrite are successively formed.

4.—That of these salts only two may be said to contain real "water of crystallisation," namely, those termed monhydrated mercurous nitrite and nitrate respectively, in that they are efflorescent, losing water rapidly in a dry atmosphere; the rest may be held to contain "water of constitution."

CHEMICAL LABORATORY, PRESIDENCY COLLEGE, CALCUTTA, July, 1896.

^{*} Some commentary is, perhaps, needed on the expression "in the cold," used throughout. The average temperature of Calcutta at mid-day may be taken as 32.9° in the summer season, whilst in winter it is nearly 22.2°. These temperatures have been obtained from sixteen years' observation of the thermograph (dry) at the local meteorological office.

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Remarks.		The "free" Hggenerally comes out too low. (See ante, p. 337.) * Estimated as total mer- curv. (See D. 337.)				and a state of the second s	The range within which the salt is formed is a wide one thus the successive	crops D I, II, III, and E I, III IV VIII and IX have	the same composition.	The crystallisation was started April 1, and the	last crop collected May 8, 1896.	+ Estimated as total mer- curv : the salt being pre-	viously oxidised by means	01 HNU ₃ .			
Formula		Hgg(NO ₂ ) ₂	$\left. \right\}_{\mathrm{Hg}_{2}(\mathrm{NO}_{2})_{2}+\mathrm{H}_{2}\mathrm{O}}$	$^{lpha}_{9\mathrm{Hg}_{2}\mathrm{O},4\mathrm{HgO},5\mathrm{N}_{2}\mathrm{O}_{3},8\mathrm{H}_{2}\mathrm{O}$	or	$ 5Hg_2(NO_2)_2 + 4Hg_2(OH)_2 + 4Hg(OH)_2$		٩	2	$\left. \right\rangle = Hg_{2}0, 2Hg0, N_{2}0, 2H_{2}0$	or	${ m Hg_2(NO_2)_2+2Hg(OH)_2}$			0-H% -0-N3 0-Hat	141180,011203,411120	
tage, tical.	N.	5-80			2.73							2.92				4.11	
Percent	Total Hg.	81-30	78-43	11-38						83.32					20.55		_
Percentage found.	N.	5.69		:	2.67	2.62			3.14	1		2.91	(mean)			4.09	
	Total Hg.	80-94 (mean) (mean) (s1-70)	(mean)	84-94 (mean)			81-29 (mean)	82-35	I	82-59	8			09.68	70.54		
Vol. of moist nitro-	gen in c.c.	6.2	(t≕32 ),(p=/35) mm.	9	at 32° and 758 mm.	16-4 at 32° and 760 mm.			6·0 at 3?° and 756 mm			6.6 at 31° and 759 mm.	8-9 at 31° and 758 mm.			7.3 at 31 5° and 751 mm.	
of	'ic Hg.	31.36	32.62 32.34	$15 \cdot 29$ $15 \cdot 28$	1	I	40.13 40.26	40.08	ł	41-04	7 - DE	I	I	41.31	TO 07		
Percentage	'ous Hg.	18.18	13-25 14-64	69-95 69-95	I	I	41 ·62 40 ·09	41.13	I	41.55	00 75	I	I		07 7 F		
	"Free" Hg.	31•4 30•26	31.02 31.08	on 70	I	ł	11	11	1	1		1	1	I	!		_
Weight found of	HgS.	0.577 1:36	$0.194 \\ 0.392$	0.148 0.1654	1	I	$0.210 \\ 0.202$	0.263	1	0.3015	0-3975	Ι	1	0.238	0.1054		
	$Hg_2Cl_2$	0.339	0.080	0.6814 0.7685	I	1	0.221 0.203	0.243 0.277	1	0.310	31	I	١	0.066			
	"Free" Hg.	0-7804 0-480	0.159 0.3248		I	I		11	1	1		1	1	1	!		
nəakat tl. .sms.	as lo .1W 12 ni	$\begin{array}{c} 2.485\\ 2.485\\ 1.586\\ 1.435\\ 0.1452\end{array}$	0.5125 1.045 0.5078	0.9331	0.3064	699-0	0.451 0.430	0.5564	0-2032	0.6336	0.4126	0.242	122.0	0.4966	0.1288	0.188	
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Table of Results of Analyses.