CHEMICAL RESEARCH AT THE PRESIDENCY COLLEGE

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BY

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ON

*Mercurous Nitrite.**

(Read December, 1895.)

Preliminary

Having recently had occasion to prepare mercurous nitrate in quantity by the action of dilute nitric acid in the cold on mercury, I was rather struck by the appearance of a yellow crystalline deposit. At first sight it was taken to be a basic salt, but the formation of such a salt in a strongly acid solution was contrary to ordinary experience. A preliminary test proved it, however, to be at once a mercurous salt as well as a *nitrite* The interesting compound promised thus amply to repay an investigation.

Historical

Lefort, Gerhardt and Marignac, especially the last, have studied and described in detail the action of nitric acid on mercury under varying circumstances. We have to labour here under the serious disadvantage of not having access to the original memoirs of these French chemists. Fortunately, a complete resumé of Marignac's work is to be found in Fremy's *Encyclopédie Chimique.* The information as regards

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* **Reprinted from the Journal, Asiatic Society of Bengal. Vol. LXV, Part II, No. 1, 1896. See also Zeit. Anorg. Chem. Bd xii. 1896.**

mercurous nitrite, however, is scarcely worth anything.* Roscoe and Schorlemmer in their well-known treatise do not so much as mention this compound, nor is there any reference to it to be found in the latest edition of Watt's *Dictionary of Chemistry*

Method of Preparation

Yellow nitric acid, sp. gr 1 410, is diluted with water in the proportion of 1 to 3 in a flask or beaker. 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 A gentle effervescence of gases at once takes place, and in the course of about an hour yellow needles resembling prismatic sulphur, begin to appear on the surface of mercury, After a few hours the liquid together with the mercury is carefully decanted off, and the salt shaken out of the vessel over porous tiles to remove the adhering mother-liquor ·

For purposes of analysis, *etc*, it is preferable to collect the first day's or at most the second day's crops only, partly because minute globules of mercury get entangled among the mass of the crystalline deposit, which it is tedious to get rid of, and partly because the composition of the salt varies on standing in the liquid. Thus it is found that if the salt, instead of being removed, is allowed to remain in contact with the mercury and the mother liquor, it gradually disappears and in its place transparent, perfectly colourless, crystals are formed, which grow in size with time. These latter will be described under the name of "Marignac's salt," which is a basic mercurous nitrate.

Qualitative tests

The new compound among others answers to the following tests.—

1. Dilute sulphuric acid slowly evolves nitrous fumes: more readily on heating.

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* The words which have a direct bearing on the present subject are quoted here. "L'azotite mercureux se forme...en meme temps que l'azotate mercurique d'apres Lefort, chaque fois que l'on attaque du mercure per de l'acide nitrique. D'autre part, Gerhardt n'admet pas l'existence de l'azotite mercureux et il considère les produtis obtenus comme de l'azotate mercuroso-mercurique.' Tome III. p. 240.

2. On warming with a large excess of water, globules of mercury separate out. In the cold the decomposition is only partial

The *perfectly clear* mother-liquor, decanted off the mercury, gives the following reactions —

(a) Boiled with an excess of pure caustic soda solution, it yields a black dense precipitate, the filtrate from which, after acidification with dilute sulphuric acid, rapidly decolorizes potassium permanganate solution and instantly sets free iodine from potassium iodide.

(b) Sodium chloride throws down a copious white precipitate; after removal of the calomel, the filtrate is now divided into several portions; to one is added caustic soda, and a yellow precipitate is the result, another portion treated with potassium iodide gives an orange precipitate; whilst a third portion on addition of hydrochloric and phosphorous acids yields a further quantity of mercurous chloride.

It is thus evident that in the clear solution we have both a *mercurous* and a *mercuric* salt as well as a *nitrite* Urea does not give the faintest opalescence to the liquid, showing the absence of mercuric *nitrate*

QUANTITATIVE ANALYSIS

A. *Estimation of Mercury*

In determining the composition of the salt, the amount of mercury in it will have the predominating voice, on account of its high atomic weight; the nitrogen playing only a minor part. The estimation of this metal will therefore be described somewhat in detail.

It has already been shewn that when the salt is heated with a large bulk of water, metallic mercury separates out, leaving in solution both an *ous* and an *ic* salt. The mercury thus liberated sometimes collects readily into a single globule; sometimes it remains as a grey powder, the whole of which it is difficult to aggregate into globules, even after continued heating with hydrochloric acid. For estimation, the mercury is now transferred to a tared crucible and kept under a dessicator. The mercury weighed in this form will be termed "free" mercury all along.

The solution decanted off the mercury with the rinsings of the vessel is considerably diluted with water and an excess of hydrochloric and phosphorous acids added to it. The mixture is now allowed to stand overnight and the precipitate of mercurous chloride weighed in the usual way When, however, it is desired to estimate the *ous* and the *ic* salts separately, treatment with sodium chloride is resorted to previous to the addition of hydrochloric and phosphorous acids, and the calomel then weighed in two instalments. Although this method yields accurate results, it often proves a very tedious one. After removal of the calomel by $HCl + H_3PO_3$, and further dilution of the filtrate with water, a small quantity of precipitate, varying from a few centi-to milligrams is generally obtained the succeeding day, and so on. Probably it was the nitrous acid necessarily present in the liquid which caused this kind of retardation in the precipitation of calomel.*

In a few cases the mercury in the *ic* salt was estimated as the *sulphide*. But this method is almost equally troublesome on account of the large quantity of sulphur set free The pores of the filter-paper get choked up, and the filtration, though carried on under reduced pressure with the aid of Bunsen's pump, proceeds very slowly Moreover the precipitate has to be digested with a strong solution of sodium sulphite, thoroughly washed with hot water, dried and re-washed with carbon bisulphide, purified by being kept over mercury and re-distilled. Unless the precipitate is treated once more with carbon bisulphide, the result is apt to be too high. There is thus not much to choose between these methods Both, however, give satisfactory results when conducted with care and patience

Preparation I —0 8695 gram substance gave 0·274 gram. "free" mercury = 31 5 per cent "free' mercury. 1·1895 gram. substance kept over $H_2 SO_4$ in the dessicator, July 27th 1895. July 30th, wt. = 1 184 gram.; after a month's stay in the dessicator, the wt was constant = 1·184 gram. 1 184 gram substance gave 0 3485 gram. ' free" Hg., = 29·43 per cent "free" Hg . 0 246 gram. Hg_2Cl_2 from the *ous* salt in solution = 17 7 per cent. Hg.; and 0 422 gram. Hg_2Cl_2 from the *ic* salt = 30·27 per cent Hg

Preparation II.—1 2865 gram. substance gave 0·3957 gram. "free" Hg., = 30·76 per cent., 0·25 gram Hg_2Cl_2 from the *ous* salt = 16·5 per

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* In the estimation of mercurous nitrate no such retardation occurs.

Hg; and 0·4645 gram. Hg_2Cl_2 from the *ic* salt=30·69 per cent. Hg. 1·224 gram. substance gave 0·3575 gram "free" Hg.,=29·2 per cent.; 0·243 gram. Hg_2Cl_2 from the *ous* portion=16·86 per cent. Hg.; and 0·437 gram Hg_2Cl_2 from the *ic* portion=30·31 per cent. Hg.

Preparation III.—1·641 gram. substance gave 0·5025 gram. "free" Hg.,=30·62 per cent.; 0·348 gram. Hg_2Cl_2 from the *ous* salt=17·8 per cent. Hg.; and 0·5965 gram HgS from the *ic* salt=31·33 per cent. Hg.

The results are presented here in a tabulated form for convenience of reference.

	"Free" Mercury	Mercury in the *ic* Salt	Mercury in the *ous* Salt	Total per cent. of Mercury	
1.	31·5		..	.	
2.	[29·43]	30·27	17·7	78·67	mean 78·56
3.	30·76	30·69	16·5	77·95	
4.	[29·2]	30·31	16·86	77·87	
5.	30·62	31·33	17·8	79·75	

The percentage of "free mercury" in analysis (2) and (4) respectively comes out too low. The cause of this has been already explained. Whenever the mercury separates out as fine grey powder it is difficult to collect the whole of it into globules; during the decantation of the liquid a part of it is carried off, and during the process of boiling with hydrochloric acid to induce coagulation, another portion is lost by volatilisation. As Fresenius himself remarks "in general a little mercury is lost." In analysis (5) the percentage of mercury in the *ic* salt is a little too high, because this was estimated as HgS (see *ante* p. 4). It would be safe to take 30·7 as the percentage of mercury both in the "free" state as well as in the *ic* salt, and this number has been actually taken in calculating the percentage in (2) and (4).

B. *Estimation of Nitrogen.*

The salt was boiled with water and after separation of "free" mercury, the clear liquid was made up to a definite volume and generally 4 c c of it treated in the nitrometer In the case of very dilute' solutions of alkaline nitrites and nitrates it is generally the custom to take a larger volume of the liquid, evaporate it to dryness and then dissolve the residue in the minimum quantity say 2 c c.) of water. But unfortunately this could not be done in the present case, as thereby insoluble basic salts were formed In dealing with small quantities any experimental errors would no doubt be highly magnified and thus tend to vitiate the result, but the method is one which admits of rigorous exactitude, as was proved by blank experiments with dilute solutions of potassium nitrate *

Preparation IV *(a)* Substance=0·2554 gram , Volume of solution =65 c.c

4 c.c. Sol.=1·5 c c NO t=33°C ; p=760 mean (mean of 4 concordant estimations). Whence NO=11·46 per cent.

(b) Substance=2 008 gram., Vol. of Sol.=226 c.c.

4 c c. Sol. =3 5 c c NO (mean of 3 estimations); t=31°C; p=760 m m Whence NO = 11·87 per cent.

(c) Substance = 2·299 gram ; Vol. of Sol. =234 c c.

4 c.c Sol = 3·9 c c NO (mean of 4 estimations), t=32°C; p=760 m m Whence NO =11·93 per cent

Evidence as to the salt being a nitrite pure and simple.

As the Crum-Frankland method does not enable us to discriminate between the *nitrate* and the *nitrite*, use was made of the well known reaction between urea and nitrous acid †

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* One who has made the estimation of nitrites and nitrates almost his life-long study testifies as regards the Crum-Frankland process, "that in the absence of organic matter and with proper manipulation in the shaking tube, the method is one of great accuracy, and capable of determining extremely small quantities of nitrates or nitrites" Warington—Chem. Soc Jour 1879, page 387.

† For details of this process see "A gasometric method of determining nitrous acid," by P. F. Frankland Chem Soc. Jour LIII, 364

It was found that the solution of the *ous* and *ic* salt was only slowly and imperfectly acted upon by dilute sulphuric acid, it was therefore treated with pure caustic soda and warmed. In this way the nitrite was converted into an alkaline salt

Substance = 0 7285 gram., Vol. of Sol = 100 c.c

After absorption of CO_2 by strong lye,

$$\begin{array}{lll} 4 \text{ c c. sol.} = 2{\cdot}85 \text{ c.c. N} & & \\ 5 \quad \text{do} = 3\ 55 \text{ do} & \left\{\begin{array}{l} t = 32^\circ C. \\ \\ p = 756 \text{ m m} \end{array}\right. \\ 10 \quad \text{do} = 7{\cdot}10 \text{ do} & \end{array}$$

Whence NO = 11 7 per cent

As the urea also gives up the whole of its nitrogen according to the equation given below, the experimental error is thus diminished by half.

$$2\ HNO_2 + CON_2H_4 = CO_2 + 2N_2 + 3H_2O$$

Dunstan and Dymond's method of estimating nitrites was also applied, but in this case it is extremely difficult to prevent leakage of traces of air. The result in general was rather high.

The mean of the several estimations of nitric oxide is 11·74

Discussion of the Results and Theoretical Considerations

The results accord well with the formula

$$HgNO_2 + 1/2\ H_2O\ *$$

		Theory.	Found.
Hg =	200 00	78 43	78 55
NO =	30·00	11·77	11·74
O =	16·00	6·27	
$1/2H_2O$ =	9 00	3·53	
	255·00	100·00	

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* While correcting the proofs I may as well mention here that the salt has the formula $Hg_2(NO_2)_2$ Since the memoir was presented to the Society, I have made repeated analyses of it, the mercury being estimated as sulphide, as phosphorous acid gives very low results in presence of nitrous acid The percentage of "free" mercury has been found to be 31·41, that in the *ic* salt, 31 41 and that in the *ous* salt, 17·8, total 80·62. Theory for $Hg_2(NO_2)2$ requires 81·3

On dilution with a sufficiently large quantity of water, the salt moreover undergoes dissociation, thus:

$$Hg_2(NO_2)_2 = Hg + Hg(NO_2)_2$$

The amount of mercury set free being equal to that contained in the *ic* salt, quantitative proof of which has been given above. The dissociation of mercurous nitrite is analogous to that of calomel[*]

$$Hg_2Cl_2 = Hg + HgCl_2$$

Diminution of pressure in one case playing the rôle of dilution in the other, nearly 22 per cent of the salt, however, dissolves *as such*, and dilution has no further effect in increasing the proportion of dissociation (*Vide* table, p 4)

The present compound throws additional light on the action of nitric acid on the copper-mercury group of metals. It is now admitted by chemists that "in their relation to nitric acid metals must be divided into two classes" To the former belong those which produce ammonia and hydroxylamine from it, *e g*, Tin, Zinc, Cadmium, Iron Aluminium, Potassium, &c, while the latter includes Copper, Silver, Mercury and Bismuth These seem to enter into direct union with the nitrogen of the acid, instead of displacing its hydrogen The formation of the *nitro* compounds of the fatty series by V. Meyer's method lends additional support to this theory. This *nitronic* constitution of nitrous acid, as Divers puts it, also explains the advantage of red or yellow nitric acid in dissolving metals of the silver-mercury class.[†]

$$\begin{matrix} Ag \\ Ag \end{matrix} + H \,\Big|\, NO_2 + HO \,\Big|\, NO_2 = \begin{matrix} Ag\ NO_2 \\ Ag\ NO_2 \end{matrix} + HOH$$

Indeed, the presence of nitrous acid seems to be *sine qua non* for the dissolution of metals like silver, mercury, &c., as was first pointed out by Russell.[‡] This chemist also showed that when silver dissolves

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[*] Harris and V Meyer's recent experiments fully bear out the conclusion arrived at by Odling years ago. See "Ueber den Molekularzustand des Kalomel dampfes" Berichte, 27 (1894) p 1482

[†] Divers: Chem. Soc Journ for 1883 Trans, p 443, also *ibid* Trans. for 1885, p. 231.

[‡] "On the action of Hydrogen on Silver Nitrate," Chem Soc Journ Trans [2] xii. 3.

in nitric acid, "silver *nitrite* is formed in quantity, partly in solution in the silver nitrite liquor, partly as crystals." The stability of silver nitrite in presence of strong nitric acid is noteworthy, as ordinary nitrites are decomposed even by the weakest acids. The nitronic nature of silver nitrite affords a ready explanation of this apparent anomaly.

Acworth and Armstrong in their classical researches found "that "the amount of gas [NO] obtained by decomposing silver nitrite by "nitric acid varies according to the strength of the acid, *being greater* '*the weaker the acid*" (the italics are ours) .again "no amount of heating will effect this [decomposition] if the acid be concentrated."* Mercurous nitrite seems to behave exactly like silver nitrite.

The traces of nitrous acid, present in the yellow nitric acid, no doubt, start the reaction, but how to account for the continued formation of mercurous nitrite? For, this small quantity is soon used up according to the equation given above There must be a parallel reaction going on to keep up the supply of nitrous acid. Acworth and Armstrong thus explain the action of copper on nitric acid.†

$$\begin{aligned} Cu + 2\,HNO_3 &= 2H + Cu\,(NO_3)_2 \\ 2H + HNO_3 &= HNO_2 + OH_2 \\ 3HNO_2 &= 2\,NO + HNO_3 + OH_2 \end{aligned}$$

Adopting this view, the mercurous *nitrite* would continue to be formed for some time, and being insoluble in the menstruum, would be precipitated, whilst mercurous nitrate would remain in solution. The strength of the acid also would go on diminishing, till a time arrives when mercurous nitrite is no longer stable in this liquid, the nitrous acid decomposing according to the equation

$$3\,HNO_2 = 2\,NO + HNO_3 + OH_2$$

and Marignac's salt begins to be formed. The transformation of the nitrite into nitrate is however very slow, the process extending over weeks.

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* On the Reduction of Nitric Acid, &c., Chem Soc. Journ, Vol LI. (1877) p. 54 *et seq.*

† Whether NO is formed through the agency of *nascent* hydrogen, or by the *direct* action of the metal on nitric acid must be left at present an open question. *Cf.* Deville: De l'état naissant, *Compt Rend*, 1870, LXX, 22, 550

During the initial stages of the reaction the reverse change seem to take place; for, on the surface of the mercury somewhat brisk effervescence goes on, but proportionally very little nitric oxide escapes. During its upward ascent most part of it is absorbed, thus —

$$2\ NO+HNO_3+H_2O=3\ HNO_2.$$

A strong proof in favour of this view seems to be the fact that as soon as the superincumbent liquid is poured off, torrents of red fumes appear on the surface of mercury.*

The place of mercury in the periodic System would naturally justify the expectation that it would yield the *analogue* of silver nitrite and the present compound is a realisation of it.

Although the compounds of monatomic mercury resemble the corresponding ones of silver, there is a sharp distinction between them Silver never gives basic or hydrated salts, whilst the compounds of mercury with nitric or nitrous acids seem to be almost invariably basic or hydrated or both.

It has already been said that for purpose of analysis the first or second day's crop should be collected; after a longer time a granular mass of yellow rhombic tabular prisms (?) is obtained, which is rather richer in the percentage of mercury and at the same time much less stable. When this salt, after being dried on the porous tile, is kept in the bottle, it constantly evolves nitrous fumes.

Temperature also seems to have an important bearing on the formation of the present salt. The ordinary temperature of the Laboratory

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* Veley also arrives at this conclusion. "If the conditions are such that "these metals [Copper, Mercury and Bismuth] dissolve, it would appear that the "metallic nitrite is at first formed, together with nitric oxide. The former is de-"composed by the excess of nitric acid to liberate nitrous acid, whilst the latter "reduces the nitric acid to form a further quantity of nitrous acid."

"Eventually the net result is the product of two reverse chemical changes "represented by the equations—

(1) $2\ NO+HNO_3+H_2O=3\ HNO_2.$

(2) $3\ HNO_2=2\ NO+HNO_3+H_2O.$"

Proc. Royal Soc. (1890), 48, page 458

in the summer season, 31° to 30°C., seems to be very favourable for the growth of the needles.

The different mercurous nitrites and nitrates and *mercuric nitrite* as also an attempt to prepare nitro-ethane with the aid of the compound now described, will form the subject of subsequent communications.

ON

The Constitution of Mercuric Hyponitrite, Nitrite and Nitrate.

I.—*Mercuric Hyponitrites* II.—*Trimercuric Sulphate and its new Modifications* III.—*Theoretical Considerations*

Preliminary

Evidence has already been adduced in favour of the *nitronic* constitution of mercurous nitrite.* It has also been found that though it is not possible to prepare mercuric nitrite in the solid state, a neutral solution of it is however easily obtained as a product of the dissociation of mercurous nitrite Such a solution on treatment with a dilute solution of sodium hyponitrite as prepared by Zorn and Dunstan and Dymock's method, which necessarily contains *potassium sulphate* was found to yield mercuric hyponitrite.† It was thought desirable to study the action of this reagent on mercuric nitrate as well with a view to gain an insight into its constitution. The investigation has led to results which seem to be of interest

I.

(a)

Mercuric Hyponitrites.

A concentrated solution of mercuric nitrate is first got ready containing the minimum amount of free nitric acid essential to its

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* Journal Asiatic Society Vol. LXV, Pt. II, No. I p. 7. Zeit. anorg. Chem. (1896), p. 372.

† Journal Chem. Soc. LXXI, 348.

very existence in a state of solution. This object is gained as follows:— The stock solution of the nitrate more or less acid is carefully diluted with water, till a flocculent white precipitate of basic nitrate just begins to separate out, and which remains suspended in shreds. The liquid is heated to boiling so as to coagulate the basic salt, which is removed by filtration. To the filtrate is now cautiously added a solution of sodium hyponitrite prepared as above, when a light gelatinous white precipitate appears at the top of the liquid, which takes a long time to settle down. Great care should be taken at this stage, for if too much of the precipitant be added all at once, a yellow powdery deposit begins to appear. It is necessary to work with a very large bulk of the nitrate solution in order to get this gelatinous substance in quantity sufficient for analysis. It shrinks to a very small amount when it is dried over sulphuric acid. In its general properties the substance resembles the hyponitrite previously described.

Analysis.

The compound has the formula $Hg(NO)_2+3HgO+5H_2O$

	Calc.	Found I	Found II
Hg	80·17	80·15	80·47
N.	2·81	2·98	——

The presence of water was proved qualitatively by gently heating in a bulb tube. The substance is apt to be contaminated more or less with the basic mercuric sulphate described below.

(*b*)

A solution of mercuric chloride was treated with sodium hyponitrite solution exactly as above. A gelatinous white precipitate was thus obtained; when dried, it had a yellowish white appearance. In the present instance *it is immaterial whether a concentrated or dilute solution of the chloride is used.* This compound corresponds to the formula $Hg(NO)_2+3HgO+3H_2O$, in fact it is the same salt as obtained from mercuric *nitrite.*

	Calc.	Found.
Hg.	83·16	82·90
N.	2·91	3·13

II

Trimercuric Sulphate and its new Modifications

a

The filtrate from the gelatinous precipitate [See prep. I (*a*)] is diluted *ad lib*, when a yellow impalpable powder comes down almost immediately, the amount of dilution depending upon the strength of the filtrate From what has been already said it would be evident that when the mercuric nitrate solution is very largely diluted to begin with and the basic nitrate precipitate got rid of as before and then treated with the precipitant the yellow powder is at once obtained without the gelatinous hyponitrite

β

It has been pointed out above that in order to obtain the yellow powder the filtrate from the gelatinous substance has to be copiously diluted with water ; now, if this filtrate instead of being diluted be allowed to stand overnight, a crystalline form of the yellow compound is obtained, which is sometimes of a bright orange colour and sometimes orange, with a brownish tint. The mother-liquor from this orange variety of the basic sulphate when largely diluted with water yields as before the yellow powder One should practise on a small scale in order to acquire the necessary experience for obtaining these modifications.

γ

When the dilute filtrate from the yellow powder (*a*) is boiled in a flask for sometime, it may be for an hour or two, and thus slowly concentrated, crystalline bright yellow scales, and sometimes a scaly powder, is gradually deposited at the bottom

The yellow powder (*a*), the formation of which has been described above, is the well-known trimercuric sulphate——mineral Turpeth. This as well as its *β* and *γ* modifications will form the subject of the next paper

III

Theoretical Considerations.

A solution of mercuric nitrite or chloride, *however highly diluted it may be*, always yields mercuric hyponitrite, when acted upon by sodium hyponitrite solution in presence of potassium sulphate ; but a solution of the nitrate under similar conditions gives tri-mercuric sulphate

It appears that in mercuric nitrite as in mercurous nitrite, the nitrogen is directly attached to the metal, whereas in the nitrate as is generally accepted, it is united to oxygen In the former there is no tendency for the NO_2 group to detach itself from the metal, but in the latter on dilution and in presence of the alkaline sulphate the split takes place as indicated by the dotted line

$Hg-O$——NO_2 The sodium hyponitrite seems to take no direct part in the reaction unless the mercuric nitrate solution be sufficiently concentrated In one respect however the alkaline hyponitrite plays a conspicuous part, in that by its solvent action upon the basic mercuric sulphate it retards immediate precipitation and thus favours the formation of its crystalline modifications

The researches of Professor Divers and of his pupils Haga and Shimidzu have thrown a flood of light on the constitution of silver nitrite and of mercuric sulphites* The "non-oxylic or haloid" character of these salts forms the ' central conception in their Chemistry Mercuric nitrite also has a *haloid* constitution It is well-known——though sufficient recognition of it has not generally been taken in the text books ——that the halogen compounds of mercury are with difficulty acted upon by sulphuric acid The nitrite of mercury also resists the action of the sulphate. This haloid constitution of the nitrites is the "central conception" in the Chemistry of the compounds which form the subject of the present investigation †

A few pertinent remarks might be made here as regards the constitution of silver and mercury hyponitrites Both these salts dissolve *as such* in dilute nitric acid and are reprecipitated on the addition of an alkali. It has also been found that mercuric hyponitrite does not readily dissolve in dilute nitric acid and is with still greater

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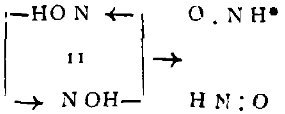
* Jour Chem Soc Trans. 1883, p 443; *ibid* 1885, p. 231, *ibid* 1886, p. 533

† Cf 'Bemerkenswerth fur alle Halogenverbindungen des Quecksilbers ist ihre grosse Widerstandsfähigkeit gegen conc Schwefelsäure. Selbst in der Hitze wird durch diese das Halogen nur langsam ausgetrieben." Richter Lehrbuch der Anorg Chem. Ed 1895, p 384.

difficulty soluble even in boiling strong nitric acid On neutralizing the solution with alkalies a voluminous flocculent precipitate of the hyponitrite is thrown down. The behaviour of hydrochloric acid towards mercuric hyponitrite is also interesting This acid in the dilute state and even in the cold readily dissolves the salt, which is reprecipitated on neutralization with an alkali. Thus, mercuric chloride is not formed in solution. In other words the affinity of mercury for the radical of hyponitrous acid (whatever its constitution might be) is greater than that for the halogen All the well-known reactions of *silver hyponitrite as well as the several methods of formation of the* hyponitrites seem to point to a "diazo" constitution of hyponitrous acid—HO—N_2—OH; it is however possible that in certain cases this acid and its salts, especially those of silver and mercury, exist in tautomeric modifications Thus —



$$\begin{array}{l} HO\,N \\ \quad \| \\ N\,OH \end{array} \longrightarrow \begin{array}{l} O\,.\,NH^{*} \\ \\ H\,N:O \end{array}$$

This imidic constitution would have the metal directly bound to nitrogen *The comparative stability of the mercury hyponitrites in* the heat does not also seem to be in accord with their *diazo* structure

It has been shewn above that the concentrated solution of mercuric nitrate under favourable conditions when treated with sodium hyponitrite and potassium sulphate gives rise to mercuric hyponitrite in preference to trimercuric sulphate In other words, mercury exchanges its place in the nitrate which is an oxylic salt, for that of the hyponitrite in which it is directly attached to nitrogen It is only when the nitrate solution is used in a dilute form that other forces come into the field of action, and a basic sulphate is the result.

In a subsequent communication entitled "the Interaction of the alkaline hyponitrites with the salts of the zinc-copper group," the author hopes to develop this theory further.

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* Annalen Bd 292, Heft 3,357 Hantzsch Zur Isomerie der Verbindungen $N_2O_2H_2$

ON

Trimercuric Sulphate and its new Modifications.

Historical

Trimercuric sulphate, the salt corresponding to hexabasic sulphuric Acid, $S(OH)_6$, has been known since the 16th century. "Das basische schwefelsaure Quecksilberoxyd kannte schon Basilius Valentinus .Inder Paracelsischen Schule wurde dies Salz meist mineralischer Turbith order Turpeth gennant" (Kopp.. Geschichte IV, 188). In the present century this compound has been described by several chemists from time to time. Kane gives to it the formula $Hg\ SO_4{\cdot}2HgO$. and his analysis bears it out. The present investigation would, however, go to show that this is really a hydrated salt having the formula $HgSO_4{\cdot}2HgO\ \frac{1}{2}H_2O$ It is probable that the percentage of water being so low as 1·22 has hitherto escaped notice. In fact the analyses of R. Phillips and of Braamcamp and Siq. Ol. conform to the latter formula.* The orange and the bright yellow crystalline modifications I do not find described anywhere.

The method of preparation of the α, β & γ modifications of this salt has been described in the previous paper. The α and the β forms are both hydrated and have the same formula, namely that given above; whilst the really anhydrous salt can only be obtained by the method of preparation given under γ.

General Properties.

All these compounds dissolve in dilute nitric and hydrochloric acids and more readily on warming; the solution in the latter acid has a faintly opalescent appearance, due to the presence of traces of calomel. When dried at 100°, the hydrated varieties α and β do not lose water nor change in colour. When heated to a higher temperature the yellow powder (α) gives up water and assumes an orange to

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* *Vide* Gmelin's Hand Book : Vol VI, p. 29.

brown coloration; but it reverts to the original colour on cooling. The orange and the orange-brown grano-crystalline variety (β) loses water under similar conditions and falls to a yellow powder. When heated to about 400° these basic sulphates behave in a remarkable way; it is true that they begin to decompose long before this temperature is reached, but at about this temperature they are converted into mercuric sulphate having given up the oxide of mercury as metallic mercury and oxygen; the mercuric sulphate then fuses to a brown liquid and volatilises as mercurous sulphate, oxygen and sulphur dioxide being at the same time liberated The decomposition can be represented by the following equation: $2[HgSO_4\ 2HgO]=Hg_2SO_4+4Hg+3O_2+SO_2$

Analysis.

Method of analysis. The mercury was estimated as sulphide in the usual way The water in the yellow variety (α) was determined by heating in a tube in a current of dry carbonic acid gas. In the cooler parts of the tube near which the calcium chloride tube was attached there was interposed a layer of gold leaf, so as to arrest vapours of mercury which might otherwise enter into the $CaCl_2$ U-tube. Perhaps, it would not be unnecessary to mention here that the yellow powder was dried at 100°, then powdered again, so as to break up the small lumps and again transferred to the steam chamber. When the weight of the substance was constant it was kept in a dessicator over sulphuric acid. The possibility of the presence of mechanically held or absorbed water was thus guarded against

Result of Analysis.

α and β

	Calc. for	Found.											
	$HgSO_4\ 2HgO\ \frac{1}{2}H_2O$	1	2	3	4	5	6	7	8	9	10	11	12
Hg	81 41	80 76	80 72	81 28	81 26	80 72	80 55	81 26	80 67	81 13	80 85	81 13	81 47
SO_4	13·02			13 48									
H_2O .	1 22		1 16		1 25								

Theory for the anlydrous salt demands Hg=82·420 It may be added here that the analyses given above are of different preparations, with the exception of 3 and 4 which belong to one and the same preparation. It will be found that the percentage of mercury generally comes out too low. The reason of this is that in these preparations minute portions of mercuric nitrate and the alkaline sulphate are invariably "carried down" during the precipitation, which cannot be got rid of even by repeated washing In a few cases the nitrogen, and the alkaline sulphate contained in the filtrate, were determined. Thus in 9 the percentage of potassium sulphate amounted to 0·73 whilst in 10 it rose so high as 1·33. The nitrogen generally came up to 0·25 to 0·75 per cent

It is well-known that wherever oxide of mercury is prepared by treating mercuric nitrate with caustic alkali, it is never chemically pure, the impurities being mercuric nitrate and alkali.* Haack has described the preparation of mercuric arsenate by double decomposition of mercuric nitrate and sodium arsenate. He found that the compound thus obtained was always contaminated with mercuric nitrate and sodium nitrate. The result of his analyses,† which is given below, will explain as to why it is that the mercury has generally come out too low and sulphuric acid too high in the estimations given above.

Calc. for		Found			
$Hg_3(AsO_4)_2$		I	II	III	IV
As_2O_5 ...	26·20	25·50	24·37	26·10	26·00
HgO ...	73.80	72.23	73·01	73.68	73.60
Na_2O ...	—	0·73	0·19	—	—
N_2O_5 ...	—	1·43	1.85	—	—
	100·00	99·89	99·42	99·78	99·60

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* Vide Encycl Chimiqe (Fremy) T 3 cahier, 14 p 154

† Annalen Bd 292, 184

This is the really anhydrous salt. When it was heated in a dry bulb tube not a trace of moisture was noticed in the cooler parts.

Analysis.

Calc. for $HgSO_4 \cdot 2HgO$		Found
Hg ...	82.42	82.53
SO_4 ...	13·19	13·33

The Action of Heat on Trimercuric Sulphate

as described above (see page 17) was studied in the following way. The compound was placed in a porcelain boat and heated in a combustion tube, 65 c. c. long, in a current of carbonic acid gas As the decomposition of the oxide of mercury is a case of dissociation, there is a tendency for the components to re-combine in the cooler parts of the tube. This was prevented by the current of the inert gas which chased away the oxygen into the collecting tube, filled with mercury and strong potash lye, the moment it was set free. (See Deville Compt Rend. 56, 729) A Hoffmann's furnace was used and the progress of decomposition could be watched from time to time. The behaviour referred to above was noticed in every case of the mass of the substance fusing and swelling up immediately before complete volatilisation. The white sublimate of mercurous sulphate was deposited near the heated portion of the tube and the "mirror" of mercury away from it.

The decomposition was quantitatively established as follows :—The white sublimate of mercurous sulphate together with the mirror of mercury was treated with dilute nitric acid and shaken up. The contents were then transferred to a beaker; the liquid, holding in solution mercurous sulphate, was decanted off the metallic mercury. The latter was warmed with hydrochloric acid to make the small globules coagulate into a single one. The mercurous sulphate solution was treated with sodium chloride and the calomel weighed in the usual way The sulphuric acid in the filtrate was also estimated. If the salt decomposes according to the equation :—

$$2\,[Hg\ SO_4 \cdot 2HgO \cdot \tfrac{1}{2}\ H_2O] = Hg_2\ SO_4 + 4Hg + 3O_2 + SO_2 + H_2O.$$

we should expect that the "free" mercury would amount to double the quantity obtained from calomel and that the sulphuric acid radical SO_4) as well as oxygen would amount to half of what is contained in the original salt.

Result of Analysis.

	Calc	Found		
		1	2	3
Hg (metallic) ...	54·28	54·00	55·42	52·92
Hg (in calomel) ...	27·14	25·90	25·80	27·36
SO_4	6·51	6·58	6·57	—
O	6·51	6·44	6·50	6·60

In (1) and (2), the wt of salt taken for analysis amounted to 0·3226 gm and 0·332 gm. respectively; but in (3) the wt was 1·969 gm. The filtrate from the calomel was tested with sulphuretted hydrogen, which imparted only a brown coloration to the liquid, but no weighable precipitate was obtained. The result of analysis is not very satisfactory; but the method itself does not admit of a high degree of accuracy.

As a check upon the method of estimation of oxygen, pure oxide of mercury was analysed The result is given below:—

Theory		Found
Hg	92·60	92·34
O	7·40	7·36
	100·00	

It was thought desirable to prepare trimercuric sulphate by the ordinary method, namely by the action of sodium sulphate on a hot solution of mercuric nitrate The lemon yellow powder thus obtained was washed and dried with the care described above (see p. 7). The result of analysis is given below. The water was kindly estimated by direct method by Mr. C. Bhaduri B. A., Demonstrator, Chemical Laboratory, with scrupulous care and rigorous exactitude.

Calc. for		Found		
$Hg\,SO_4\cdot 2HgO\cdot \frac{1}{2}H_2O$		1	2	3
Hg .	81·41	81·47	81·64	81·36
SO_4 ...	13·02	13·78	—	—
H_2O ..	1·22	1·21		

As was to be expected a much purer product was obtained in this case The analyses recorded above are of three different preparations

NOTE ON THE DECOMPOSITION OF MERCURIC SULPHATE UNDER HEAT —when trimercuric sulphate is gradually heated it undergoes decomposition as pointed out above When the brown liquid, before it is completely volatilised, is allowed to cool down quickly, a white, porous, vitreous mass of mercuric sulphate is obtained. When this compound is heated it gradually decomposes, then fuses and is completely volatilised, the products being metallic mercury, mercurous sulphate, oxygen and sulphur dioxide The description in Roscoe and Schorlemmer's standard work is thus fully borne out by my own experiments No sublimate of mercuric sulphate is however obtained, as stated by Mohr. (Gmelin Vol. VI p. 29.) In one case 0·331 gm. $HgSO_4$ yielded 6 mgs. of HgS in the filtrate from calomel when the solution of the sublimate of mercurous suphate was treated with sodium chloride It is however possible that when the mercurous sulphate was warmed with dilute nitric acid to get it into solution, a small portion of it underwent oxidation.

The decomposition goes on in two directions.

Thus

$$2\,Hg\,SO_4 = Hg_2\,SO_4 + SO_2 + O_2 \quad \dots \quad (1)$$

$$Hg\,SO_4 = Hg + SO_2 + O_2 \quad \dots \quad (2)$$

By far the larger proportion of the salt decomposes according to equation (1), a small portion only, sometimes less than one-fifth of the total quantity, breaks up according to (2)
