

XV.—*Hyponitrites; their Properties, and their Preparation by Sodium or Potassium.*

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THE hyponitrites have received the attention of many chemists besides myself since their discovery in 1871, and even this year new ways of forming them and the new working of an old method have been published. Yet much has been left to be put on record before a fairly correct and full history of these salts can be said to have been given, and the present paper is meant to be the necessary supplement to what has already been published.

Ways of forming Hyponitrites.

No writer on hyponitrites in recent years has shown himself acquainted with all the known ways of getting these salts, or even with the most productive. The following complete list is valuable,

therefore, and is of special interest as bringing together the various modes of formation of these salts.

1. Reduction of an alkali nitrite by the amalgam of its metal (Divers, 1871).

2. Reduction of an alkali nitrite by ferrous hydroxide (Zorn, 1882; Dunstan and Dymond).

3. Reduction of (hypo)nitrososulphates by sodium amalgam (Divers and Haga, 1885).

4. Reduction of nitric oxide by alkali stannite (Divers and Haga, 1885).

5. Reduction of nitric oxide by ferrous hydroxide (Dunstan and Dymond, 1887).

6. Decomposition of a hydroxyamidodisulphonate by alkali (Divers and Haga, 1889).

7. Oxidation of hydroxylamine by sodium hypobromite (Kolotow, 1890).

8. Oxidation of hydroxylamine by mercuric oxide, silver oxide, or cupric hydroxide (Thum, 1893).

9. Interaction of hydroxylamine and nitrous acid (Thum, H. Wislicenus, Paal and Kretschmer, Tanatar, 1893).

10. Oxidation of hydroxylamine by benzenesulphonic chloride and alkali (Piloty, 1896).

11. Interaction, in methylic alcohol, of hydroxylamine with nitrous gases (Kaufmann, 1898, *Annalen*, 299, 98).

12. Interaction, in methylic alcohol, of hydroxycarbamide and nitrous gases (Hantzsch, 1898).

13. Interaction of dimethylhydroxynitrosocarbamide and alkali (Hantzsch and Sauer, 1898).

Menke's reduction of fused alkali nitrate by iron, and Rây's reduction of mercuric nitrite by potassium cyanide in solution, are not included in the list, because both reductions are very doubtful, and require confirmation before they can be accepted. In the present paper, only the original method of preparing hyponitrites will be treated of.

Preparation of Sodium Hyponitrite Solution by the Reduction of Sodium Nitrite with Sodium Amalgam.

Sodium nitrite can be converted by sodium amalgam in the easiest and quickest imaginable way into fully one-sixth of its equivalent of sodium hyponitrite; this remains in solution, and is pure but for the presence of much sodium hydroxide. From this solution, the sodium salt itself, as well as silver hyponitrite, can be at once prepared, nearly pure and with hardly any loss. The solution, if

cautiously neutralised, is also at once fit for preparing lead, copper, mercury, and some other salts. The neutralisation is known to be complete when a little of the solution just ceases to give black oxide when mixed with a drop of a dilute solution of mercurous nitrate. Others who have tried this method, and particularly Hantzsch and Kaufmann, got far less favourable results.

Pure sodium nitrite is necessary, but that can now be prepared very simply (this vol., p. 85). In order to get as much hyponitrite as possible and as little hydroxylamine, the nitrite must be in concentrated solution; three times its weight of water seems to be the best quantity to dissolve it in when operating in the way to be described. Using these proportions, there is enough water to form, with the sodium oxide produced, a solution of the composition $\text{NaOH} + 3\text{H}_2\text{O}$, which is a nearly saturated solution of $\text{NaOH}, \text{H}_2\text{O}$ at the mean temperature.* In presence of so much hydroxide, the water is also quite saturated with hyponitrite, a small quantity of this salt even separating when the solution is kept at 0° for a time.

To reduce sodium nitrite in cold concentrated solution, $2\frac{1}{2}$ atoms of sodium are needed, the additional half atom being consumed in the unavoidable formation of some nitrogen, hydroxylamine, and ammonia. This accords well enough with the statement in my first paper, as a first approximation, that not more than 4 atoms are active on sodium *nitrate*. In practice, however, 3 atoms of sodium should be used in reducing sodium nitrite, partly because it is wanted afterwards to reduce hydroxylamine, and partly because it is important that all the nitrite should be reduced, and this, notwithstanding statements to the contrary, can only be accomplished quickly in presence of a good excess of sodium. The strength of the amalgam is not an essential point; I have, however, found it most convenient to work with a soft, solid amalgam having the composition $(\text{NaHg}_8)_2$, or 23 grams of sodium to 1600 grams of mercury.† The temperature, also, is not of importance if only the solution of nitrite is concentrated, and although it may in fact rise nearly to 100° without harm, it is better to follow my original direction to keep the flask in a stream of cold water during the reduction. It is, however, preferable to cool it, particularly in warm weather, by means of a brine and ice bath, as then the amalgam can be added much faster without producing any great evaporation. The temperature of the solution during the reduction then ranges, with a convenient rate of

* Sodium hydroxide forms a saturated solution at 15° in its own weight of water. When cooled, this solution deposits large pointed prisms of the monhydrate.

† Tanatar erred in supposing that I recommended the use of hard amalgam, and his supposed improvement of my process is not one in fact.

working, from 5° to 25° , and the time taken to add 23 grams of sodium need not be more than 10 minutes.

From a quarter to a half gram-molecule of sodium nitrite is a convenient quantity to work on, and the solution is best contained in a 350 to 450 c.c. pear-shaped, wide mouthed flask, lying very obliquely in the cooling bath while the amalgam is added by means of a spatula. The last fourth of the amalgam may be put into the flask as rapidly as it can be, and the flask may then be removed from the bath. It is kept actively rotated for 10—15 minutes, during which the temperature will rise to about 40° and then fall. The solution and mercury are next poured into a narrow mouthed stoppered bottle so as to half fill it, the thick, aqueous solution adhering to the flask being washed into the bottle, but the water used should be limited to 2 or 3 c.c. if it is desired to obtain the solid sodium salt. The whole is now violently shaken for 10 minutes or so, so as to destroy all the hydroxylamine. To ascertain this, a drop of the solution is tested by diluting it and adding a drop of silver nitrate solution, and a slight excess of dilute nitric acid; there should not be the slightest black tint due to silver reduced by hydroxylamine. No gas is liberated during the shaking, but a very strong odour of ammonia is developed. Strange to say, a minute quantity of nitrite is still present, and it seems almost impossible to entirely remove it, although it can be so far reduced by an hour's shaking of the solution with the amalgam that the acidified solution does not blue potassium iodide and starch until it has stood for about an hour.

On separating the solution from the amalgam and exposing it in a dish overnight over sulphuric acid, under reduced pressure, it will be free from ammonia, and is virtually a pure and stable concentrated solution of sodium hyponitrite and hydroxide.

As here described, the preparation of a solution of sodium hyponitrite ready for use is the same as that followed by me in 1871 (with nitrate), except the important modification in the manner of removing the hydroxylamine. When silver hyponitrite is prepared from the crude solution, the hydroxylamine gets destroyed by silver oxide, as I pointed out in the addendum to my first paper. Zorn, as an improvement, introduced the use of mercuric oxide, on the ground that destruction of some silver hyponitrite was thus avoided, but he overlooked the fact that it is the silver oxide, just as it is mercuric oxide, which becomes decomposed, the hyponitrite or any other acid radicle being untouched by the hydroxylamine in alkaline solution. Whether, therefore, mercuric oxide, or silver nitrate, or mercuric nitrate is used, and the precipitated metal then separated, the result is just the same in concentrated alkaline solutions, except that the dropping in a solution of the nitrate is more easy to carry out

than stirring up with mercuric oxide. Further, where the alkaline solution is very weak, the use of mercury compounds is not without objection, as a little mercuric oxide remains in solution. But whether silver or mercury oxide is employed, the result is unsatisfactory, for, as Thum has pointed out, both these oxides, in destroying the hydroxylamine, regenerate nitrite. Not, however, that Thum himself found this prevented him from successfully purifying the silver hyponitrite from nitrite by thorough washing and reprecipitation. Berthelot and Ogier, Paal and Kretschmer, and I myself, have not, however, met with the same success, as I found it necessary, in order to get silver hyponitrite free from all trace of nitrite, to begin by precipitating it in the absence of nitrite. Nevertheless, far from casting doubt on Thum's statement, I believe his silver salt to have been some of the purest ever prepared, from the account he has given of the properties of hyponitrous acid. No one, however, will be disposed to deny the superiority of sodium as a means of removing the hydroxylamine from the solution.

An almost pure solution of sodium hyponitrite can be conveniently got by dissolving the freshly prepared, hydrated, solid salt in water. Sodium iodide, or potassium iodide and the silver salt, will also furnish a solution of alkali hyponitrite. To get a solution for precipitating purposes, Thum proceeded in an indirect way, first preparing a solution of hyponitrous acid, and then adding enough sodium hydroxide to make the solution neutral to phenolphthalein, an effective but very wasteful process. Kirschner also, wanting a solution for precipitating purposes, used sodium chloride and silver hyponitrite, which, in a complex and wasteful way, he made to yield a solution which although mixed with much chloride and nitrate, was practically free from silver.

Sodium Hyponitrite.

In 1878, Menke gave full analyses of crystals of a stable salt having the composition of sodium hyponitrite containing $6\text{H}_2\text{O}$, which he had prepared by deflagrating in an iron crucible a mixture of sodium nitrate and iron filings, keeping the product at a red heat for an hour in a fire of charcoal rather than of gas, boiling the mass with water, filtering off iron oxide, evaporating, and leaving to crystallise. He makes no reference in his paper to the large amount of sodium hydroxide he must have had to deal with, although this should have seriously affected the procedure. In 1882, Zorn submitted Menke's method to a thorough examination, but failed to obtain the least trace of hyponitrite; he found, however, that ferrous hydroxide, acting on a solution of sodium nitrite, did produce sodium hyponitrite (in solution). His suggestion that Menke had mistaken

carbonate for hyponitrite takes no account of the fact that the nitrogen and water in the salt were repeatedly determined. It can now, however, be stated with certainty that Menke's salt was not the sodium hyponitrite obtainable by reducing sodium nitrite by sodium amalgam and water, for this differs from it in degree of hydration, stability, and in other properties.

D. H. Jackson (Proc., 1893) described two ways in which he had succeeded in preparing sodium hyponitrite, but with such difficulty that he was deterred from investigating its properties; indeed, he merely mentions, in proof of his success, that he obtained crystals which contained the theoretical proportion of sodium, but this happens to be no proof at all, as sodium carbonate has just the same content of sodium; moreover, the hyponitrite is a hydrated salt which cannot be rendered anhydrous without some decomposition, and although of crystalline texture, the salt can hardly be described as occurring in crystals. Nevertheless, his success in getting the salt is not to be doubted. One of the methods he adopted was to reduce a concentrated solution of sodium nitrate by sodium amalgam, evaporate the solution in a vacuum until the salt crystallised, and wash the crystals with alcohol to free them from sodium hydroxide. With some modification, the process he followed is an excellent one.

To obtain sodium hyponitrite from the somewhat thick solution prepared as already described, it is first passed through a Gooch asbestos filter well covered from the air; it contains 1 mol. of sodium hydroxide to 3 mols. of water, and is a saturated solution of the hydroxide, whilst there are about $21\frac{1}{2}$ atoms of sodium present as hydroxide to 1 as hyponitrite. Cooling alone will cause the separation of the hyponitrite, and the solution readily loses water in a vacuum over sulphuric acid until it retains only about 2 mols. to 1 mol. sodium hydroxide, when almost the whole of the sodium hyponitrite will have separated; at $25-30^{\circ}$, this will happen in about 40 hours, the salt separating as minute, crystalline granules, some of which adhere to the walls of the dish, but most of them being deposited as a thick crust on the surface of the solution. Below 15° , the mother liquor readily deposits crystals of the monhydrate of sodium hydroxide, and as evaporation is slower in the cold, it is better, for both reasons, to conduct the operation in a warm room.

The only effective way of separating the salt from its viscid mother liquor is by the pump and a Gooch crucible unlined with asbestos; draining on a tile is impossible. In the same apparatus, it is washed with absolute alcohol and then transferred to a basin and gently triturated with fresh portions of alcohol until all the sodium hydroxide has been removed. If now drained on a good tile, it is the nearly pure hydrated salt, but very unstable, losing both water and nitrous

oxide, and consequently becoming contaminated again with sodium hydroxide ; if, however, it is promptly dried in a vacuum desiccator, it becomes anhydrous before it has undergone much decomposition, and is then quite stable in dry air. The amount of the hydrated sodium hyponitrite should be quite one-sixth of the calculated quantity, and the mother liquor will then be too poor in hyponitrite to be used as a source of silver hyponitrite.

A modification of the method, which gives an equally good yield, is to precipitate the salt by absolute alcohol instead of evaporating ; the only precaution necessary is to prevent, as far as possible, the salt from becoming attached to the walls of the vessel. A large quantity of alcohol is required, because of the very large proportion of sodium hydroxide which is present. A few drops of the solution are added to the alcohol in a flask and at once violently shaken with it until the hyponitrite has completely solidified ; then gradually the rest of the solution is poured in with very active agitation. If abundance of alcohol is used from the first, with thorough mixing, very little of the salt will remain in solution and very little adhere to the flask ; with less alcohol at first, a notable quantity of the salt is lost by being kept in solution, for although it is afterwards slowly deposited, it is not then in a serviceable condition, and much salt is liable to adhere to the flask, which can, indeed, be dissolved out in water, and be reprecipitated by alcohol, but only with very great loss.

The action of sodium chloride on silver hyponitrite (see p. 106) is complex and quite unsuitable for the preparation of a solution of pure sodium hyponitrite. Nevertheless, such a solution, charged as it is with sodium chloride, and containing, besides, some silver hyponitrite dissolved in it, deposits sodium hyponitrite when mixed with much absolute alcohol, and this constitutes Jackson's second method of getting the salt ; it always, however, contains a little chloride mixed with it.

The granular form of sodium hyponitrite is most marked in it when it has been separated from a highly concentrated solution of sodium hydroxide ; when it is redissolved in a very little water and the solution rapidly evaporated in an exhausted desiccator, the salt separates as an almost structureless membrane on the surface, and there readily becomes opaque and apparently anhydrous. In the ordinary desiccator, a finely granulated crust forms. I have never obtained it in crystals. The salt, when quite freshly prepared, has an exceedingly mild, alkaline taste.

The attempts to determine the degree of hydration of the salt have been unsatisfactory because of its instability, but they point to the formula $(\text{NaON})_2 + 5\text{H}_2\text{O}$. That formula requires 23.47 per cent. sodium, whilst analysis of the salt weighed as soon as it was almost

free from alcohol, gave 23·66 per cent. In place of 30·61 per cent. for the hyponitrite ion, 28·10 per cent. was obtained by dissolving the salt in water and precipitating with silver nitrate, a deficiency fairly attributable to decomposition before the silver nitrite could be added; for, as proved by Zorn, this way of estimating hyponitrous acid is accurate. Loss of weight in the vacuum desiccator gave 44·91 per cent., whilst the calculated quantity of water is 45·92 per cent., but the difference is easily accounted for as due to loss of nitrous oxide, and, indeed, would be even greater but for the fact that this loss involves fixation of water by sodium oxide.

The anhydrous salt, somewhat decomposed, is non-coherent and opaque, and in appearance much like that of *magnesia alba*; heat is evolved when it dissolves in water, and it is insoluble in alcohol. The anhydrous salt only slowly takes up water from a solution of sodium hyponitrite. Heated in a closely-covered vessel, it yields nitrogen and sodium oxide mixed with some nitrate, $3(\text{NaON})_2 = 2\text{N}_2 + 2\text{Na}_2\text{O} + 2\text{NaNO}_2$. The salt bears a heat of 300° without decomposing, and then melts and effervesces; glass, platinum, and even silver are freely attacked by the fused mass, and the product hisses when water is added to it. Sodium hydroxide and nitrite are the solid products when the hydrated salt is quickly heated, and nitrous oxide, as well as nitrogen, is given off. Strong sulphuric acid decomposes the salt, with production of odourless, white vapours, and does not form nitrosylsulphate if the sodium salt is pure.

The salt, or a fairly concentrated solution of it, effervesces with a dilute acid like a carbonate. The solution, with the respective reagents, gives a precipitate of calcium hyponitrite and of most other hyponitrites at once. It dissolves a little silver hyponitrite and decomposes silver chloride (see the account of silver hyponitrite, p. 106). Dry sodium hyponitrite is not decomposed by carbon dioxide, and, since the hydrated or dissolved salt partly decomposes by interaction with the water, its power of fixing carbon dioxide does not indicate that it is directly decomposable by that substance. The solution, when boiled, decomposes moderately fast into hydroxide and nitrous oxide. If allowed to stand for a day, a trace of nitrite is formed (see p. 114).

Potassium Hyponitrite; Potassium Amalgam.

The preparation of a solution of potassium hyponitrite is throughout like that of a solution of the sodium salt. It is only necessary, therefore, to say something concerning the potassium amalgam which is required, concerning which as a reagent little or nothing has been published.

Merely for convenience in working, the composition of the potassium amalgam should correspond pretty closely, in parts by weight, to that recommended for the sodium amalgam, namely, $(\text{Hg}_{14}\text{K})_2$, or 2800 of mercury to 39 of potassium, this being the weakest amalgam that is solid, a pasty amalgam like that of sodium not being obtainable. Although it crystallises in simple cubes, often very large, which are so sharp angled that they can hardly be introduced into a flask without fracturing it, these crystals are very easily crushed in a porcelain mortar, and are then in a state quite convenient for use. Sodium or potassium amalgam not stronger than here recommended (1 kilo. of mercury to 14 grams of alkali metal) is particularly easy to prepare in Draper's way, that is, by melting the sodium or potassium under solid paraffin and adding the mercury to it, at first very gradually. The operation can be performed on the open table. In spite of the fact that more heat is evolved, according to Berthelot's numbers, the action is less violent in preparing potassium amalgam than it is in the case of sodium amalgam. Potassium, also, nearly always requires to be well stirred with a glass rod to bring about its first contact with the mercury under the paraffin;* sodium never does. When all the mercury has been added, either amalgam requires good stirring in order to dissolve all lumps, and should again be stirred when solidifying, in order to disturb crystallisation as much as possible. The specific gravity of the paraffin is about the same as that of potassium, but paraffin expands so very greatly in melting that the potassium readily sinks in it when it is in the liquid state. Muhlhaeuser, many years ago, melted sodium under petroleum and then added the mercury to it, and, in recent years, Nef has recommended the use of toluene, which boils freely by the heat produced in the union of the metals. But toluene could hardly be used in making potassium amalgam, because of its specific gravity.

A highly concentrated solution of potassium hyponitrite and hydroxide having been prepared, the hyponitrite can be precipitated by absolute alcohol, but only very incompletely, and some of what is precipitated is afterwards dissolved away in washing it with more alcohol. The preparation of this salt is, therefore, less satisfactory than that of the sodium salt.

Another way of making potassium hyponitrite is to decompose silver hyponitrite with exactly the right quantity of solution of potassium iodide. By rapid evaporation under reduced pressure, the solution can be concentrated, although with partial decomposition, preparatory to treating it with absolute alcohol, and it can even be dried up, so as to

* This is probably due to the fact that the potassium presses but lightly upon the mercury on account of its specific gravity not greatly exceeding that of the paraffin, and not because of any chemical difference.

yield the impure solid salt. The cold of evaporation in a vacuum has sometimes caused the separation from the concentrated solution of hydrated crystals, which, however, melt when placed on filter paper ; otherwise, the salt is obtained anhydrous in minute, prismatic crystals. The salt decomposes more rapidly than the sodium salt, but is stable when quite dry. It is soluble in 90 per cent. spirit, and slightly even in absolute alcohol. Its aqueous or alcoholic solution yields silver hyponitrite with silver nitrate, dissolves silver hyponitrite to some extent, and in other respects behaves like one of sodium hyponitrite. It has not been obtained sufficiently undecomposed to be fit for quantitative analysis.

Preparation of Silver Hyponitrite.

The hyponitrites were discovered through the production of the silver salt, and since that discovery this hyponitrite has been prepared and redescribed by many chemists ; all deviations from the account I first gave of it are, however, incorrect, and the only additional observations that have been made are that it can be obtained in a purer state than I got it at first, and that it gives off nitric peroxide when heated. The very poor success in obtaining it in satisfactory quantity in recent years is remarkable (see p. 97) ; this seems to be due to erroneous methods of procedure, either in reducing the nitrite or in converting the sodium hyponitrite into the silver salt.

The concentrated solution of sodium hyponitrite and hydroxide, already described, is diluted and mixed with just sufficient silver sulphate or silver nitrate, dissolved in much water, to precipitate the hyponitrite ; for it is unnecessary to neutralise the sodium hydroxide. (Neutralisation can, indeed, precede precipitation, if desired, as in preparing mercury and other hyponitrites, but in the case of the silver salt it is quite unnecessary, and there is a risk of loss of hyponitrite.) Silver sulphate should be used if it is essential to exclude nitrate from the silver hyponitrite ; for, as will be shown, washing and reprecipitating are but imperfect means of purifying the precipitate. Supposing a half gram-molecule of sodium nitrite to have been reduced, the alkaline solution, diluted to three times its volume or more, is mixed with 13 grams of silver sulphate or 14 grams of silver nitrate dissolved in about 3 litres of water, and the mixture stirred vigorously at once and continuously for 5 minutes, in order to convert the silver oxide into silver hyponitrite. After the precipitate has nearly all subsided, the turbid liquor, if bright yellow rather than brownish, is decanted and more silver solution added to it until, after stirring well, some brown silver oxide remains, when the whole is poured back and stirred up with the main precipitate, and then left to settle. Good daylight is almost essential

for judging the colour of the precipitate when finishing, but the precipitate should not be exposed to light more than is absolutely necessary.

After washing somewhat by decantation, the precipitate is stirred up with successive portions of highly dilute sulphuric acid (3 or 4 per mille) until this fails to become fully neutralised, and shows, therefore, when poured off and mixed with a drop of sodium carbonate, a slight yellow opalescence due to silver hyponitrite. The precipitate, after being washed with water by decantation until the washings no longer contain sulphate, is stirred up with water containing a trace of sodium carbonate, and, finally, again washed with water. It is then collected on a filter and dried in the dark in a vacuum. When thus dried, it may be heated for a time to 100° in dry air without change and become still drier. It is now usually as pure as it is possible to get it. As, however, the operations are not always so perfectly carried out as to ensure this degree of purity, it is desirable sometimes to submit the salt to further treatment, preferably before it has been dried. In that case, it is dissolved, in portions at a time, in 3 per mille ice cold dilute sulphuric acid, and is either expeditiously filtered, if necessary, into some sodium carbonate solution, or, if not, is at once made alkaline with sodium carbonate. The reprecipitated salt is then treated with sulphuric acid and washed in exactly the same manner as the original precipitate. Even after reprecipitation, the silver hyponitrite obtained from 34.5 grams of sodium nitrite will weigh about 11 grams.

The process for preparing silver hyponitrite just given differs from that contained in my first paper in not neutralising the sodium hydroxide with acetic acid, in taking silver sulphate instead of nitrate, sulphuric acid in place of nitric acid, and sodium carbonate in place of ammonia, and in some minor details. The use of sulphuric acid is not new, that acid having been first used by van der Plaats, but the motive for the change is new and has been already given. Cold dilute sulphuric acid is not in the least less active than nitric acid in decomposing silver hyponitrite; in fact, unless very dilute, it is more active in consequence of silver sulphate crystallising out. Sodium carbonate (used by Haga and me in 1884, *Trans.*, 45, 78) is to be preferred to ammonia for precipitating the salt, as being more sensitive, and because the last trace of ammonia is difficult to wash out of the silver salt (as Hantzsch and Kaufmann found, see p. 114). It is easy to ensure absence of all silver carbonate, along with complete precipitation of the hyponitrite, because of the solubility of the carbonate in the excess of carbon dioxide always present in the solution.

Properties of Silver Hyponitrite.

Silver hyponitrite is bright yellow, and when pale in colour it generally contains a trace of ammonia or loosely combined silver oxide. If along with such impurity there is also black silver sub-oxide, the colour becomes dull greyish-yellow, but when other impurities are absent, the presence of a little black oxide renders it somewhat bright green, as seen principally in the crude salt prepared by the hydroxamidodisulphonate method. The difference in colour observed has even suggested the possibility of the existence of different modifications, but there is really nothing to support this notion.

If precipitated from strongly alkaline solution, or from concentrated solutions of the sodium salt and silver nitrate, or in rubbing the calcium salt with strong solution of silver nitrate, silver hyponitrite is dense, but when precipitated by neutralising its solution in dilute acid, it is flocculent and bulky. When deposited from its ammoniacal solution through evaporation or large dilution with water, it is crystalline (Kirschner ; but also see Paal and Kretschmer).

It is slightly more soluble in water than silver chloride, and is dissolved by very dilute nitric or sulphuric acid, so as to be recoverable on quickly neutralising the acid. The nitric acid required to dissolve it is considerable, being about 3 equivalents. The sulphuric acid solution very soon deposits silver sulphate. Acetic acid dissolves it only very slightly in the cold ; phosphoric acid dissolves it, but not very freely. It is dissolved by ammonia solution, but only sparingly when this is very dilute, and the same salt can be recovered either by neutralising or dissipating the ammonia. It is also soluble in ammonium carbonate solution, and very slightly in ammonium nitrate solution. Of particular interest is its solubility to a slight extent in hyponitrous acid solution, and to a greater degree in solution of an alkali hyponitrite.

It is readily oxidised by strong nitric acid. Strong sulphuric acid acts energetically, the heat of reaction being itself quite sufficient to decompose some of the salt, a fact which accounts for the production of some nitric peroxide and nitrosyl sulphate (see effects of heating, p. 108). It is not decomposed by a cold solution of sodium carbonate, or by one of sodium hydroxide if it is weak. It is fully decomposed by its equivalent of potassium iodide in solution, but only imperfectly by a solution of sodium chloride, if the latter is not in considerable excess. When a solution of sodium chloride is shaken with excess of undried silver hyponitrite, decomposition ceases when the two sodium salts in the solution are in the proportion of 18 eq. of chloride to 25 eq. of hyponitrite, or, by weight, 4 of chloride to 5 of anhydrous

hyponitrite. Absolute alcohol in large excess effects a partial separation of the two sodium salts, as already described.

Silver hyponitrite in the moist state is not entirely stable, for it decomposes even at the ordinary temperature, although exceedingly slowly; light and heat quicken the change, the former modifying it to some extent. The decomposition is made evident by the salt losing its bright colour, by its answering to the iodide and starch test for a nitrite, and by its yielding up to water more silver salt (not nitrite, but nitrate apparently) than its own very slight solubility would account for. The salt may be washed with boiling water, or even be boiled with water, without any very apparent result, but continuous boiling not only has marked effect in decomposing it, but an action which grows in intensity, even though the water is frequently replaced. The water is found to contain silver nitrate, whilst the solid salt gives the reaction for nitrite. Masses of moist precipitate retain their colour outside while drying in a thermostat, but become greyish inside. Silver hyponitrite dissolved in a solution of sodium or potassium hyponitrite decomposes on standing, and very quickly on boiling, reduced silver being deposited and sodium nitrate formed in solution.

Bright diffused light causes enough change in a few hours—bright sunlight in a few minutes—to allow of nitrite being detected. The colour change caused by light has been variously described; as a matter of fact, in the sufficiently pure salt under water, it is such that the bright yellow hyponitrite becomes covered with a somewhat bright brown, flocculent substance, very like silver oxide, which, perhaps, it is; the blackening or greying, which has been observed by others to be caused by light, must have been due to impurities, although time, as just described, brings about a greying of the salt. Silver hyponitrite is least sensitive to light when dry and exposed to dry air. The main change which occurs in the moist salt, slight as it is, is evidently similar to that caused by heat. The salt prepared by the hydroxyamidodisulphonate method generally shows an unreal stability, due apparently to presence in it of a trace of sulphite, as will be explained when the properties of a hyponitrous acid solution are treated of; for, in that connection, it has to be taken into consideration that, like many other precipitated substances, silver hyponitrite is difficult to obtain of high purity. The very slight atmospheric oxidation of moist silver hyponitrite, described by Haga and me (*Trans.*, 1884, 45, p. 78) I now regard as being, not the oxidation of the salt itself, but of nitric oxide produced by the very slowly decomposing salt, which is then retained as nitrate and nitrite in the salt; the result would be the same as if the salt itself were oxidised.

Effects of Heating Silver Hyponitrite.

In my first paper, it is stated that silver hyponitrite is decomposed by a moderate heat into nitric oxide, metallic silver, and a little silver nitrate—in this respect resembling silver nitrite, and that it does not fuse or exhibit any other change except that from a bright yellow to a silver-white colour. That is still a correct statement, so far as it goes, but it is imperfect. In 1887, van der Plaats stated that silver hyponitrite decomposes explosively when heated; presumably his preparation contained acetate. Thum, who, in 1893, rightly denied its explosive character, observed that, in decomposing by heat, the bright yellow salt becomes dark brown before assuming the white colour of silver, while Kirschner found (1898) that the salt became temporarily black. Thum's observation was due, I think, to the very dense red, almost opaque, hot nitric peroxide which then pours forth, and through which at times the solid mass does look very dark. Kirschner's observation may be due also to this cause, or to his hyponitrite having contained sulphite. However this may be, the salt decomposes with only the change of colour I have described, and in a lump of the precipitate the change can be followed by the change in position of the sharp boundary line between the bright yellow salt and the bright white metal, just as it can be followed in calcium oxalate decomposing by heat; there is no brown or black intermediate stage. Thum seems to have found no silver nitrate, but observed the production of dense red fumes even when the salt was heated in an atmosphere of carbon dioxide, and at a temperature not much (\dagger) above 100° . From the important observation of the generation of nitric peroxide, he concluded that the decomposition of silver hyponitrite by heat is probably into silver, nitrogen, and nitric peroxide. I had, of course, seen, in my early work, the production of red fumes, but had attributed this to the nitric oxide meeting the air, and to the decomposition at a higher temperature of the silver nitrate which had been formed. The further study of the decomposition which I have made has proved that metallic silver, silver nitrate, nitric peroxide, nitric oxide, nitrogen, and possibly a trace of nitrite are always produced.

Having assured myself that nitric peroxide, as well as nitric oxide, is evolved by silver hyponitrite when heated, I exposed some to heat in a rapid current of carbon dioxide, in order to sweep away as fast as I could the nitric peroxide that was produced; for the production of nitric peroxide may sufficiently account for that of silver nitrate secondarily. The nitric peroxide and the metallic silver could give the nitrate (Divers and Shimidzu, *Trans.*, 1885, 47, 630), but it seems improbable that these two substances being produced would then

immediately interact at the same temperature. There is, however, no reason why the nitric peroxide of the decomposed part of the salt should not act on the undecomposed portion and thus produce nitrate, such interaction readily taking place. My experiment recorded above was instituted to see whether I could not almost prevent the formation of nitrate. The attempt failed, for I found silver nitrate in the residue equivalent to as much as $\frac{1}{17}$ th of the total silver, but this result does not disprove that the nitrate really is formed in the way suggested.

The nature and composition of the gaseous products were ascertained by heating the salt in a vacuum. The quantity of salt taken was in each experiment so proportioned to the capacity of the little flask or bulb in which it was heated that the volume of the gases at the common temperature and pressure should be a little less than the capacity of the bulb. The air was removed from the bulb holding the salt by means of the mercury pump, while the bulb was kept in boiling water to ensure the dryness of the salt. When exhausted, the bulb was sealed off, and the silver hyponitrite decomposed by heating the bulb in a bath. Thus heated in the absence of air and moisture, the salt exhibits scarcely any change below 140° , and only slow decomposition between 140° and 160° , but above these temperatures the change is soon complete. The metallic silver is slightly caked together, presumably by the silver nitrate, and the gases are faintly red between 140° and 150° , and orange-red at 160° and above. On allowing the vessel to cool, the gases become colourless, but regain their colour just as before when the vessel is again heated, and these changes can be repeated any number of times.

To examine the contents of the bulb when cold, its point was broken off under water, and the small rise of water into the neck of the bulb marked; then the bulb was transferred to a small trough of strong solution of sodium sulphite in order to absorb the nitric oxide (this vol., p. 82). After an hour or longer, the residual gas was examined and measured by bringing the bulb mouth upwards, testing the gas as to odour and power to support combustion, and then filling it with water from a burette up to the mark already made, and afterwards to the mouth in order to learn the volumes of the gases when corrected for temperature and pressure. The volumes could be only approximately measured in this way, but quite well enough for the purpose. The metallic silver was weighed, and from its weight and that of the hyponitrite, that of the silver nitrate became known. In one experiment, the bulb was at once freely opened to the air, and the gases rapidly blown out; in this way, the nitric oxide showed its presence by reddening in the air, and both the silver and the silver nitrate were directly determined.

These experiments established the production of nitrogen, as well as that of the other substances, and the non-production of any appreciable quantity of nitrous oxide. The quantitative results were that, when the decomposition is slowly effected, as between 140° and 160° , silver hyponitrite yields about 27 per cent. of its nitrogen in the free state, and about 20 per cent. when the decomposition is rapidly accomplished at higher temperatures. The silver nitrate was formed in quantities corresponding with those of the nitrogen, according to the equation $3(\text{AgON})_2 = 4\text{Ag} + 2\text{AgNO}_3 + 2\text{N}_2$, but that, of course, proved nothing, since the whole of the nitrate might have been formed by the nitric peroxide during the cooling, as certainly much of it must have been. On the other hand, the limited quantities of nitrogen generated gives full proof that much nitric oxide is either primarily formed or comes from interaction between hyponitrite and peroxide, besides what undoubtedly comes from the interaction of the nitric peroxide and metallic silver during the cooling. Were none of the nitrogen of the salt to become nitric oxide, the free nitrogen would be half of the total nitrogen, instead of only three- or four-fifteenths as found.

From the facts observed, it seems to me to be highly probable that silver hyponitrite decomposes into silver, nitrogen, and nitric peroxide, according to the equation $2(\text{AgON})_2 = 4\text{Ag} + \text{N}_2 + 2\text{NO}_2$, and that interaction then occurs between the hyponitrite not yet decomposed and some of the nitric peroxide, thus: $(\text{AgON})_2 + 4\text{NO}_2 = 2\text{AgNO}_3 + 4\text{NO}$, and, therefore, that the decomposition of silver hyponitrite into silver and nitric oxide does not occur directly.

It remains to explain the absorption and regeneration of nitric peroxide by cooling and heating the gases in contact with the solid residue of the decomposed hyponitrite. The interaction of silver and nitric peroxide in the cold, already referred to, explains the disappearance of the nitric peroxide, half of its nitrogen becoming nitrate and half nitric oxide. The regeneration of nitric peroxide at such low temperatures as those in the neighbourhood of 150° is explained by experiments of mine recorded in a separate note (this vol., p. 83). The silver nitrate and nitric oxide interact to produce nitric peroxide, and at first nitrite, but ultimately silver itself, $\text{AgNO}_3 + \text{NO} = \text{Ag} + 2\text{NO}_2$.

As to the Existence of Silver Nitrito-hyponitrite, Nitrato-hyponitrite, and Nitrato-nitrite.

Silver Nitrato-nitrite.—I have made new experiments on the union of silver nitrate with silver nitrite, first examined by me in 1871 (Trans., 24, 85). Silver nitrite, mixed with a little less than its equivalent of silver nitrate, suffers only slight decomposition until it

melts along with the nitrate at about 130° . The fused salts solidify at about 125° to a translucent, greenish-yellow, crystalline mass, except in the uppermost part, where it is opaque from the presence of bubbles and metallic silver. This upper part removed, the rest can be fused again without suffering further change, and even be heated nearly to 180° without decomposing. Silver nitrite, heated alone, shows marked change of colour when the temperature has reached 120° , gives red fumes at about 140° , and very freely decomposes below 180° without showing signs of fusing. Silver nitrate does not fuse below 217° (Carnelly). The low melting point of the mixture of the two salts, and the increased stability of the nitrite, are, however, the only facts showing that there is any chemical union, for water separates the two salts.

Non-existence of Nitrato-hyponitrite.—Silver hyponitrite (4 parts) and silver nitrate (5 parts), in intimate mixture, were heated in a bath. No change was observed until 175° was reached, when fusion and the evolution of red fumes occurred. The hyponitrite had then disappeared, and the fusion may be attributed to the decomposition of the hyponitrite, as usual, into nitric oxide, among other things, and to the interaction of this nitric oxide with some of the nitrate to form the fusible nitrate-nitrite.

The attempt was also made to prepare a compound of the two salts in presence of water, there being some grounds to expect success. Calcium hyponitrite, a nearly insoluble salt, was ground up with excess of a very concentrated solution of silver nitrate, and a dense and strongly yellow precipitate obtained, which was washed with water until all the calcium salt had been removed; the precipitate was still yielding up a little silver nitrate when the washing was stopped. Drained on a tile and dried in a vacuum, it proved to be somewhat sensitive to light and to heat, but, as it contained 76.94 per cent. of silver, and could have been washed more free from silver nitrate, a combination of the two salts stable in water does not exist. All that can be said is that silver hyponitrite requires long washing to remove the last portions of silver nitrate.

Nitrito-hyponitrite also non-existent.—In a paper already referred to, I have recorded obtaining a minute quantity of what appeared to be hyponitrite, when partially decomposing silver nitrite by heat, that is, a bright yellow substance insoluble in water and soluble in ammonia. I have failed to get this again. Silver hyponitrite and silver nitrite, heated together, show no change until decomposition and the escape of red fumes occur, and then all hyponitrite has been destroyed.

When making known his observation of the interaction of hydroxylamine and nitrous acid in 1893, Paal stated that, from a solution of

alkali hyponitrite which also contained nitrite, silver nitrate had precipitated a substance which, although it was like silver hyponitrite, proved to be a silver nitrito-hyponitrite. It gave no silver nitrite, even to hot water, and could be dissolved in cold dilute nitric acid, and be reprecipitated with ammonia without suffering change in composition. It was less stable than the simple hyponitrite when heated, gave the reactions of a nitrite along with those of a hyponitrite, and yielded numbers (not quoted), on analysis for silver, which agreed nearly with that required by the formula $\text{Ag}_2\text{N}_2\text{O}_3$. Ten years previously, Berthelot and Ogier, probably under similar conditions, got similar results, except that they were led by their analysis to give the formula $\text{Ag}_4\text{N}_4\text{O}_5$ to the substance they had obtained. It is true that, in spite of endeavours to purify it, silver hyponitrite retains with obstinacy enough nitrite to give the iodide and starch reaction for a nitrite, and that it often, through the presence of impurities, gives low results for the silver; but, beyond these admissions, I cannot subscribe to the accounts given by the chemists just named as to the existence of compounds of silver hyponitrite with silver nitrite.

I have reduced sodium nitrite by sodium amalgam as usual, and dissolved in the solution one-sixth as much more sodium nitrite as had been reduced, thus getting hyponitrite and nitrite together in solution in about equivalent proportions, in accordance with the experience recorded in this paper. The precipitation of silver hyponitrite was then proceeded with, in one experiment, without previous neutralisation of sodium hydroxide, and in another experiment after neutralisation of the alkali. The result was the same in both experiments. There was a bright yellow precipitate, not noticeably different from ordinary hyponitrite, and the mother liquor retained much alkali nitrite or silver nitrite in the respective cases; the precipitate was repeatedly washed with cold water, but the washing was stopped when very little silver was being extracted. It proved to be somewhat sensitive to light and heat. It was dried in the cold and in a vacuum, and the silver was then determined; this was 76.9 per cent. Nitrite could be easily detected in it, but the compound $\text{Ag}_2\text{N}_2\text{O}_3$ would have only 74 per cent. of silver, and $\text{Ag}_4\text{N}_4\text{O}_5$ only 76 per cent. Besides this, by prolonged washing the hyponitrite can be made much purer. These experiments, therefore, afford no evidence of the existence of such a compound as Paal has described.

Properties of a Solution of Hyponitrous Acid.

Solutions of hyponitrous acid are always prepared in one way, namely, by decomposing silver hyponitrite with just sufficient dilute hydrochloric acid. Hyponitrous acid has been obtained by Hantzsch

and Kaufmann in crystals very deliquescent and very unstable, by using dry ether in place of water in its preparation. The acid in dilute solution reddens litmus not so strongly as nitric acid, but much more than carbonic acid. On drying the reddened litmus paper, it becomes blue again. A solution of the acid becomes neutral to litmus when half the quantity of baryta water or alkali required to form the normal salt has been added (Zorn), and such a solution, by decomposition, soon acquires the property of blueing red litmus paper. When neutral to litmus, the solution is also neutral to phenolphthalein (Thum). When neutralised with baryta, and very rapidly evaporated under reduced pressure, hyponitrous acid yields an acid salt which is crystalline and extremely unstable (Zorn).

It decomposes silver carbonate, if not also lead and other carbonates; it also decomposes silver nitrate and sulphate. It does not oxidise hydrogen iodide (iodide and starch reagent), and is not oxidised by iodine solution or by the air. It is oxidised by nitrous acid and the stronger oxidising agents. No way of deoxidising or hydrogenising hyponitrous acid is known; it entirely resists the action of sodium amalgam, and also, according to Thum, that of zinc and sulphuric acid. Ethylic hyponitrite is reduced, apparently, by tin and acetic or hydrochloric acid to alcohol and nitrogen, according to Zorn, but as, also according to him, it slowly decomposes by itself, when moist, into nitrogen, alcohol, and aldehyde, there is sufficient reason to doubt that this reduction by tin and acid is anything more than the hydrogenisation of the aldehyde.

Hyponitrous acid slowly decomposes into nitrous oxide and water. A strong solution soon effervesces, gently in the cold, freely when heated, just like a solution of carbon dioxide, and some hyponitrites in presence of only a little water effervesce with an acid. A solution of one or two grams of the acid in a litre of water kept in ice hardly falls noticeably in strength in one hour, but at 25—30° it may lose a sixth of the acid by decomposition in 24 hours; at a lower temperature, Thum observed a loss only half as great in the same time. Alkali hyponitrites in solution also decompose into nitrous oxide and alkali, gradually in the cold and rapidly when heated; alkali hydroxides impede the decomposition, and when highly concentrated stop it altogether, apparently (see p. 98); neutralisation of the alkali even by carbonic acid hastens the decomposition, as a matter of course, but there is no evidence that carbonic acid is able to decompose a hyponitrite, as it has been said to do.

Hyponitrous acid solution dissolves silver hyponitrite slightly. The alkali salts of hyponitrous acid dissolve silver hyponitrite somewhat more freely, and also decompose silver chloride (see p. 102);

they give precipitates with barium and calcium salts, and with solutions of most metallic salts.

Other substances are liable to be present in the solution of hyponitrous acid, and this fact has certainly caused the properties of the acid to be wrongly described in some respects. In one point, this is the case in my first paper, in which, however, there was a warning that the crude solution of the acid, which had been examined, might have reacted as it did partly through the presence of other unrecognised substances in it. That solution decolorised iodine water, and prevented the action of nitrous acid on an iodide; this, however, was not due to the hyponitrous acid, but to a very little hydroxylamine, the presence of which was unrecognised. Kirschner has again given to hyponitrous acid the property of decolorising iodine water to a slight extent. In his case, the substance acting on the iodine must have been a trace of sulphur dioxide, for he made his solution of the acid from silver hyponitrite that had been prepared by the hydroxyamidodisulphonate method. I can confirm the accuracy of his observation. Even when the silver hyponitrite has been most carefully precipitated so as to avoid all sensible precipitation of sulphite, and has been dissolved in dilute acid and reprecipitated, it still gives a solution of hyponitrous acid capable of acting on a very little iodine water; but then no more iodine was taken up although there was hyponitrous acid in the solution. On the other hand, the acid prepared from silver hyponitrite not derived from hydroxyamidodisulphonate does not decolorise iodine at all, as Thum first pointed out.

Hyponitrous acid, according to van der Plaats, liberates iodine from potassium iodide; according to Thum and my first paper, it does not, whilst according to Hantzsch and Kaufmann it is only just at first that it does not do so. The last-named chemists, therefore, state that the acid does not itself liberate iodine, but quickly begins to yield nitrous acid which does liberate it. They also found hyponitrous acid to yield ammonia, but in a later publication Hantzsch and Sauer state that the ammonia was an impurity in the silver hyponitrite from which the acid had been prepared. Even with the simultaneous formation of the ammonia, it is difficult to understand the generation of nitrous acid. These authors, invoking the aid of tautomerism, suppose that the hydrogen leaves oxygen for nitrogen, giving the unknown substance $\text{HN}:\text{O}$, which then becomes $\text{NH}_3 + \text{N}_2\text{O}_3$, and these again pass into $\text{HNO}_2 + \text{N}_2 + \text{OH}_2$. In place of this series of improbable—I would say, unnatural—changes, I suggest that, if indeed such change occurs at all, it must be into water, nitric oxide, and nitrogen, the nitric oxide then oxidising to nitrous acid. But I am strongly disposed to deny that hyponitrous acid decomposes

of itself into anything but what are certainly its main products, nitrous oxide and water. My reasons are several. First, there is the unlikelihood that the diazo-radicle, $N:N$, should resolve itself into mono-nitrogen compounds, such as NO , NH_3 , $NO \cdot OH$ or $(NO)_2O$, instead of $(N_2)O$. Secondly, there is the fact that time comes in as the condition of the production of nitrous acid, and that a rise in temperature does not. A solution of hyponitrous acid of fair purity, if boiled or quickly evaporated gives nothing but nitrous oxide and water; and only very slowly and to a very small extent does nitrous acid appear in a cold solution of the purest acid. Thirdly, the greater the care taken to reduce and exclude all nitrite in preparing the hyponitrous acid solution, the longer will be the time before any sensible quantity of nitrous acid develops, and the more gradually will the quantity increase. From these facts, the almost necessary inference is that the whole of the nitrite has never been entirely removed or excluded in preparing the acid, and that what has been left, although too minute in quantity to affect the iodide test (which requires 1 in 20 millions, according to Warington), yet multiplies itself by interaction with the hyponitrous acid, forming nitric oxide, which is further oxidised to nitrous acid by the air dissolved in the solution $(HNO)_2 + 2HNO_2 = 2H_2O + 4NO \rightarrow 4HNO_2$. This aerial oxidation can be demonstrated in such a solution of hyponitrous acid as that which Hantzsch and Kaufmann employed in their experiments, which gave the blue of the iodide test almost immediately; it is only necessary to leave one portion of the solution in a deep, narrow vessel, such as a test tube half full, and another portion in a shallow basin for 10 minutes, and then apply the test, when the solution in the basin will be found to liberate more iodine than that in the tube. If, in reducing the sodium nitrite, its concentrated solution is shaken with excess of the amalgam for an hour or two after its main reduction, and the solution is then either diluted, acidified cautiously with dilute sulphuric acid, and tested, or is precipitated by silver sulphate, away from the light as far as practicable, and the precipitate washed in the dark and converted into the acid and tested, either solution, when mixed with the iodide reagent, will not blue in the least for an hour or more in the dark, and provided the constituents of the reagent are pure enough and properly used.*

Against the view, which may be advanced, that hyponitrous acid becomes nitrous acid through oxidation by the air, I must point out

* My way of applying the test is that followed by Warington (*Chem. News*, 1885, 51, 39), except that, having potassium iodide of high quality, I used it instead of Trommsdorf's zinc iodide solution. In the dark, a blank test will remain for hours without the least blueing. There is no advantage in using acetic acid in place of pure sulphuric or hydrochloric acid.

that it is difficult to admit that if the nitrous acid has such origin, it should form so very slowly. A way occurred to me which must be used for deciding this point, so far as the exclusion of nitrous acid goes, but it has, in my opinion, not served to do so. If, in preparing sodium oximidosulphonate, the sulphur dioxide is used in excess, every trace of nitrite ought, presumably, to be sulphonated; if, then, the oximidosulphonate is fully hydrolysed into hydroxyamidossulphonate, as it presumably can be, then, when the latter is converted into hyponitrite and sulphite by potassium hydroxide, there will be no oximidosulphonate present to simultaneously revert to nitrite and sulphite. Therefore, the silver hyponitrite from such a source should be obtainable absolutely free from nitrite, and should furnish a solution of hyponitrous acid also free from nitrous acid. Such silver hyponitrite I endeavoured to prepare, and then tested the acid got from it. The issue was, however, complicated by the fact that such an acid is not quite free from sulphurous acid, as was shown by its decolorising a minute quantity of iodine solution. That it also did not act for a time on the iodide and starch reagent was due in part to this cause. The solution did, however, give a blue coloration with the reagent sooner than a corresponding blank test. But this was no proof that hyponitrous acid passes spontaneously into nitrous acid, for, first, there is the possibility of nitrous acid having been present through incomplete sulphonation and hydrolysis in preparing the hyponitrite; this nitrous acid would, indeed, have been converted into nitric oxide by the sulphurous acid retained by the silver salt, but when all this was gone, the nitric oxide would have become nitrous acid again by oxidation. Secondly, it is almost certain that the oxidation of the sulphurous acid by the air would have induced oxidation of some hyponitrous acid, in accordance with the observations of Mohr, M. Traube, van't Hoff and Jorissen, Engler and Wild, Bach, &c.

Quantitative Estimation of Hyponitrous Acid.—Hyponitrous acid can be estimated accurately, both gravimetrically (Zorn) and volumetrically (Thum). Solutions of the free acid, or of its alkali salts in water, or of its other salts in very dilute and cold nitric acid are mixed with excess of silver nitrate, and then the free acid is just neutralised with sodium carbonate or with ammonia. The washed precipitate is either dried and weighed as such, or weighed as metal or as chloride.

Volumetrically, the acid can be estimated in solution in the free state and unmixed with any other acid, by adding excess of solution of potassium permanganate, leaving it for a quarter of an hour, then adding sulphuric acid, allowing it to remain for another quarter of an hour, warming to 30°, adding a known quantity of oxalic acid sufficient to decolorise, and, finally, titrating back with permanganate. The hyponitrous acid is thus oxidised to nitric acid. The oxalic acid should

be decinormal, and the solution of permanganate be volumetrically equivalent to it. Ferrous sulphate is unsuitable for use in place of oxalic acid. The process is an excellent one. Hantzsch and Sauer failed to get good results, because they deviated from Thum's directions by acidifying the permanganate before adding it to the hyponitrite. Kirschner also was unsuccessful with this process, but his failure is also explained by his deviation from Thum's directions. He added nearly insoluble salts, such as the barium, strontium, or silver hyponitrite, to the potassium permanganate, so that the base of the salt was present, and the hyponitrous acid locally in excess of the permanganate; he then added the sulphuric acid, apparently immediately, and used ferrous sulphate for titrating back.

Taking 5 c.c. of normal hydrochloric acid, largely diluting it, adding ice and a cream of precipitated silver hyponitrite so as to exactly use up all the hydrochloric acid, making up to 100 c.c., and decanting from the bulk of the silver chloride, I obtained a solution which, although somewhat turbid from silver chloride, gave, in successive portions of 20 c.c., all tested within an hour, quantitative results corresponding well with 0.155 gram hyponitrous acid in 100 c.c., that is, the quantity equivalent to the hydrochloric acid taken; next day, the remainder of the solution (in very hot weather) showed the presence of 0.131 gram of the acid in 100 c.c.

Thum found that, in alkaline solution, alkali hyponitrite is quantitatively converted into nitrite by permanganate. Although I have not examined this point myself, I find that nitrite is thus formed, and that nitric acid is formed in Thum's acid permanganate method. Kirschner doubts that either is produced.

Barium, Strontium, and Calcium Hyponitrites.

Barium hyponitrite has been obtained by Zorn, Maquenne, and Kirschner, and is most simply prepared by adding barium chloride to a concentrated solution of sodium hyponitrite and stirring well. It is crystalline, almost insoluble, and an unstable and exceedingly efflorescent salt, but Kirschner has succeeded in determining its water of crystallisation satisfactorily. Its formula is $\text{BaN}_2\text{O}_2 + 4\text{H}_2\text{O}$. A crystalline acid salt exists (Zorn).

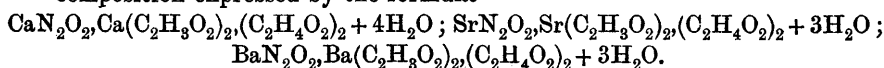
Strontium hyponitrite, $\text{SrN}_2\text{O}_2 + 5\text{H}_2\text{O}$, Maquenne, Kirschner.

Calcium hyponitrite, $\text{CaN}_2\text{O}_2 + 4\text{H}_2\text{O}$, Maquenne, Kirschner. This is crystalline, very sparingly soluble, stable, not losing its water even over sulphuric acid. I find that it can be easily precipitated from a fairly concentrated solution of sodium hyponitrite, and can thus be prepared more easily than in the ways followed by Maquenne and by

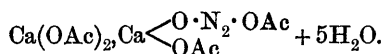
Kirschner, using the silver salt. On account of its stability, it is a good hyponitrite to keep in stock. It is sufficiently soluble for its solution to serve to show the reactions of a hyponitrite with silver, mercuric, mercurous, copper, lead, and other salts.

Calcium, Strontium, and Barium Hyponitrosoacetates.

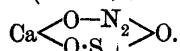
Some remarkable salts have been described by Maquenne, having the composition expressed by the formulæ



I have prepared and partly analysed the calcium salt, following Maquenne's process, which is to dissolve calcium hyponitrite in 30 per cent. acetic acid until the new salt begins to crystallise out. I kept the acid at about 50° while dissolving in it nearly as much of the calcium salt as it would take up, the salt being deposited on cooling. It is remarkable that this can be done without causing more than very slight effervescence. The salt crystallises in short prisms, stable for many days, very soluble in water, in which it gives, with silver nitrate, the yellow hyponitrite. In spite of its acid composition, it is neutral or even slightly alkaline to litmus. To account for its existence and neutral reaction, I suggest for it the constitution expressed by the formula



This represents it as being normal calcium acetate with one-fourth of its oxylic oxygen replaced by the hyponitrite radicle, or as a double anhydride of calcium acetate and hyponitrite. It is thus made out to have a constitution analogous to that of a (hypo)nitrososulphate, as determined by Haga and me (Trans., 1895, 67, 1098),



Simple hyponitrosoacetic acid, $\text{C}_2\text{H}_3\text{O} \cdot \text{O} \cdot \text{N}_2 \cdot \text{OH}$, would be isomeric with acetoneitrosohydroxamic acid, $\text{C}_2\text{H}_3\text{O} \cdot \text{N}(\text{NO}) \cdot \text{OH}$, which Hantzsch and Sauer have been trying to prepare. The hyponitrosoacetates are much more stable in water than the (hypo)nitrososulphates, a difference perhaps connected with the fact that sulphuric acid ionises largely, while both acetic acid and hyponitrous acid ionise very little. Heated with water, the hyponitrosoacetates decompose like the (hypo)-nitrososulphates do in cold water.

Mercuric Hyponitrite.

Mercuric hyponitrite is a particularly interesting salt and has not as yet been described. Rây has, indeed, described some compounds which he regards as being basic mercuric hyponitrites, but obtained under conditions suggesting the probability that they are something quite different; moreover, he has not as yet proved them to be compounds of this class. One of them he obtained by the interaction of solutions of mercuric nitrite and potassium cyanide, a very interesting and remarkable result, should it be confirmed. In any case, his precipitates appear to have nothing at all in common with the normal salt here described, and cannot be obtained in the ordinary way. The existence of this salt was indicated by me in 1871.

Mercuric hyponitrite is obtained from sodium hyponitrite and mercuric nitrate by precipitation; the solution of sodium hyponitrite and hydroxide, obtained by reducing sodium nitrite, is largely diluted and, while ice cold, nearly or quite neutralised with dilute nitric acid; it is then (mercurous nitrate serving as indicator, see p. 97) poured into a mercuric nitrate solution, which must not be in excess and should contain as little free acid as possible. The slightly turbid mother liquor is quickly decanted from the precipitate formed, and after being neutralised with sodium carbonate is mixed with more mercuric nitrate, the whole poured back on to the main precipitate, stirred up with it, and soon again decanted. The precipitate should be washed quickly by decantation, since it is liable to be quickly destroyed by the slightly acid mother liquor.

It is a flocculent, cream-coloured precipitate, easily washed on the filter, and dries up to a light buff-coloured powder, this colour being due, probably, to incipient change into the mercurous salt. Dried quickly in the air, on a porous tile, it is hydrated, having the formula $(\text{HgN}_2\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, but if dried in the desiccator it is anhydrous. Being a little sensitive to light, it should be dried in the dark. It dissolves in hydrochloric acid and in sodium chloride solution, but it is unstable, changing into the mercurous salt, and, therefore, is liable to show turbidity in the chloride solutions. The mercury, precipitated as sulphide from a solution of the anhydrous salt in hydrochloric acid, was found to be 76.71 per cent., the formula HgN_2O_2 requiring 76.92 per cent. Its solubility in excess of sodium chloride does not prevent mercuric chloride giving a precipitate with sodium hyponitrite. The solubility of the salt in sodium chloride is a qualitative proof of its normal composition. The alkalinity of the solution is caused by the sodium hyponitrite generated in it. Potassium hydroxide at once decomposes mercuric hyponitrite into oxide, without showing any

tendency to produce basic salts. In very dilute alkali, the precipitate is slightly soluble.

What makes this salt so remarkable, not only as a hyponitrite, but as a mercuric salt, is the nature of the decomposition which it undergoes. Slowly or quickly, it decomposes into mercurous hyponitrite and nitric oxide—some of the latter, oxidised by the air, converting some hyponitrite into nitrate. No other mercuric salt decomposes into mercurous salt, although many cupric salts change into cuprous salts. Ferric oxalate shows just the same kind of change, namely, into ferrous oxalate and carbon dioxide. The most closely related change, however, is that of sodium (hypo)nitrososulphate into sulphite and nitric oxide, the very phenomena being similar, so that, except for the colour change, I might describe my experience with this salt in the words of the paper by Haga and me on sodium (hypo)nitrososulphate (Trans. 1895, 67, 1095). Thus, having on one occasion left some grams of salt all night in the desiccator in the form of a pressed cake, just as removed from the filter, I noticed, when weighing it between watch-glasses, that it was losing weight on the balance-pan. When the glasses were opened, a strong nitrous odour was observed, the cake soon became grey, white on the surface, and, being left loosely covered, grew very hot and gave out torrents of nitric oxide; it then cooled, and underwent no further change, even in the course of months. The whitish colour of the cake was found not to penetrate beyond a millimetre into it, the inside being of a uniform yolk-yellow, and consisting of mercurous hyponitrite. The surface-coating proved to be mercurous nitrate, largely soluble in water, and had evidently been produced with the assistance of the oxygen of the air. Not always, however, does the change occur in this striking and rapid way, its progress being gradual and almost imperceptible until complete.

Mercuric hyponitrite is decomposed by heat largely into mercuric oxide and nitrous oxide, but partly into metal and nitric oxide.

Other Hyponitrites.

Mercurous Hyponitrite.—This salt has been prepared and analysed by Thum (*Inaug. Diss.*, Prag. 1893), who used sodium hyponitrite and mercurous nitrate in obtaining it. The possibility of getting it by the spontaneous decomposition of mercuric hyponitrite has just been described. Rây has also evidently obtained it in a very impure state, not further examined. It can be prepared in the same way as mercuric hyponitrite, using mercurous nitrate in place of mercuric nitrate. It is of a full yellow colour, is blackened by even the weakest solution of alkali, and is soluble in dilute nitric acid, from

which it can be precipitated by sodium carbonate. It is a stable salt, but is blackened by bright light. Its decomposition by heat resembles that of the mercuric salt, except that much more metal is produced, as is natural. Composition, $(\text{HgON})_2$.

Cupric Hydroxide Hyponitrite.—This salt was described by me in 1871, and was also obtained by Kolotow in 1890, but was first fully examined by Thum, and has again been examined by Kirschner; being a basic salt, its precipitation from normal sodium hyponitrite leaves an acid mother liquor, on neutralising which much more of the salt precipitates. It is of a bright pea-green colour, and very stable. It may be boiled with water without losing its colour, but is decomposed by sodium hydroxide and is soluble in dilute acids and ammonia. Thum has shown its composition to be $\text{Cu}(\text{OH})\text{NO}$. It gives water, cupric and cuprous oxides, and nitrous and nitric oxides when heated. By adding copper sulphate in excess to hydroxylamine sulphate and then a very little ammonia, it can also be precipitated in small quantity.

Cuprous hyponitrite cannot be formed. I have tried to get it by precipitating sodium hyponitrite by copper sulphate in presence of free hydroxylamine, but, first, cuprous oxide precipitated and then, by aerial oxidation, the basic cupric hyponitrite, which in composition is equivalent to that of cuprous hyponitrite combined with hydroxyl (see above).

Lead Hyponitrite.—This salt was also briefly described by me and has been prepared and analysed by Thum; Kirschner has again prepared and analysed it, but not in a pure state. The precipitate is cream-yellow and flocculent, but soon becomes very dense and sulphur-yellow; its first state is probably that of a hydrate; Kirschner has mistaken it for a basic salt. The yellow salt is PbN_2O_2 . As Thum has pointed out, the yellow precipitate, when formed in a weak acid solution, is crystalline and just like ammonium phosphomolybdate. It is soluble in dilute nitric acid, and is decomposed by sodium hydroxide, but not by sodium carbonate in the cold.

Ammonium Hydrogen Hyponitrite.—This salt has been described by Hantzsch and Kaufmann, who found it to be exceedingly unstable, as was to be expected. That the normal salt could not exist had already been pointed out by me, and by Zorn; D. H. Jackson believes, however, that he did obtain it in small quantity in prismatic crystals, but this is exceedingly improbable.

Ethylic Hyponitrite.—This alkylic salt was prepared by Zorn, and its vapour-density taken by him. It is very explosive, and is not saponified by potassium hydroxide. In the moist state, it slowly decomposes into nitrogen, alcohol, and aldehyde.

Benzyllic Hyponitrite.—Hantzsch and Kaufmann have prepared

benzylic hyponitrite and determined its molecular magnitude cryoscopically. It undergoes similar decomposition to the ethylic salt.

Constitution of the Hyponitrites.

Molecular Magnitude.—In my first paper, nothing could be said as to the molecular magnitude and constitution of the hyponitrites. In 1878, Zorn fully determined their molecular magnitude, finding it to be that containing N_2 , first, by establishing the existence of an acid barium salt and illustrating the similarity of hyponitrites to carbonates (a point which had already been noticed by me), and then by preparing ethylic hyponitrite and taking its vapour-density at reduced pressure (Hofmann's method). It would, therefore, be unjust to the memory of this chemist to admit Hantzsch's claim (*Annalen*, 1898, 299, 68) to have finally established this point by determining cryoscopically, in conjunction with Kaufmann, the molecular magnitude of hyponitrous acid in water and of benzylic hyponitrite in acetic acid, valuable as these determinations are. The possibility of determining the molecule of the acid in its solution in water rests upon the fact, also ascertained by these chemists, that the acid only slightly ionises even in very dilute solution. Maquenne, by a somewhat uncertain form of the cryoscopic method, has also shown that, in calcium hyponitrosoacetate, the hyponitrite radicle cannot be less than N_2O_2 . The strong alkalinity of the alkali salts, and the want of action on litmus of their partially-neutralised solution, first pointed out by me, and the solubility, although only slight, of silver hyponitrite in hyponitrous acid solution (Thum) and in alkali hyponitrite solution, are also facts in accordance with the dihydric composition of the acid. Other chemical evidence of the diazo-grouping in hyponitrites is afforded by the fact of the difficulty, if not impossibility, of deoxidising or hydrogenising them (see p. 113). The derivation of hyponitrites from the interaction of hydroxylamine and nitrous acid would only afford evidence of the diazo-magnitude of the molecule, if the hyponitrite produced were much larger in quantity than what can be obtained from hydroxylamine by other oxidising agents, or from nitrous acid by other reducing agents.

My colleague, Assistant Professor Ikeda, has kindly made some determinations of the molecular magnitude of sodium hyponitrite by Loewenherz's method (*Zeit. physikal. Chem*, 1896, 18, 70), in which the lowering of the freezing point of melted hydrated sodium sulphate by another sodium salt is observed; Loewenherz found that sodium salts behave towards the water of hydrated sodium sulphate almost as non-electrolytes. Prof. Ikeda, in his experiments, employed sodium thiosulphate in place of sulphate, but only because he had been working

with that salt, and had had large experience with it. Unfortunately, the anhydrous sodium hyponitrite I could furnish at the time was contaminated with 4 or 5 per cent. of carbonate (same mol. wt.), so that the determination of the molecular magnitude can only be regarded as approximate. But it is amply sufficient to decide between $\text{NaON} = 53$, and $(\text{NaON})_2 = 106$, if that were any longer necessary, after Zorn's decisive researches, supplemented by those of Hantzsch and Kaufmann. Prof. Ikeda has given me the following details.

M. p. of $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O} = 48.4^\circ$ (Tilden found 48.5°);

H. of fusion = 42.8 Cal. (Ikeda);

Wt. of thiosulphate used = 40.9 grams;

Wt. of sodium hyponitrite used = g grams;

Dp. of solidifying pt. = ΔT° ;

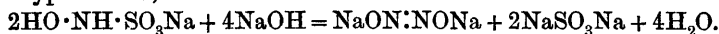
Mol. wt. of hyponitrite = m .

$$m = \frac{1}{\Delta T} \cdot \frac{g}{40.9} \cdot \frac{2(273 + 48.4)^2}{42.8} = \frac{g}{\Delta T} 118.1.$$

<i>g.</i>	ΔT°	<i>m.</i>
0.152	0.115	156
0.467	0.509	108
1.066	1.260	100
1.238	1.507	97

In cases where no decomposition of the salt occurs, the method gives results too high, as, for example, 78.6 instead of 69 , for sodium nitrite; but taking into consideration the partial hydrolysis of the hyponitrite that certainly takes place, its molecular weight is clearly indicated as 106 rather than 53 .

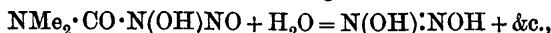
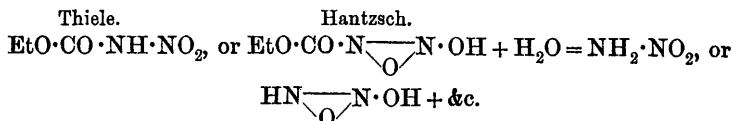
Constitution.—The constitution $(\text{HNO})_2$ seems to be excluded by considerations of valency, but the positive evidence for $(\text{HON})_2$ is ample. Zorn's observation that ethylic hyponitrite decomposes into nitrogen and alcohol (and aldehyde), even in presence of reducing agents, establishes the diazo-grouping in hyponitrites. Ammonia or other amine is never produced in the decomposition of any hyponitrite. Then the conversion of a hydroxyamidodisulphonate into hyponitrite affords a beautiful demonstration of the oxylic constitution of the hyponitrites,



Hantzsch and Sauer have also given an equally convincing proof of the same point, by introducing nitrosyl into dimethylhydroxycarbamide and decomposing the product by alkali (see below). The facts that cuprous hyponitrite cannot exist, and, on the other hand, that the mercurous hyponitrite, and not the mercuric salt, is stable, point also to the metals being united to the oxygen, and not to the nitrogen.

Hantzsch and Sauer, in their desire to prove that nitramine is not $\text{H}_2\text{N}\cdot\text{NO}_2$, but a stereoisomeride of hyponitrous acid, would have it that their interesting formation of hyponitrous acid from dimethyl-hydroxynitrosocarbamide is analogous to that of nitramine from nitrosourethane,

$\text{EtO}\cdot\text{CO}(\text{N}_2\text{O}_2\text{H}) + \text{HOH} = \text{H}(\text{N}_2\text{O}_2\text{H}) + \text{EtO}\cdot\text{COOH}$;
 $\text{NMe}_2\cdot\text{CO}(\text{N}_2\text{O}_2\text{H}) + \text{HOH} = \text{H}(\text{N}_2\text{O}_2\text{H}) + \text{NMe}_2\cdot\text{COOH}$ (decomposing).
 However, by displaying what $(\text{N}_2\text{O}_2\text{H})$ conceals, namely, the difference between the nitramine and the isonitramine,



it becomes evident that the hydrogen of the water (or metal of the alkali) goes, in the case of the nitramine, to the amidic nitrogen united to the carbonyl, whilst, in the case of the isonitramine, it goes to the nitroxy- or nitroso-nitrogen not united to the carbonyl, even if Hantzsch and Sauer's free resort to tautomerism could be justified. Surely, this difference is too great to allow of nitramine being treated as a probable or actual stereoisomeride of hyponitrous acid. Hantzsch's formula, $\text{KO}\cdot\text{N} \begin{array}{c} \diagup \diagdown \\ \text{O} \end{array} \text{N}\cdot\text{SO}_3\text{K}$, for potassium(hypo)nitrososulphate has been shown

by Haga and me to have nothing favouring its preference to that of $\text{KO}\cdot\text{N}\cdot\text{N}\cdot\text{O}\cdot\text{SO}_3\text{K}$, which has so much to be said for it.

Analogy of Hyponitrites to Carbonates—of N_2 to CO.—In hardly forming salts with the feebler metal radicles, such as aluminium and ferricum; in decomposing readily into anhydride and water; and in having its soluble normal salts with very alkaline reaction, hyponitrous acid resembles carbonic acid, as was indicated in my first paper. Zorn, also, in one of his papers, dwells on the analogy of the one acid to the other, pointing out that the salts have the same molecular magnitude, since N_2 and CO are both 28.

As is well known, the physical properties of nitrogen and carbon monoxides are throughout almost identical. The radicles, carbonyl and dinitrogen, also are both bivalent, and occur combined with oxylic, imidic, and alkyl radicles. Thus, $\text{CO}(\text{ONa})_2$ and $\text{COONa}(\text{OH})$ find their analogues in $\text{N}_2(\text{ONa})_2$ and $\text{N}_2\text{ONa}(\text{OH})$. Just as ferric oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, becomes $\text{Fe}_2(\text{C}_2\text{O}_4)_2 + 2\text{COO}$, so $\text{Hg}_2(\text{N}_2\text{O}_2)_2$ becomes $\text{Hg}_2(\text{N}_2\text{O}_2) + 2\text{NO}$. COO corresponds with N_2O ; also $\text{CO}\cdot\text{NAg}$ to $\text{N}_2\cdot\text{NAg}$. Lastly, ketonic compounds are perhaps represented by azo-compounds.

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