X.—*Preparation of Hyponitrite from Nitrite through
Hydroxyamidosulphonate.*

By EDWARD DIVERS, M.D., D.Sc., F.R.S., and TAMEMASA HAGA,
D.Sc., F.C.S.

SULPHONATION, followed by hydrolysis, readily converts an alkali nitrite into the unstable hydroxyamidosulphonate, which, in a solution saturated with potassium hydroxide, has all its hydrogen replaced by

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potassium, and is simultaneously resolved into hyponitrite and sulphite,

This remarkable change was made known by us in 1889 (*Trans.*, 1889, 55, 760), along with the fact that it afforded a rich source of hyponitrite, since the quantity of the latter formed is equivalent to at least half the nitrite taken. But this, it was pointed out, depended on our method of preparing hydroximidodisulphonate being employed, and as the description of that method was not published until five years later, the new source of hyponitrite could not be used advantageously by others. Even since then, the method has escaped the notice of seven separate workers on hyponitrites, namely, Thum, W. Wislicenus, Paal and Kretschmer, Tanatar, D. H. Jackson, Piloty, and Hantzsch and Kaufmann, to be at last, however, taken up by Kirschner (*Zeit. anorg. Chem.*, 1898, 16, 424). Indeed, it may be said to have been rediscovered by Piloty, who in a paper on "an oxidation of hydroxylamine by benzenesulphonic chloride" (*Ber.*, 1896, 29, 1559), describes the resolution of benzenesulphonic hydroxylamide by potassium hydroxide into hyponitrite and benzenesulphinate, with a yield also of half the calculated quantity of the former salt.

As we have each of us very frequently employed the hydroxyamido-sulphonate method of preparing hyponitrite, and the details requisite in order to get high yields have not been published, it seems it will be of service to chemists to describe the method fully.* So far as our experience goes, we can be certain of getting a yield of 60 per cent. of the theoretical, and occasionally much more, although we have not succeeded in discovering the cause of this. In what follows, we assume that the convenient quantity of 2 decigram-molecules of sodium nitrite is taken, from which about 17 grams of silver hyponitrite may be obtained.

In order to limit the quantity of potassium hydroxide required, which is very large in any case, no more water than is necessary must be used, and except that particular attention must be given to this point, the process begins exactly like that of making hydroxylamine sulphate from nitrite (*Trans.*, 1896, 69, 1665). In a tared, wide-mouthed, round-bottomed flask of 200—250 c.c. capacity, 14.4 grams of 96 per cent. sodium nitrite,† together with sodium carbonate containing 10.6 grams of anhydrous carbonate, are dissolved by heat in enough water to make the total weigh 83.5 grams. Some lead salt

* Kirschner's method is an excellent form of our process, but I prefer that described in this paper.—E. D.

† But preferably, 13.8 grams of pure sodium nitrite, this being now very easy to prepare (this vol., p. 85).

in the nitrite is deposited, but goes into solution when the potassium hydroxide is added and gives no trouble. Sodium carbonate of any hydration may be used, but as, subsequently, more of this salt has to be added, and then should be approximately the monhydrate, it is convenient to use this form throughout. Such a carbonate, almost pure, is generally found in the "dried" pure carbonate of commerce. Keeping the flask in active motion in an ice-and-brine bath, sulphur dioxide is passed in until a short time after the temporarily precipitated acid carbonate has redissolved, and just when a bit of lacmoid paper in the solution becomes fully red. About 0.1 c.c. strong sulphuric acid is then dropped in. If the temperature is kept below 0° , the conversion of the nitrite into hydroximidosulphonate is complete, whereas if it rises much above 0° some nitrilosulphonate would form, and interfere with the result. If higher temperatures have been avoided, the nitrite and carbonate taken in molecular proportions, and the sulphur dioxide not used in excess, the solution is ready to be hydrolysed; but as the salts may not have been in exact proportion, and sulphur dioxide may also be present, it is best to blow a strong current of air through the solution at 0° , so as to expel any sulphur dioxide or nitric oxide that may be present.

After this treatment, the solution is brought to about 30° , in order to start hydrolysis, and set aside for a day in a warm place with the flask corked. Complete hydrolysis to hydroxyamidosulphonate without further hydrolysis to hydroxylamine is thus secured,* and, consequently, just the calculated quantity of sodium carbonate (10.8 grams anhydrous) is found to be required, including that for the three or four drops of sulphuric acid added. The approximately monhydrated carbonate, added in fine powder, is briskly shaken with the solution, so as to hinder its caking, the last portions being dissolved by warming the flask. The solution of hydroxyamidosulphonate and sulphate, thus prepared, contains almost exactly half its weight of water, is therefore supersaturated, and is the strongest solution practically obtainable; it will be found to approach closely 113 grams in weight, so smoothly do the reactions proceed. The solution may

* That the production of hydroxylamine is avoided if this detail is attended to, has been proved by shaking the solution, after it has been made alkaline, with sodium amalgam, which readily converts hydroxylamine into ammonia, but does not act on the hydroxyamidosulphonate. On testing in this way, no odour of ammonia can be recognised, and moist red litmus paper held in the bottle is barely affected. Kirschner, using potassium hydroximidosulphonate, had to heat to boiling to effect hydrolysis, which is difficult then to complete without some of the hydroxyamidosulphonate passing on into hydroxylamine. When the hydrolysis is incomplete, nitrite will be regenerated later on by the alkali; and when it is carried too far, nitrite will also be formed during the oxidation of the hydroxylamine by the silver (or mercury) oxide.

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be made weaker, and then concentrated, but the adjustment is troublesome, and the formation of hard cakes of sodium sulphate, which interferes with the proper working at the next stage of the operation, is difficult to avoid.

The contents of the flask are now well drained into a basin, preferably a hemispherical nickel basin, or, lacking that, a stout porcelain one, capable of holding about 500 c.c. Potassium hydroxide, free from chloride, assayed for real alkali and for water, and having not less than two-thirds and not more than 1 mol. of water to 1 of the hydroxide, is required, for if it were anhydrous it would cause much heating and consequent decomposition of the salts; generally, the potassium hydroxide purified by alcohol and the more translucent varieties of stick potash contain about the right proportion of water, and dissolve in water without much rise of temperature. From 130 to 165 grams of it, according to its degree of hydration, are quickly crushed in a warm mortar, thrown into the solution in the basin, and incorporated with it by means of a pestle. There is marked heating only just at first, which is better met by keeping the basin in water or resting it on snow or pounded ice for a very short time. On stirring in the potassium hydroxide, the solution sets to a stiff paste, if kept cold, quickly becoming thin again on further stirring, but full of an opaque, white precipitate of sulphate. If the basin has been cooled, hardly any gas escapes at first, but gentle effervescence and much frothing occur before long in any case. When the potassium hydroxide has been all ground up and dissolved, the basin is placed under close cover from atmospheric moisture and carbonic acid, and left in a warm place for 30 hours; if kept for more than 50 hours, the quantity of hyponitrite sensibly, but slowly, diminishes. As much even as one-fourth of the hydroxyamidosulphonate may sometimes, in cold weather, still be present, and can be partly destroyed by keeping the basin at 55—60° for half an hour, although not with noticeable increase of the quantity of hyponitrite, but this heating, with the attendant risk of over-heating, is better omitted, on the whole. Besides undecomposed hydroxyamidosulphonate, the contents of the basin now consist of precipitated sulphate and sulphite, and solution of potassium hydroxide in slightly less than its weight of water (almost exactly $\text{KOH} : 3\text{H}_2\text{O}$), together with the potassium hyponitrite. It is, apparently, only to secure this concentration of the potassium hydroxide, a practically saturated solution, that hardly less than 10 mols. of it to 1 of hydroxyamidosulphonate have to be used. More of it may be added without effect, good or bad, unless the solution of the salts is weaker than is here recommended, for in that case additional potassium hydroxide must be used to bring the concentration to the right point.

Treatment with a silver salt is the only way of separating the hyponitrite from the other salts, and for this purpose the presence of the alkali is essential, together with large dilution when precipitating. The best way is to use the silver solution exceedingly dilute, because this checks the precipitation of silver oxide and sulphite until some time after all the hyponitrite has separated. Now the necessity for large dilution, and the advantage of still larger dilution, remove the only objection that can be raised to the use of silver sulphate instead of silver nitrate, and since it is generally important to feel assured that no trace of nitrate or nitrite can have been carried down with the hyponitrite, the sulphate should have the preference, although the nitrate can almost certainly be used with as good results. A cold saturated solution contains only 5 or 6 grams of the sulphate to the litre, and is most easily prepared by boiling excess of the salt with water and pouring the solution into an equal volume of cold water.

Whichever salt is used, the contents of the basin are first washed into a very capacious precipitating vessel, and the highly dilute silver solution is poured in until it ceases to produce any more black precipitate. When this is at all abundant, as it sometimes is in cold weather, an hour's interval is given for subsidence of most of it, the still dark solution is decanted, and the precipitate washed by decantation before rejecting it. With or without this interruption, the addition of the silver solution is continued until the bright yellow hyponitrite suddenly appears, and so long after as the joint precipitation of brown oxide can be easily checked by stirring. When the point is reached where the oxide only redissolves slowly and no longer gives place to a yellow one of hyponitrite, no more silver solution should be added. If much more were added, there would be permanent precipitation of silver oxide, which is apt to be accompanied by silver sulphite. The quantity of silver sulphate required may be as much as 40 grams, which means 7 or 8 litres of solution; if silver nitrate be used, about 44 grams will be wanted, dissolved in 4 litres, or more, of water.

Half-an-hour after precipitation, the solution is to be poured off, even though still a little turbid, and the precipitate washed by decantation, for there is a very slow deposition of a mirror of metallic silver from the sulphite solution, which goes on for days. In order to separate the hyponitrite from the metallic silver and its oxide, and perhaps chloride, it has to be dissolved in dilute acid and reprecipitated. If every trace of nitrite is to be kept out of the hyponitrite, nitric acid can hardly be used, because I find that it always contains some nitrous acid, and it is, therefore, necessary to use sulphuric acid. Since the hyponitrite must be kept in solution as short a time as possible, it is advisable to have the acid not very

dilute, in order to reduce the volume of liquid to be filtered. But high dilution is better, because the stability of hyponitrite falls off rapidly with increasing concentration; moreover, if the sulphuric acid is not dilute enough, silver sulphate will separate; a 1 per cent. solution of the acid, well cooled in ice, is suitable, some 5 litres of it being required. The precipitate should be treated with the acid in portions at a time, not all together; and, as far as possible, the undissolved precipitate should be kept off the filter until the last. For so long a filtration a Lunge filter-tube-extension of the funnel is more suitable than the filter pump, the filtrate being allowed to fall directly into excess of sodium carbonate solution. Working with these precautions, the silver hyponitrite can be dissolved and reprecipitated, even in hot weather, with hardly any appreciable loss.

Having replaced the alkaline mother liquor by water, dilute sulphuric acid is cautiously added, until, after stirring up the precipitate well, the solution is no longer alkaline, and some of it, when filtered, is found to contain a trace of the silver hyponitrite; this is best ascertained by adding one or two drops of sodium carbonate solution to about 100 c.c. of it, which should cause a permanent, yellow, very slight, opalescence.

The precipitate, thoroughly washed by decantation and dried on a filter at the ordinary temperature in a desiccator, in the dark, and then at 100°, will give 78 per cent. silver (calc. 78.26). But in order to preserve the bright colour of the salt and its entire freedom from nitrite, all work on it should be done with very little exposure to bright daylight. The weight of silver hyponitrite obtained from the quantity of sodium nitrite employed should be not less than 17 grams.

IMPERIAL TOKYO UNIVERSITY, JAPAN.