CXCI.—*Reduction of Nitrites, Nitrates, and Nitric Acid with Magnesium Amalgam: A New Method of Preparing Hyponitrites.*

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It has been shown that magnesium reacts very slowly with solutions of many metallic salts to give hydroxides (Lemoine, *Compt. rend.*, 1899, **129**, 291; Tommasi, *Bull. Soc. chim.*, 1899, **21**, 885; Kahlenberg, *J. Amer. Chem. Soc.*, 1903, **25**, 380; Senbert and Schmidt, *Annalen*, 1892, **267**, 218). Since magnesium amalgam is much more reactive, its reducing action on metallic nitrates and nitrites has now been studied, and found to afford a convenient method for the preparation of hyponitrites. Among those thus prepared are several not hitherto described, *viz.*, *cadmium*, *zinc*, *lithium*, *rubidium*, and *cæsium hyponitrites*, and that of magnesium has been obtained in solution.

Most of the known hyponitrites depend for their preparation on double decomposition with sodium nitrite (compare Divers, J., 1899, **75**, 95), but the method now described is direct. Moreover, the use of magnesium amalgam possesses advantages over that of sodium amalgam (as used by Divers) in that magnesium hydroxide is much more readily removed than sodium hydroxide and that it does not enter into secondary reactions (*e.g.* precipitation of metallic hydroxides) or tend to decompose unstable hyponitrites.

The reduction of nitrates by magnesium amalgam takes place in several stages, the presence of nitrites, hyponitrites, hydroxylamine, and ammonia having been established in many cases. Hydroxylamine is frequently produced in considerable quantities, but not a trace was observed in the preparation of rubidium and cæsium hyponitrites; its isolation as sulphate in good yield is described.

In testing for hyponitrites by silver nitrate it is first necessary to remove the hydroxylamine by shaking with mercuric oxide. The silver nitrate test may be applied in the case of lithium, sodium, potassium, barium, strontium, and calcium hyponitrites even in the presence of their hydroxides, for the silver oxide first formed reacts with the soluble hyponitrites, precipitating the characteristic yellow silver hyponitrite; but in the case of rubidium and cæsium hyponitrites, the silver oxide does not undergo this double decomposition, and the solution has to be neutralised with dilute nitric or acetic acid before the test is applied.

EXPERIMENTAL.

Preparation of Magnesium Amalgam.—20 G. of magnesium, either as filings or as small pieces of clean ribbon, are placed in a flask containing 400 g. of mercury and gently heated for 2 or 3 minutes on a wire gauze over a flame. The flask is then removed and vigorously shaken at intervals during 10 minutes, the heat evolved being sufficient to keep the elements in a state of reaction. (If heating is continued for too long, the whole mass takes fire.) When all the magnesium has dissolved, the liquid mass is solidified by being poured on a porcelain tile, and while still soft it is cut into small pieces and stored in a stoppered bottle which is protected from moisture. It was found unnecessary and even undesirable to conduct the amalgamation in an atmosphere of carbon dioxide or hydrogen, for the whole mass sometimes took fire in the latter gas.

Procedure.—Owing to the exothermic nature of the reduction and to the instability of hyponitrites, all solutions were immersed in a freezing mixture and thoroughly stirred during the reaction, so that the temperature did not exceed 5°. Also, it was found essential to continue the reduction until no nitrite remained before attempting to concentrate the solution, for nitrates and nitrites appear to accelerate the decomposition of the hyponitrite.

It is advisable to filter off the bulky precipitate of magnesium hydroxide from time to time during the reduction, for it is difficult to remove it all at once at the end of the reaction.

Lithium Hyponitrite.—To a concentrated neutral solution of lithium nitrate, cooled in an ice-salt mixture, magnesium amalgam was slowly added in small pieces. The mixture was kept for a short time, and the precipitated magnesium hydroxide was filtered off and washed once or twice with small quantities of ice-cold water. The filtrate was again reduced, and the operation repeated until the solution was free from nitrate and nitrite; it then contained ammonium and lithium hydroxides, hydroxylamine, and lithium hyponitrite, but no magnesium salt. The solution was placed in a vacuum desiccator over concentrated sulphuric acid, the hydroxylamine decomposing and the resulting ammonia being absorbed in the acid. After about a fortnight, the whole set to a solid, white mixture of lithium hydroxide and hyponitrite. The hyponitrite was extracted with absolute alcohol, in which it was moderately soluble, and then precipitated with ether. Several repetitions of the extraction and precipitation gave *lithium hyponitrite* free from hydroxide; it was dissolved in the minimal quantity of water and again evaporated to dryness in a vacuum desiccator over sulphuric acid (Found, by conversion into Li_2SO_4 : Li, 19·34. $Li_2N_2O_2$ requires Li, 18·79%). The slightly high result was due to hydrolysis during the final crystallisation, as was shown by the alkalinity of the aqueous solution.

Sodium Hyponitrite.—Sodium nitrite (35 g.) in water (200 c.c.) was reduced as above, 420 g. of 5% amalgam being used. The solution smelt strongly of ammonia and contained hyponitrite and hydroxylamine. After 20 days' evaporation the solid hyponitrite was obtained together with caustic soda; the latter was extracted by washing with absolute alcohol, and the hyponitrite dried in a vacuum desiccator. (Divers's method of precipitating the hyponitrite by the addition of absolute alcohol gave a smaller yield.) (Found: Na, 43·63. Calc.: Na, 43·4%).

Potassium Hyponitrite.—The nitrite (40 g. in 250 c.c. of water) was reduced exactly as in the foregoing example. The solution was strongly alkaline and contained ammonia, hydroxylamine, caustic potash, and potassium hyponitrite, and the hyponitrite was worked up as before (Found: K, 56·49. Calc.: K, 56·58%).

Reduction of the nitrate instead of the nitrite proceeded similarly, but was less convenient.

Rubidium Hyponitrite.—Rubidium nitrate solution (from 7 g. of the chloride, by reaction with silver nitrate) was completely reduced as usual; the resulting solution contained rubidium hydroxide and hyponitrite, and ammonia, but no hydroxylamine. After keeping over-night in a vacuum desiccator over sulphuric acid, the solution was neutralised with dilute acetic acid, and then concentrated as before. The resulting long, needle-shaped, colourless crystals were repeatedly washed with absolute alcohol to remove all the acetate, and the *rubidium hyponitrite* was dried in a vacuum desiccator (Found, by conversion into Rb_2SO_4 : Rb, 63·6. $Rb_2N_2O_2,2H_2O$ requires Rb, 64·0%).

The solid hyponitrite was very deliquescent. When heated in a test tube it melted in its water of crystallisation, and decomposed at a higher temperature without explosion.

Cæsium Hyponitrite.—The nitrate (from 5 g. of the chloride) was reduced as before. The solution, containing cæsium hydroxide and hyponitrite, together with ammonia but no hydroxylamine, ultimately yielded a white mass from which alcohol extracted the hydroxide and left the *hyponitrite* (Found : Cs, 56·69. $Cs_2N_2O_2,8H_2O$ requires Cs, 56·54%).

Magnesium Hyponitrite.—This hitherto-unknown hyponitrite has been prepared by us, but not isolated, by reduction of the nitrate (40 g. in 250 c.c. of water). The hyponitrite is found with the precipitated hydroxide and not in the solution. The washed precipitate was added to dilute acetic acid (6%) until no more dissolved and a slight excess remained. The filtered solution gave a positive test for hyponitrite with silver sulphate, but on keeping over-night in a vacuum desiccator, the magnesium hyponitrite was totally decomposed. It was also found that the hyponitrite was not reprecipitated by any alkali, but was decomposed.

That magnesium hyponitrite is soluble in ether and acetic acid has been shown by our attempts to isolate it in organic media. The precipitate of hydroxide and hyponitrite was extracted with a mixture of glacial acetic acid (1 vol.) and ether (6 vols.), and the extract evaporated in a vacuum desiccator to remove the ether. The remaining acetic acid solution responded to the tests for hyponitrites, but further evaporation caused decomposition.

Zinc Hyponitrite.—Reduction of the nitrate (20 g. in 200 c.c. of water, to which a few drops of nitric acid had been added) gave a solution containing hydroxylamine and a little magnesium but no hyponitrite. The precipitate, however, showed the presence of hyponitrite, and was therefore washed, dissolved (with cooling) in the minimum quantity of dilute acetic acid (6%), neutralised with ammonia, and kept for 2—3 hours; the gelatinous precipitate which separated was filtered off, washed, dissolved in acetic acid, and reprecipitated by neutralisation, the process being repeated five times in order to get rid of magnesium hydroxide and zinc hydroxide. The gelatinous white precipitate ultimately obtained had the appearance of boiled arrowroot and was free from magnesium; on drying in a vacuum desiccator it yielded a white powder (Found, by heating to ZnO: Zn, 45·5. ZnN_2O_2,H_2O requires Zn, 45·6%). *Zinc hyponitrite* explodes on heating unless it is warmed very gently at first.

Cadmium Hyponitrite and Hydroxyhyponitrite.—After reduction of the nitrate in the usual way, the filtered solution contained nitrate, hydroxylamine, and ammonia, but no hyponitrite. The washed precipitate, however, showed the presence of hyponitrite, and was therefore treated as in the case of zinc. The white precipitate which was slowly formed in the neutralised solution was filtered off after 3 hours, washed, redissolved in dilute nitric acid, and again neutralised. After six repetitions of this process, the precipitate was dried and obtained as a yellowish powder of *cadmium hyponitrite* (Found: Cd, 64·8. CdN_2O_2 requires Cd, 65·2%). This had $d_{4°}^{22°}$ 2·121.

During the process of dissolution and reprecipitation, the colour of the hyponitrite gradually changed from white to light yellow. The *white* substance has been found to be the *oxyhyponitrite* [Found: Cd, 70·6. Cd(OH)(NO) requires Cd, 70·5%]. This case is analogous to that of lead hyponitrite (Kirschner, *Z. anorg. Chem.*, 1898, **16**, 424). The basic hyponitrite was very explosive, like silver hyponitrite, so for analysis a weighed quantity was dissolved in concentrated nitric acid in a crucible and cautiously heated to the oxide.

Action of Heat on Cadmium Hyponitrite.—0·2892 G. of the yellow salt was placed in a hard-glass tube, which was exhausted by a Sprengel pump, and heated gradually in a bath of sulphuric acid. At 185° the substance decomposed suddenly into cadmium oxide and a gas, which was collected in a graduated tube and occupied 40 c.c.; as it was almost totally, though slowly, absorbed by cold water, it was assumed to be nitrous oxide, especially as no nitrous fumes were formed when air was admixed with it. The gas was completely soluble in alcohol.

Calcium Hyponitrite.—After reduction of the nitrate as usual, the solution contained hydroxylamine, ammonia, and calcium hyponitrite, but no magnesium. The precipitate also gave tests for hyponitrite. Calcium hyponitrite being partially soluble in water, the precipitate was repeatedly extracted with small quantities of water, and the extract added to the main solution, which was then kept over sulphuric acid in a vacuum desiccator for a day, to remove hydroxylamine and ammonia, neutralised with phosphoric acid, to remove calcium hydroxide, filtered, and the filtrate was evaporated over sulphuric acid in a vacuum. The solid crystalline mass was washed with small quantities of absolute alcohol and again dried (Found : Ca, 23·17. Calc. for $CaN_2O_2,4H_2O$: Ca, 23·26%).

Strontium Hyponitrite.—This was prepared exactly as in the preceding case (Found : Sr, 37·1. Calc. for $SrN_2O_2,5H_2O$: Sr, 36·9%).

Barium Hyponitrite.—This salt, which is more soluble in water than that of calcium or strontium, was prepared in the same way (Found : Ba, 51·66. Calc. for $BaN_2O_2,4H_2O$: Ba, 50·98%).

Lead Hyponitrite and Oxyhyponitrite.—Reduction of lead nitrate (30 g. in 200 c.c. of water) gave a solution containing hydroxylamine and ammonia, but no magnesium or hyponitrite. The precipitate was dissolved with cold dilute acetic acid, the solution neutralised, and the dissolution and precipitation were repeated. The white precipitate thus formed was filtered off, washed, and dried (Found : Pb, 77·8. Calc. for PbN_2O_2 : Pb, 77·6%).

The white salt, after treatment with acetic acid and ammonia four or five times at room temperature, became yellow; it was then filtered off, washed, and dried in a vacuum (Found : Pb, 84·2. Calc. for PbO,PbN_2O_2 : Pb, 84·5%).

Reduction of Other Nitrates.—In the cases summarised below hyponitrites were not obtained.

1. *Mercuric nitrate* gave a red precipitate of mercuric oxide; ammonia was evolved, and the solution contained magnesium nitrite.

2. *Mercurous nitrate* gave at first a brown precipitate, which gradually turned black; ammonia was evolved and magnesium nitrite was detected in the solution.

3. *Cobalt nitrate* gave at first a blue precipitate (perhaps a basic salt), which gradually turned to brown cobaltic hydroxide; ammonia was evolved and the solution contained magnesium nitrate and nitrite only.

4. *Copper nitrate* gave a precipitate of basic copper nitrate, $Cu(NO_3)_2,3Cu(OH)_2$ (Found : Cu, 52·88. Calc.: Cu, 52·92%), and the solution contained magnesium nitrate and nitrite, hydroxylamine, and ammonia. Nitric oxide is at first evolved, followed by ammonia.

5. *Nickel nitrate* gave at once a black precipitate of nickelic hydroxide, and the contents of the solution were the same as in the preceding case.

6. *Silver nitrate* was at once reduced to the metal; the solution contained magnesium nitrate and nitrite and ammonia.

7. *Ammonium nitrate* gave the nitrite and ultimately ammonia only.

Reduction of Nitric Acid : Preparation of Hydroxylamine Sulphate.—Nitric acid (200 c.c. of 10%) and sulphuric acid (20 c.c. of 10%) were cooled in ice and reduced in the usual way. The precipitate was separated and the filtrate reduced with the addition of 5 c.c. of 10% sulphuric acid, this operation being repeated three times. The solution was finally evaporated on a water-bath, and the hydroxylamine sulphate removed from the magnesium and ammonium sulphates by repeated extraction with warm absolute alcohol. Evaporation of the extract gave hydroxylamine sulphate in a yield of 60% of the nitric acid used; its purity was 97·8% as estimated by Raschig's method.

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