

LXXXVII.—*Disodium Nitrite, an Additive Compound of Sodium Nitrite and Sodium.*

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IN the course of work on the preparation of alkali metals by the electrolysis of non-aqueous solutions, the author had occasion to examine the products obtained by electrolysing a solution of sodium nitrite in perfectly anhydrous liquid ammonia. A deposit was observed to form on the cathode, resembling metallic sodium in that it dissolved in water with violent evolution of hydrogen, but completely differing from the metal by reason of its bright yellow colour and by its failure to dissolve in excess of ammonia with the production of the characteristic blue coloration.

It was found, further, that the same compound may be obtained in a state of purity, as a brilliant yellow precipitate, by bringing together free metallic sodium and dry sodium nitrite, each dissolved separately in anhydrous ammonia. An analysis of the precipitate showed it to possess the empirical composition Na_2NO_2 , the ammonia acting merely as a solvent. By the action of water, decomposition takes place with regeneration of sodium nitrite and of sodium hydroxide. No hyponitrite could be detected in the solution.

EXPERIMENTAL.

Direct Preparation of Disodium Nitrite.

For the preparation of the compound in a pure condition, it is essential first of all to free the ammonia, which is to be used as a solvent, from all traces of moisture. This may be done by introducing into a distilling flask a suitable quantity of liquid ammonia and dissolving in it sufficient sodium to impart to it a blue colour. The ammonia is freed from sodium hydroxide and from excess of sodium by distillation and recondensation in the vessel which is to be used for the preparation of disodium nitrite.

The preparation may most conveniently be carried out by dissolving in the clear, anhydrous ammonia thus obtained a known weight of metallic sodium, this being added in small pieces. Freshly fused and finely powdered sodium nitrite in a solid condition is next introduced. It is found unnecessary to dissolve this separately provided that sufficient time is given for the sodium to pass into solution and that the nitrite is added gradually. The addition of sodium to a solution of sodium nitrite, on the other

hand, does not result in a satisfactory preparation on account of the formation of an insoluble layer round the sodium as added.

The completion of the reaction is easily recognised by the discharge of the deep blue colour. This is found to take place on the addition of one molecule of sodium nitrite to each atom of sodium, disodium nitrite being thrown down as a bright yellow precipitate, from which the excess of ammonia is removed by evaporation. Any access of moisture is accompanied by an explosion, which is usually sufficiently intense to shatter the reaction vessel and to cause a dangerous spray of liquid ammonia.

In an experiment, about 100 c.c. of pure anhydrous ammonia were condensed in the long-necked flask used as a reaction vessel. At this stage, the rubber stopper at its mouth was withdrawn and replaced by a second one fitted with a Bunsen valve. One gram of metallic sodium was now introduced gradually in small pieces, the reaction vessel being allowed to remain for about ten minutes after the final addition to ensure complete solution of the sodium. Three grams of finely powdered sodium nitrite, previously dried by fusion, were next weighed out in a small stoppered tube and added gradually to the solution of sodium, the vessel being shaken gently. On adding the last portion of nitrite, the blue coloration in the reaction vessel disappeared, showing that one atom of sodium reacted with each molecule of sodium nitrite, and a yellow precipitate of disodium nitrite was seen to have formed. The reaction vessel was now removed from its cooling-bath and allowed to attain the ordinary temperature, with consequent evaporation of the layer of colourless liquid ammonia with which the compound was covered. At this point, the reaction vessel, together with its stopper and valve, was weighed in order to ascertain whether ammonia was being retained as an integral part of the compound, the following results being obtained:

	Grams.
Weight of empty reaction vessel	52.77
Weight of sodium added	1.00
Weight of sodium nitrite added	3.00
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	56.77
Weight of vessel plus compound after evaporation of ammonia	56.79

The yellow compound contains, therefore, no ammonia.

Preparation of Disodium Nitrite by the Electrolysis of Sodium Nitrite.

For this purpose, a reaction tube about 35 cm. long and 3 cm. in internal diameter was provided with concentric cylindrical

platinum electrodes separated from one another by an asbestos diaphragm. The area of the electrode used as cathode was about 25 sq. cm. After half filling the electrolysis tube with pure, dry liquid ammonia in the manner already described, about 5 grams of dry powdered sodium nitrite were introduced and the whole allowed to remain. No metallic sodium was, of course, introduced into the electrolysis vessel.

The two electrodes with their asbestos diaphragm were next introduced into the nitrite solution, care being taken to avoid access of atmospheric moisture, and a current of 2 amperes at a potential of 110 volts from the laboratory mains was led through for one hour. On interrupting the current, the cathode was seen to be covered with and surrounded by a yellow deposit similar to that obtained by the direct action of sodium on the nitrite. The platinum cathode was quickly immersed in a test-tube of dry ether, and on bringing it under water, the vigorous evolution of a considerable quantity of hydrogen was noted. A somewhat striking demonstration of the violence with which the compound combines with water was obtained by repeating the experiment and allowing the yellow cathodic deposit, separated as far as possible from the ammonia, to rise to the ordinary temperature in contact with the air. A series of sharp decrepitations, accompanied often by fire, was observed.

Action of Water on Disodium Nitrite.

In order to examine the moderated action of water on the compound, 4 grams were prepared in a pure, ammonia-free condition by the first method. Hydration was now carried out by the passage of a current of moist nitrogen, distilled water being added as soon as hydration was complete.

The solution was found to exert no reducing action on Fehling's solution, showing the absence of hydroxylamine and similar compounds. A second portion was tested for hyponitrite by neutralising with *N*/100-sulphuric acid, followed by silver sulphate, in accordance with the procedure recommended by Divers and Haga (T., 1899, 75, 97). No yellow precipitate of silver hyponitrite was obtained. A further sample was now neutralised, without dilution, with *N*/10-nitric acid, and silver nitrate added. A white precipitate soluble in much water was obtained. In order to investigate the composition of this precipitate, which was suspected to be silver nitrite, a further 4 grams of disodium nitrite was hydrated in the manner previously described, made up to approximately 100 c.c., and neutralised as before with *N*/10-nitric

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acid. The precipitate obtained by the addition of excess of silver nitrate solution was collected and carefully washed with cold distilled water, after which it was dried in a vacuum desiccator in the dark. A silver salt (2.1 grams) was obtained which was found on analysis to contain $\text{Ag}=69.8$; AgNO_2 requires $\text{Ag}=70.1$ per cent.

It is intended, as soon as time permits, to investigate the whole subject more closely, and to examine also the possibility of obtaining alkyl derivatives, which may throw light on the constitution of disodium nitrite.

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