CCLXXXII.—*Investigations on Hyponitrites. Part I. Sodium Hyponitrite: Preparation and Properties.*

By James Riddick Partington and Chandulal Chhotalal Shah.

Sodium hyponitrite required for the present work was prepared by a modification of the method of Divers (J., 1899, **47**, 97). Three other methods (Joanis, *Compt. rend.*, 1894, **118**, 718; Weitz and Vollmer, *Ber.*, 1924, **57**, *B*, 1015; Scott, *J. Amer. Chem. Soc.*, 1927, **49**, 986) were tried and found to give hyponitrite, but the method adopted here was found to be the most suitable, as regards both cost and purity of the product. We were not able to obtain it in the pure white form by the method of Weitz and Vollmer.

Three solid hydrates of the salt have been reported, the penta- (Divers, *loc. cit.*), the hexa- (Menke, J., 1878, **33**, 401), and the ennea-hydrate (Weitz and Vollmer, *loc. cit.*). We find that the solid salt exists in the form of two different hydrates. From a concentrated solution of sodium hydroxide, it separates on standing in a vacuum over sulphuric acid in the form of small granules of the pentahydrate. If this or the anhydrous salt is redissolved in water, and the solution concentrated over sulphuric acid in a vacuum, or the solid precipitated by a large excess of alcohol, the *octahydrate* is formed. In the first case, the octahydrate forms short thick needles, and in the second it appears as very small crystals. The hexa- and the ennea-hydrate could not be obtained, and very probably these have been mistaken for the above two hydrates. Divers could not obtain the salt in the crystalline form, and denied the statement made by Jackson (P., 1893, **12**, 210), who obtained it as needles.

Analysis.—The salt, in either the anhydrous or the hydrated state, has not been analysed previously, except one analysis each by Divers, Menke, and Weitz and Vollmer (*locc. cit.*). Menke estimated the nitrogen in the substance by heating it with soda-lime and determining the amount of ammonia formed. We found no trace of ammonia either under these conditions or when the salt was treated with Devarda's alloy and potassium hydroxide. Nitrogen in hyponitrites, in general, however, can be estimated by a modification of Dumas's method. The dry salt is mixed with fused sodium hydrogen sulphate and heated in a combustion tube, the gases evolved being passed over hot reduced copper gauze, and the liberated nitrogen measured. Kirschner (*Z. anorg. Chem.*, 1898, **16**, 424) used copper powder instead of sodium bisulphate. This method gives good results with other salts, but fails in the case of the sodium compound, the results of the nitrogen analysis being always too low, apparently because some nitrogen as sodium nitrate remains undecomposed by sodium hydrogen sulphate, even at a red heat. The residue was, in fact, found to contain sodium nitrate. Since no suitable method could be found for the determination of nitrogen in the sodium salt, the hyponitrite radical was determined as the silver salt; but as silver carbonate and nitrite are also insoluble in a neutral solution, the sodium salt was examined for the presence of both of these. The amount of nitrite in the salt was found to be less than 0·001%, and no carbonate was detected.

Action of Hydriodic Acid.—Various views are held as to the action of hydriodic acid on hyponitrites. A solution of the sodium salt does not immediately give any blue colour with hydriodic acid and starch, although this colour develops in 2—3 minutes. We believe that this result is due to small traces of nitrous acid present in the preparation. A solution which has been kept for 24 hours behaves similarly, showing that the amount of nitrous acid does not appreciably increase, though a sensitive colorimetric determination with Griess reagent shows that nitrous acid does increase somewhat in such a solution. In a freshly prepared solution, the content of sodium nitrite was found to be $4{\cdot}2 \times 10^{-4}\%$, and in the same solution after 24 hours it was $6{\cdot}3 \times 10^{-4}\%$, which increased to $7{\cdot}3 \times 10^{-4}\%$ at the end of one week. Probably in solution the salt decomposes according to the equation

$$3Na_2N_2O_2 + 2H_2O = 2NaNO_2 + 4NaOH + 2N_2 \quad . \quad (1)$$

but the amount of nitrous acid formed is too small for macro-estimation. The solution does not give the diphenylamine test.

Thermal Decomposition of the Solid.—The action of heat on the solid anhydrous salt has been studied by Divers (*loc. cit.*), who states that it is stable up to 300°, but at higher temperatures decomposes as follows

$$3Na_2N_2O_2 = 2NaNO_2 + 2Na_2O + 2N_2 \quad . \quad . \quad (2)$$

Ray and Ganguli (J., 1907, **91**, 1399) find that the products of the action of heat on the silver salt consist of silver, silver nitrate, nitrogen, and nitric oxide; and on the mercury salt, of mercury, mercuric oxide, nitric and nitrous oxides, together with some nitrogen and mercurous nitrate. In contrast to these two salts, we find that the sodium salt decomposes according to the equation given by Divers [(2) above] when heated in a vacuum, the decomposition occurring suddenly and explosively at 260—265°, leaving a red residue which becomes yellow on cooling. The solid on analysis was found to consist of equimolecular proportions of sodium nitrite and sodium oxide, while the gas evolved was pure nitrogen.

When the dry salt is heated with sodium hydrogen sulphate, the gaseous products consists of nitrous and nitric oxides and nitrogen, while, as stated above, even at a red heat some sodium nitrate remains in the solid residue. Probably the decomposition proceeds simultaneously according to the equations

$$Na_2N_2O_2 + 2NaHSO_4 = 2Na_2SO_4 + H_2O + N_2O \quad . \quad (3)$$

$$3Na_2N_2O_2 + 4NaHSO_4 = 2NaNO_2 + 4Na_2SO_4 + 2H_2O + 2N_2 \quad (4)$$

$$2Na_2N_2O_2 + 4NaHSO_4 = 4Na_2SO_4 + N_2 + 2H_2O + 2NO \quad . \quad (5)$$

$$3NaNO_2 + 2NaHSO_4 = 2Na_2SO_4 + NaNO_3 + H_2O + 2NO \quad (6)$$

Aqueous solutions of the salt instantaneously decompose in a vacuum to the extent of 50%, giving nitrous and nitric oxides and nitrogen, the main product being nitrous oxide (68·5%). The action may be represented by equations (3) and (5), H_2O being substituted for $NaHSO_4$. If the pressure is not below 40 mm., the solution does not decompose abruptly, but does so slowly, the decomposition mainly proceeding according to equation (3). No nitrate or nitrite can be detected in the solution.

Action of Acids.—Ray and Ganguli (J., 1907, **91**, 1866) studied the action of dilute mineral acids on the silver and the mercurous salt, and showed that the former is completely decomposed by these acids, whilst the latter is only partly decomposed, except by hydrochloric acid. We have examined the action of dilute sulphuric and hydrochloric acids on the sodium salt, and find that the reaction is the same as in aqueous solution; the percentage decomposition is a little higher and the proportion of nitrogen and nitric oxide is slightly greater, thus showing that the reaction (5) is favoured by acids. No nitrate or nitrite appears to be formed during the reaction.

The salt is completely decomposed by concentrated sulphuric acid. Nitric acid and traces of nitrous acid are formed besides nitrous and nitric oxides and nitrogen. The reaction is very vigorous and the whole vessel becomes filled with white fumes, the solid salt being so much heated at places that it glows. The main reaction (65%) is represented by equation (3). All the reactions (3), (4), (5), and (6) probably occur, and also probably, in addition:

$$5Na_2N_2O_2 + 8H_2SO_4 = 2NaNO_3 + 8NaHSO_4 + 4H_2O + 4N_2 \quad (7)$$

Oxidation with Potassium Permanganate.—Various workers have examined the oxidation of hyponitrous acid and of sodium and other hyponitrites in presence of sulphuric acid, by means of permanganate, but have reached very different conclusions. Hantzsch and Sauer (*Annalen*, 1897, **299**, 67) prepared a solution of the free acid by shaking $N/100$-hydrochloric acid with a weighed amount (excess) of silver hyponitrite; the amount of potassium permanganate used by such a solution was less than that required by the equation

$$H_2N_2O_2 + 4O = 2HNO_3 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Similarly, Kirschner (*loc. cit.*) treated weighed amounts of the barium, calcium, strontium, and silver salts with acid potassium permanganate and also obtained low values. On the contrary, Divers (*loc. cit.*), using $N/20$-solution of the acid, and Thum (*Monatsh.*, 1893, **14**, 294), using $N/100$-solution of the acid, in both cases prepared from silver hyponitrite and hydrochloric acid, obtained values showing that the oxidation proceeds to completion according to equation (8). Recently, Raschig (" Schwefel- und Stickstoffstudien," 1924) has shown that the action of acidified potassium permanganate proceeds according to the equation

$$H_2N_2O_2 + 2O = 2HNO_2 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and differs from the action of subsequently acidified potassium permanganate (acid added 15 minutes after the permanganate solution), which proceeds according to equation (8) above. As is well known, nitrous acid is oxidised quantitatively to nitric acid by potassium permanganate in presence of acids. To avoid this difficulty, Raschig supposes that an anhydride, N_2O_3, different in constitution from the anhydride of nitrous acid and stable towards permanganate in acid solution, is formed. In his experiments he used a solution of the sodium salt obtained by shaking silver hyponitrite with saturated sodium chloride solution.

We have repeated these experiments, using solutions of different concentrations and prepared in different ways, and we think that a portion of the hyponitrous acid is always oxidised to nitric acid according to equation (8), the other portion decomposing into nitrous oxide and water according to equation (3). Owing to the spontaneous decomposition of solutions of hyponitrites and hyponitrous acid, the results obtained are invariably low as can be seen from Table II. Another cause for the low values is the fact that silver hyponitrite is not completely decomposed by shaking with hydrochloric acid (Ray, De, and Dhar, J., 1913, **103**, 1562), or with sodium chloride (Divers, *loc. cit.*).

Since aqueous solutions of the salt decompose in a vacuum, as shown above, they were not used for examining the products of oxidation formed in a vacuum. The results obtained with the solid sodium salt show that the above conclusion regarding the action of permanganate on hyponitrous acid, *viz.*, that a portion of it is oxidised to nitric acid and the other portion decomposes into nitrous oxide, is correct. In the presence of acidified potassium permanganate, 65% of the salt decomposes, giving nitrous oxide and nitrogen. The remaining 35% is oxidised to nitric acid. But if the acid is added 15 minutes after the potassium permanganate solution, 48% of the salt decomposes into nitrous oxide and nitrogen, and the rest is oxidised to nitric acid. The formation of nitrogen probably occurs according to equation (5), the nitric oxide simultaneously formed being oxidised to nitric acid. Thus the low values obtained by Raschig are to be attributed rather to the greater decomposition suffered by hyponitrous acid than to the formation of a hypothetical oxide, N_2O_3. In his attempt to separate this N_2O_3, he failed to account for one-third of the total nitrogen, which very probably escaped before he began his estimation.

Reduction.—Among the products of reduction of hyponitrous acid, four substances, *viz.*, nitrogen, hydroxylamine, hydrazine, and ammonia, are likely to be formed. By reduction with zinc and acetic acid, Devarda's alloy and potassium hydroxide, aluminium amalgam, sodium bisulphite, stannous chloride, titanous chloride, and sodium hydrosulphite (hyposulphite), we find that none of the last three is formed, though von Brackel (*Ber.*, 1900, **33**, 2115) claims to have obtained hydrazine by reduction with zinc and acetic acid and also with sodium bisulphite. In the case of sodium hydrosulphite (alkaline), no nitrogen either appears to be formed. Coblens and Bernstein (*J. Physical Chem.*, 1925, **29**, 750) claim to have reduced silver hyponitrite to ammonia by the successive action of stannous chloride and titanous chloride. We were unable to obtain any ammonia by the action of these reagents on sodium hyponitrite solution. Traces of ammonia sufficient for colorimetric estimation by Nessler reagent were found in the solution, but this is probably due to impurities rather than to the reduction of the hyponitrite.

Table I summarises the foregoing results in the form of a nitrogen balance.

EXPERIMENTAL.

Preparation of Sodium Hyponitrite.—25 G. of pure sodium nitrite (Divers, J., 1899, **47**, 85) are dissolved in 50 c.c. of water. Sodium amalgam, prepared by dissolving 25 g. of sodium in 140 c.c. of mercury, is slowly added to the above solution contained in a round-bottomed flask. During the addition the solution is kept cold by running water. After all the amalgam is added, the flask is vigorously shaken and cooled till no more heat develops. The whole is then transferred to a thick-walled separating funnel, the solid adhering to the flask being twice washed with very small amounts of water, and shaken continuously for one hour to reduce any nitrite which might have been precipitated along with the hyponitrite from the strongly alkaline solution. The amalgam is then separated. The sodium hyponitrite is filtered off through asbestos, without unduly exposing the liquid to the action of air, which can best be done by passing a current of carbon dioxide-free air or nitrogen over the solution being filtered. The solid is then taken out and repeatedly triturated with alcohol till the pulp-like mass falls to a fine powder, which is then filtered and washed with the same reagent. It is redissolved in the least amount of water, and filtered from suspended impurities. The solution is then concentrated over sulphuric acid in a vacuum. The vessel should preferably be covered, as considerable bumping occurs. On the third or fourth day thick short needles separate. These are crushed and triturated with alcohol, filtered, and washed with alcohol and ether. The salt so prepared is the *octahydrate* (Found : Na, 18·05; N_2O_2, 24·7; H_2O, 55·5. $Na_2N_2O_2,8H_2O$ requires Na, 18·4; N_2O_2, 24·0; H_2O, 57·6%). When left for 24 hours over concentrated sulphuric acid in a vacuum, it becomes anhydrous (Found : Na, 42·3; N_2O_2, 54·1. Calc. for $Na_2N_2O_2$: Na, 43·4; N_2O_2, 56·6%). The yield of the anhydrous salt is 19%. Its specific gravity is 1·726 at 25°.

For preparing the pentahydrate, the sodium nitrite is dissolved in 75 c.c. of water. After separation of the amalgam, the solution is filtered through asbestos, and the filtrate left in a vacuum over sulphuric acid. After about 25 days, small granules separate. These are filtered in a small Gooch crucible without asbestos and washed with alcohol. They are then taken out, triturated with alcohol, filtered, and washed with alcohol and ether (Found : Na, 23·9; N_2O_2, 29·8; H_2O, 45·1. Calc. for $Na_2N_2O_2,5H_2O$: Na, 23·5; N_2O_2, 30·6; H_2O, 45·9%).

In studying the action of various reagents in a vacuum, the apparatus shown in Fig. 1 was used. The substance was weighed out in the small tube A and carefully introduced into the flask. The solution, the action of which it was desired to study, was contained in the side tube B or D. In cases where it was necessary to study the action of two reagents in succession, these were separately introduced into B and D. The vessel was then attached to the Sprengel pump and evacuated, and the solutions added to the substance through the three-way tap E. A small amount of air remains in the tap (calculated, 1·1 c.c.) and in the analysis this volume is deducted from the amount of nitrogen.

For studying the action of heat, the substance was weighed in the tube shown in Fig. 2. The spiral at the top, which contains some glass wool, prevents escape of solid when it suddenly decomposes. This tube is heated in a Pyrex tube, having a ground-in glass thermometer and attached to the pump.

Action of Heat.—(i) 0·1006 G. of the hyponitrite gave 13·9 c.c. of nitrogen (at S.T.P.). The residue weighed 0·0826 g. and required 13·9 c.c. of 0·0935*N*-hydrochloric acid for neutralisation (phenolphthalein) and 11·2 c.c. of 0·11*N*-potassium permanganate solution. (ii) 0·1236 G. left a residue weighing 0·0994 g. and required 17·0 c.c. and 14·4 c.c. of the above reagents respectively.

The hyponitrite remains unchanged to 260°. At 260—265°, it begins to melt, effervesces, and suddenly decomposes, turning first yellow and then red. After cooling, the residue is yellow.

FIG. 1.

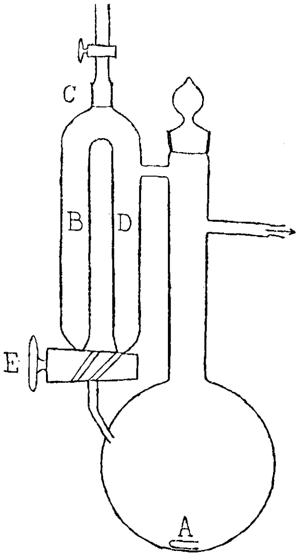
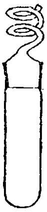


FIG. 2.



Action of Sodium Hydrogen Sulphate.—The hyponitrite was weighed in a porcelain boat, mixed with 1 g. of sodium hydrogen sulphate, and introduced into a short length of combustion tubing, which was then evacuated. (i) 0·1730 G. gave 7·6 c.c. of nitrous oxide, 3·6 c.c. of nitric oxide, and 16·1 c.c. of nitrogen. The residue contained nitrate (diphenylamine test) and traces of nitrite (potassium iodide and starch). (ii) 0·1297 G. gave respectively 9·8, 2·2, and 13·2 c.c. of these three gases. The residue gave 4·0 c.c. of nitric oxide (estimation of nitric acid by Crum-Frankland method).

In this experiment, and in the action of concentrated sulphuric acid, a washing tube containing potassium hydroxide was interposed between the pump and the apparatus, but no nitrate or nitrite was detected in it (diphenylamine test).

Action of Water.—(i) 0·1038 G. of hyponitrite gave with 20 c.c.

of water 7·9 c.c. of nitrous oxide, 2·5 c.c. of nitrogen, and 1·0 c.c. of nitric oxide; on the next day 2·3 c.c. more of the first gas were evolved. (ii) 0·1142 G. gave with 10 c.c. of water 8·1, 2·7, and 1·1 c.c. of these gases respectively. The solution did not give any test for nitrate or nitrite, but showed the presence of undecomposed hyponitrite by giving a yellow precipitate with silver nitrate.

Action of Acids.—This is shown in the following table. With the dilute acids the resulting solution gave the same reactions as with water, but with concentrated sulphuric acid, it contained nitrate and nitrite (the latter too small for estimation) and gave 1·6 c.c. of nitric oxide from the first solution.

Acid.	$Na_2N_2O_2$, g.	N_2O, c.c.	N_2, c.c.	NO, c.c.
H_2SO_4(app. 3*N*), 20 c.c.	0·1557	15·5	4·8	7·4
	0·1040	11·2	3·2	4·0
HCl (app. 3*N*), 20 c.c.	0·1060	11·5	3·5	4·2
	0·1270	14·0	3·8	3·5
H_2SO_4 (*d* 1·84), 20 c.c.	0·1032	14·3	5·6	1·3
	0·1042	14·5	6·2	1·7

Action of Acidified Potassium Permanganate.—The solution used contained 0·5 g. of permanganate in 20 c.c. of 2*N*-sulphuric acid. The results of a second experiment are in parentheses. 0·1000 (0·1249) G. gave 12·3 (16·4) c.c. of nitrous oxide and 2·2 (2·5) c.c. of nitrogen. The solution was concentrated, and decolorised with oxalic acid, the excess of the latter being removed by slowly adding permanganate solution till a slight pink colour remained. An aliquot portion was taken for estimating nitric acid. The whole gave 14·0 (20·7) c.c. of nitric oxide.

Action of Potassium Permanganate followed by Sulphuric Acid.—The acid (20 c.c. of 2*N*) was added after the gases evolved during the addition of the permanganate (0·5 g. in 20 c.c. of water) had been collected (about 30 mins.): 0·1054 g. gave before addition of acid 2·1 c.c. of nitrous oxide and 2·1 c.c. of nitrogen; and after addition of acid 5·1 and 1·2 c.c. respectively.

The solution gave 23·3 c.c. of nitric oxide.

In examining the products of reduction, the presence of ammonia was tested with Nessler reagent, hydrazine by reduction of Fehling's solution and benzalazin test, and hydroxylamine by the benzoyl chloride–ferric chloride test.

Summary.

It has been shown that sodium hyponitrite occurs in the form of two hydrates—the penta- and the octa-hydrate. The action of heat and various reagents on the solid salt in a vacuum has been studied. The anhydrous salt, when heated, decomposes into sodium oxide, sodium nitrite, and nitrogen. It is partly decomposed by

TABLE I.

Percentages of the various products calculated in terms of nitrogen. (Theoretical total, 26·4%.)

Reaction :	N_2O.	N_2.	NO.	HNO_2.	HNO_3.	Total.
Heat	—	17·3	—	8·6	—	25·9
,, ...	—	—	—	9·0	—	—
Water	9·5	3·0	0·6	—	—	13·1
,, ...	8·9	3·0	0·6	—	—	12·5
H_2SO_4, dil.	12·5	3·9	3·0	—	—	19·4
,, ...	13·5	3·8	2·4	—	—	19·7
HCl, dil.	13·6	4·1	2·5	—	—	20·2
,, ...	13·8	3·7	1·7	—	—	19·2
H_2SO_4, conc.	17·3	6·8	0·79	—	0·8	25·69
,, ...	17·4	7·4	1·0	—	—	25·8
$NaHSO_4$	5·5	11·6	1·3	—	—	18·4
,, ...	9·4	12·7	1·1	—	1·9	25·1
$KMnO_4$, acidified	15·4	2·8	—	—	8·8	27·0
,, ,, ...	16·4	2·5	—	—	10·4	29·3
$KMnO_4$ then acid	8·5	3·9	—	—	13·8	26·2

TABLE II.

Source of solution.	Conc. of HNO, g.-mol. per litre.	Amount of 0·1*N*-$KMnO_4$ required by 10 c.c. of the sol. if its conc. was 0·1*N*.		Ratio, (II)/(I).
		Acid at same time (I).	Acid after 15 mins. (II).	
Solid $Na_2N_2O_2$ dissolved in water	0·050	16·7	32·2	1·93
	0·050	14·2	27·4	1·93
Moist $Ag_2N_2O_2$ shaken with 0·1*N*-NaCl and diluted ...	0·025	—	9·0	—
BaN_2O_2 shaken with 0·1*N*-Na_2SO_4 and diluted	0·025	2·1	6·6	3·1
Moist $Ag_2N_2O_2$ shaken with 0·0935*N*-HCl and diluted ...	0·0467	7·0	20·5	2·93
	0·0701	15·7	31·1	1·98
Moist $Ag_2N_2O_2$ shaken with satd. NaCl sol. and diluted	0·1335	14·6	29·3	2·07
	0·0482	11·1	23·8	2·16

water, dilute sulphuric acid, and dilute hydrochloric acid, forming nitrous oxide, nitric oxide, and nitrogen; and completely by concentrated sulphuric acid, forming nitrous and nitric acids besides the above products. By the action of potassium permanganate, a portion of the salt is oxidised to nitric acid and the other portion decomposes into nitrous oxide and sodium hydroxide, the proportions of the two depending on the experimental conditions, thus explaining the variable results obtained by different workers under slightly different conditions. The salt could not be reduced by stannous chloride, titanous chloride, sodium hydrosulphite, etc.

One of the authors (C. C. S.) takes this oportunity of expressing his gratitude to the University of Bombay for a scholarship, and to the Trustees of the N.M. Wadia Charities for a loan, which enabled

him to carry out this work, and both authors thank the Chemical Society for a grant which has partly defrayed the expenses incurred in the research.

EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

[*Received, July* 16*th*, 1931.]