

Estimation of Sodium Hyponitrite in the Presence of Sodium Nitrite, Sodium Nitrate, and Sodium Carbonate

Action of Nitrogen Tetroxide or Dioxide on Hyponitrites

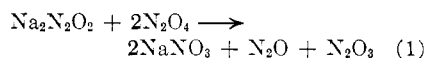
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► Experiments conducted in this laboratory indicate that when sodium hyponitrite reacts with nitrogen tetroxide at a low temperature the only solid product of the oxidation is sodium nitrate. Because liquid nitrogen tetroxide dissolved in low concentration in an organic solvent, such as carbon tetrachloride or chloroform, does not react with sodium nitrite, sodium nitrate, or sodium carbonate, it is thus possible to determine sodium hyponitrite in their presence. Details of the low temperature procedure are given.

SODIUM hyponitrite is oxidized ultimately to sodium nitrate by the action of nitrogen tetroxide through several intermediate reactions (1). Nitrogen tetroxide reacts with sodium carbonate dried at 600° C. on prolonged contact. The ultimate product of reaction is nitrate and the percentage conversion only 10.2% in 19 hours (2).

Sodium hyponitrite, though isosteric with sodium carbonate, was found to react vigorously even with chlorine and bromine. When a solution of chlorine or bromine in dry carbon tetrachloride was added to dry sodium hyponitrite, vigorous reaction took place with evolution of heat and gas. The reaction was carried out at 0° C. The residue, after being dried with dry ether and dissolved in water, gave a distinct test for chlorate in admixture with chloride or bromate in admixture with bromide, but both hypochlorite and hypobromite were absent. Dry sodium carbonate under similar conditions was stable, even on prolonged contact. If sodium hyponitrite reacts in the same way as sodium carbonate with nitrogen tetroxide the reaction should proceed completely as follows:

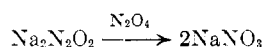


No nitrogen should be formed and the amount of nitrous oxide formed should be the same as the amount of nitrogen trioxide formed. An experiment carried out in vacuum (9) at 0° C. revealed the presence of nitrogen, nitrous oxide, nitrogen trioxide, and nitrogen tetroxide

in the gas mixture and only sodium nitrate in the solid residue. Thus, it is clear that the reaction is not as simple as shown by Equation 1.

Nitrogen tetroxide or dioxide does not react with sodium nitrite below 140° C. (3, 4). These experiments were also performed by the author in vacuum, and the same conclusion was reached from the analysis of the solid residue and gaseous products.

Liquid nitrogen tetroxide diluted with organic solvent at a much lower concentration than in experiments cited in the literature has been found to be inert toward sodium nitrite, sodium nitrate, or sodium carbonate. However, it reacts with sodium hyponitrite which may exist in different forms (7), giving undoubtedly only one solid product, sodium nitrate, at low temperature.



EXPERIMENTAL

Materials. Sodium hyponitrite was prepared according to Partington and Shah (11). Its purity was established by methods worked out by Oza and co-workers (6, 8, 10). Sodium nitrite, sodium nitrate, and sodium carbonate were extra pure analytical reagent chemicals. Anhydrous sodium carbonate was dried at 900° F. (482° C.) in an electric furnace for 2 hours, kept in a desiccator over phosphorus pentoxide, and analyzed. All organic solvents used in experiments were redistilled over phosphorus pentoxide. Nitrogen tetroxide (or dioxide) was prepared and sealed in tubes as described by Oza, Oza, and Thaker (9). These tubes (Figure 1, A), containing liquid nitrogen tetroxide, were made specially and sealed at the end, so that they could be broken easily in the tube containing organic solvent.

Procedure. About 20 ml. of carbon tetrachloride or chloroform was placed in a tube (Figure 1, B) and cooled to approximately 0° C. by an ice-water mixture. A tube, A, containing nitrogen tetroxide (approximately 0.5 gram) was inserted in tube B and placed as shown in Figure 1 in order to facilitate its breaking in the solvent. This assembly was kept in the bath for about

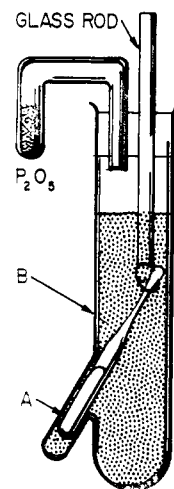


Figure 1. Assembly for determination of sodium hyponitrite by reaction with nitrogen tetroxide at low temperature

15 minutes. Tube A was then broken; nitrogen tetroxide was released slowly (the temperature being kept low) and allowed to dissolve in the organic solvent. The tube was shaken carefully in the bath to make the solution homogeneous.

Sodium hyponitrite was placed in a dry test tube and weighed. This tube was placed in the same bath to attain low temperature. Approximately 5 ml. of the previously prepared solution of nitrogen tetroxide in organic solvent was added to this hyponitrite and the solution and solid mixture were shaken carefully and allowed to remain in the bath for 10 to 15 minutes. Effervescence indicated the escape of some gas; this ceased within 2 or 3 minutes, but the test tube was allowed to remain at low temperature for 10 or 15 minutes.

The liquid was then carefully removed by decantation and the residue washed repeatedly with pure, cold solvent until the final washing gave no color, even at 50° C. The residue was then washed with dry ether, dried in hot air at about 70° C., and weighed. The residue was then dissolved in water

and analyzed qualitatively for hyponitrite ion, nitrite ion, and nitrate ion. Hyponitrite and nitrite were absent, and only nitrate was found. The material was then analyzed quantitatively for nitrate (5).

The experiments were conducted in a similar manner with pure sodium nitrite, sodium nitrate, and sodium carbonate, and in admixture with the hyponitrite. Carbonate and nitrite in aqueous solution were determined by standard methods.

RESULTS

Experiments 1, 2, and 3 (Table I) were carried out with sodium hyponitrite alone, and the nitrate formed was determined by a standard method (5). In experiments 4, 5, and 6 the nitrate formed from hyponitrite and that from the sodium nitrate taken were determined (column 4). Total sodium nitrate formed from hyponitrite was calculated (column 5), and the weight thus obtained, if subtracted from the weight of residue formed (column 3), was in close agreement with the amount of nitrate taken. In Experiments 7, 8, 9, and 10, only sodium hyponitrite reacted with nitrogen tetroxide or dioxide; sodium carbonate remained unaffected. Chemical determination of nitrate formed gave results in close agreement with those calculated for its formation from hyponitrite only. In Experiments 11, 12, 13, and 14, the nitrite content of the residue was estimated by a standard method. The nitrite was converted to nitrate by standard permanganate solution, and this along with the other formed from

Table I. Estimation of Sodium Hyponitrite^a

No.	Substance Taken	Gram	Weight of Residue, Gram	Nitrate (Total) Found by Chemical Estimation, Gram	Nitrate (Calcd. from Hyponitrite Taken), Gram
1	Na ₂ N ₂ O ₂	0.0525	0.0843	0.0841	0.0842
2		0.0735	0.1182	0.1190	0.1179
3		0.0852	0.1370	0.1368	0.1367
4	Na ₂ N ₂ O ₂ + NaNO ₃	0.025 + 0.020	0.0600	0.0602	0.03999
5		0.0352 + 0.030	0.0864	0.0865	0.05644
6		0.0485 + 0.040	0.1177	0.1178	0.07773
7	Na ₂ N ₂ O ₂ + Na ₂ CO ₃	0.0387 + 0.0412	0.1040	0.06210	0.06205
8		0.0465 + 0.0525	0.1268	0.07460	0.07457
9		0.0565 + 0.0425	0.1330	0.0907	0.09067
10		0.0156 + 0.0415	0.0665	0.0250	0.02501
11	Na ₂ N ₂ O ₂ + NaNO ₂	0.0210 + 0.025	0.0587	0.06448	0.03368
12		0.0280 + 0.045	0.0899	0.1005	0.04490
13		0.0325 + 0.045	0.0963	0.1070	0.05122
14		0.0415 + 0.050	0.1164	0.1285	0.06655

^a Solvent used to dissolve nitrogen tetroxide was chloroform

hyponitrite was then determined by the standard method. These results are given in column 4.

ACKNOWLEDGMENT

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Sensitive Photometric Technique for Determination of Organophosphorus Compounds

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► A brief examination was made of a technique for determining small amounts of organophosphorus materials, which involves initial reduction to a phosphine with a solution of lithium aluminum hydride. The phosphine vapors generated are allowed to react with either silver nitrate or gold chloride on paper. A qualitative estimation may be made visually, or a more precise determination can be made by photometric examination of the test papers. Of the several compounds tested, organocompounds could be detected in microgram

amounts, while inorganic materials produced but small response.

CETYL PHOSPHATE and benzenephosphonous acid can be reduced with lithium aluminum hydride in boiling diethyl ether solution. Karrer and Jucker (5) and Weil, Prijs, and Erlenmeyer (8) have recently published work on these experiments, in which they obtained phosphine and phenylphosphine, respectively, and swept it out of the reaction system with a stream of nitrogen. Similar reductions

have been effected by Horvat and Furst (4) and by Freedman and Doak (2). These observations suggested an analytical method based on reduction with lithium aluminum hydride and subsequent determination of the phosphines.

The Gutzeit test (3, 6, 9) for detection of arsine or phosphine, which is based upon the ability of these vapors to react with silver ions or with other metal ions to produce a colored product, appeared suitable for detection of the phosphines produced. The procedure finally developed involved reduction