70. *The Ultra-violet Absorption Spectra of Sodium Hyponitrite and Sodium α-Oxyhyponitrite : the Analysis of Mixtures with Sodium Nitrite and Nitrate.*

By C. C. Addison, G. A. Gamlen, and R. Thompson.

The ultra-violet absorption spectra of sodium hyponitrite ($Na_2N_2O_2$) and sodium α-oxyhyponitrite ($Na_2N_2O_3$) in alkaline solution have been redetermined, over the range 230—370 mμ. (The α and β nomenclature for these compounds is defined.) Sodium hyponitrite shows one peak at 248 mμ, log $\varepsilon_{max.}$ = 3·60; sodium α-oxyhyponitrite gives an absorption curve of similar shape, with one peak at the same wave-length and log $\varepsilon_{max.}$ = 3·92. Absorption-spectra measurements have been applied to the analysis of mixtures of these ions with nitrate and nitrite. Modes of decomposition in alkaline solution have been studied; solutions of sodium hyponitrite, on long storage at room temperature, decompose to give solutions containing only sodium hydroxide, whilst sodium α-oxyhyponitrite is quantitatively oxidised to nitrite by atmospheric oxygen according to the equation $Na_2N_2O_3 + O = 2NaNO_2$. The structures of the hyponitrite and α-oxyhyponitrite ions are discussed.

Reactions of liquid dinitrogen tetroxide with sodium hyponitrite ($Na_2N_2O_2$) and sodium α-oxyhyponitrite ($Na_2N_2O_3$) are discussed in the following paper. The products of these reactions when dissolved in water give solutions which may contain hydroxide, nitrite, and nitrate together with the more complex oxyacid ions, and chemical methods of analysis for a particular ion are subject to appreciable interference from the other ions present. For example, hyponitrite alone in aqueous solution may be determined by direct titration with strong mineral acids (Oza, Dipali, and Oza, *J. Indian Chem. Soc.*, 1950, **27**, 409). This method cannot be employed in the presence of hydroxide, and owing to the decomposition of the indicator, the end-point is not sharp in the presence of nitrite. Nitrite again interferes with the determination of hyponitrite by means of potassium permanganate (see Partington and Shah, *J.*, 1931, 2071). Since the hyponitrite ion is less stable in solution than the nitrite ion, the difficulties involved in the chemical determination of nitrite in the presence of hyponitrite are even greater. In view of the possible interconversion of certain of these ions in solution, and the instability of solutions of sodium hyponitrite and α-oxyhyponitrite, it was clear that a rapid physical method was preferable for both the identification of the ions and their determination. The most suitable method was considered to be that of ultra-violet spectrophotometric analysis, and some of the conclusions in the following paper are based upon this form of analysis of reaction products. However, before such analyses could be carried out it was necessary to establish accurate values for the absorption of the oxyacid ions, both singly and in mixtures. Results of this preliminary work are considered in the present paper.

Nomenclature.—By the accepted use of the prefix hypo-, the name hyponitrous acid should be applied to the unknown acid HNO. However, this name has now been widely accepted for the acid $H_2N_2O_2$ and has been approved in the I.U.P.A.C. Rules.

The name hyponitric acid has been applied to the compound $H_2N_2O_3$ by each of the authors to whom reference is made in this paper. There appears to be no justification for this and, since the chemistry of salts of this acid has been studied less extensively than those of hyponitrous acid, the use of the name hyponitric acid should be discontinued. The name oxyhyponitrous acid is preferred, at least until the structure of the acid is known with certainty.

The salt $Na_2N_2O_3$ occurs in two forms. The compound prepared from hydroxylamine and ethyl nitrate will be termed sodium α-oxyhyponitrite, and only this form of the compound is considered in the present paper. The compound obtained by oxidation of sodium hyponitrite with dinitrogen tetroxide (described in the following paper) will be termed sodium β-oxyhyponitrite.

Sodium Hyponitrite.—Baly and Desch (*J.*, 1908, **93**, 1747) first determined the ultra-violet absorption spectrum for aqueous solutions of sodium hyponitrite (without added

alkali) over a limited wave-length range which did not include the peak of the curve. Their measurements were not expressed in modern terminology, and the curve is difficult to interpret quantitatively. Kortum and Finckh (*Z. physikal. Chem.*, 1941, *B*, **48**, 42), using a photographic method, obtained the values shown as curve *C*, Fig. 1, for a solution in 0.1N-sodium hydroxide. The curve passes through a maximum and log $\varepsilon_{max.} = 3.54$. The present measurements (curve *A*, Fig. 1) confirm the general shape and position of Kortum and Finckh's curve; we find the curve to pass through a maximum at a similar wave-length (248 mμ) but curve *A* is displaced slightly towards higher ε values, with log $\varepsilon_{max.} = 3.60$. The measurements recorded on curve *A* were completed within one hour of preparation of the solution. Identical ε values were obtained for solutions in N- and in 0.1N-sodium hydroxide, so that 0.1N-sodium hydroxide is adequate to prevent detectable
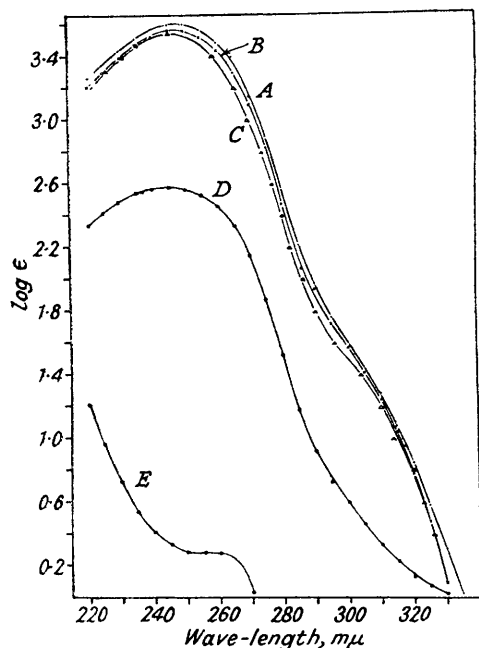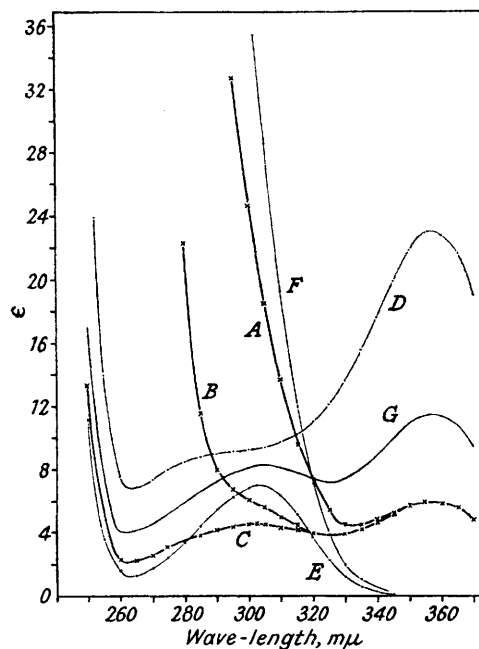

FIG. 1.

FIG. 2.

hydrolysis during the time required for determination of the spectrum. Abel and Proisl (*Monatsh.*, 1938, **72**, 1) studied the decomposition of sodium hyponitrite solutions by titration with potassium permanganate solution, and observed that the rates of decomposition, at 25° and above, varied considerably with the alkalinity of the solution. The same effect is illustrated in Fig. 1. A solution of sodium hyponitrite in N-sodium hydroxide was kept in the dark at about 20° for 9 days, and curve B was then obtained. Under these conditions only slight decomposition occurs; comparison of the $\varepsilon_{max.}$ values showed that about 90% of the hyponitrite still remained. A similar experiment, employing 0.1N-sodium hydroxide, gave curve *D*, and the $\varepsilon_{max.}$ value shows that only 9% of the hyponitrite remained. It is of interest that after 10 weeks in 0.1N-sodium hydroxide (curve *E*), the presence of a trace of hyponitrite is still detectable in the ultra-violet spectrum of the solution, although this is not detectable by chemical methods.

Analysis of Hyponitrite–Nitrite–Nitrate Mixtures.—Curve *A* (Fig. 2) is a portion of the absorption curve on a linear scale, obtained for the mixture, in 0.1N-sodium hydroxide, when the components are present in the ratio $2 : 1 : 1$. This mixture was selected since it is typical of the products of reaction between sodium hyponitrite and liquid dinitrogen tetroxide (following paper). Beer's law is obeyed by this system, since curve *A* is identical with that constructed from the separate absorption curves for the pure constituents. The curves for pure sodium nitrite and sodium nitrate (obtained from solutions of the

" AnalaR " oven-dried salts) and the relevant portion of the sodium hyponitrite curve (D, E, and F, respectively) are superimposed in Fig. 2.   The nitrite peak was obtained at 357 mμ, and $\varepsilon_{max.} = 23\cdot0$, compared with Kortum's value of $21\cdot9$ (*Z. physikal. Chem.*, 1939, *B*, **43**, 421).   The nitrate curve shows a peak at $302\cdot5$ mμ, $\varepsilon_{max.} = 7\cdot01$, compared with $7\cdot2$ (Kortum and Finckh, *loc. cit.*), and the value $7\cdot06$ deduced from the mean value of E (1%, 1 cm.) obtained in a collaborative test on aqueous potassium nitrate (Photoelectric Spectrometry Group, Bull. 1, 1949).

It is convenient, for analytical purposes, that the absorption of both nitrate and hyponitrite are negligible at the wave-length corresponding to the nitrite peak, and the ε value for the composite curve (A) at sufficiently high wave-lengths may be used directly for the estimation of nitrite.   Since the peak wave-length for nitrite (357 mμ) is only slightly above the wave-length at which nitrate and hyponitrite become inappreciable, it was considered advisable to employ a somewhat higher wave-length for purposes of estimation.   During this work ε values have been determined, and compared, at 365 mμ; this gives a high ε value ($21\cdot7$) for pure nitrite (curve D) without the possibility of interference from the other components.

The estimation of nitrate and hyponitrite may be carried out in two ways, as follows.

(a) *Simultaneous-equation method.*   The standard method involves the use of the equation

$$d_\lambda = \varepsilon_1 C_1 + \varepsilon_2 C_2 + \varepsilon_3 C_3$$

where d is the optical density ($\log_{10} I_0/I$), C_1, C_2, and C_3 are the molar concentrations of nitrite, nitrate, and hyponitrite respectively, and ε_1, ε_2, and ε_3 are the corresponding molar extinction coefficients.   Since C_1 can be determined directly, C_2 and C_3 can be obtained from simultaneous equations obtained by taking d values for two wave-lengths. The choice of suitable wave-lengths is influenced by the relatively small absorption of the nitrate, compared with the hyponitrite, ion; 305 and 320 mμ have been found in practice to be convenient wave-lengths, and the following ε values are considered here to be standard for the wave-lengths concerned.

λ, mμ	ε_1	ε_2	ε_3	λ, mμ	ε_1	ε_2	ε_3	λ, mμ	ε_1	ε_2	ε_3
305	9·43	6·95	28·6	320	11·1	3·67	7·10	365	21·7	—	—

In view of the method of calculation involved, and the magnitude of the above constants, the accuracy with which nitrate or hyponitrite can be determined depends to some extent on the relative quantities of the ions present as well as on their actual concentrations.   The table below shows the calculated percentage error resulting from an error of $0\cdot001$ in the measured value of ($d_{305} - d_{320}$), for three typical mixtures.

| Mol. ratio $N_2O_2^{2-} : NO_2^- : NO_3^-$	$d_{305} - d_{320}$	Error, %, in determination of : Na$_2$N$_2$O$_2$	NaNO$_3$
2 : 1 : 1	0·180	0·8	3·4
1 : 1 : 1	0·093	1·6	3·4
1 : 1 : 2	0·106	1·6	1·7

The above errors are calculated on the assumption that no error is involved in the original determination of nitrite; in fact, nitrite may be determined with an accuracy of about 1%, but this has no significant influence on the above figures.

(b) *Removal of hyponitrite.*   Solutions of sodium hyponitrite decompose on long storage, or more rapidly on boiling, according to the equation $Na_2N_2O_2 + H_2O = 2NaOH + N_2O$.   Since the only decomposition product remaining in the system is sodium hydroxide, which is already present in excess, the removal of hyponitrite provides an alternative, and more accurate, method of analysis.   After 9 days in the dark at about $20°$, the absorption curve for the $2 : 1 : 1$ mixture (originally curve A) changed to curve B (Fig. 2); curve C was obtained after twelve weeks.   Curve G is the absorption curve derived for an equimolecular mixture of nitrate and nitrite; the curve obtained on complete removal of hyponitrite (curve C) will have an ε scale which is half that of curve G (since in a $2 : 1 : 1$ mixture the original molar concentration used in the calculation of ε from d is twice that used for computing curve G) but, when allowance is made for this, curves C and G are identical.

For any mixture, *e.g.*, that corresponding to curve *A*, the nitrite content may be determined directly from d_{365}, as before. The value of *d* at 305 mμ is determined before and after the decomposition of the hyponitrite, and the concentration of hyponitrite is available directly from the change in *d*. The value of d_{305} given by curve *C* then represents the total absorption due to nitrate and nitrite. Knowing d_{365} for nitrite, we can calculate the value of d_{305} for nitrite by proportion from curve *D*, and *d* for nitrate can be obtained by difference.

Sodium α-oxyhyponitrite. Curve *A* (Fig. 3) represents the absorption of sodium α-oxyhyponitrite ($Na_2N_2O_3$) when dissolved in 0·1N-sodium hydroxide. The only measurements on such solutions reported in the literature are those of Kortum and Finckh (*loc. cit.*), whose curve is shown in Fig. 3 as curve *C*. There is a considerable discrepancy

FIG. 3.
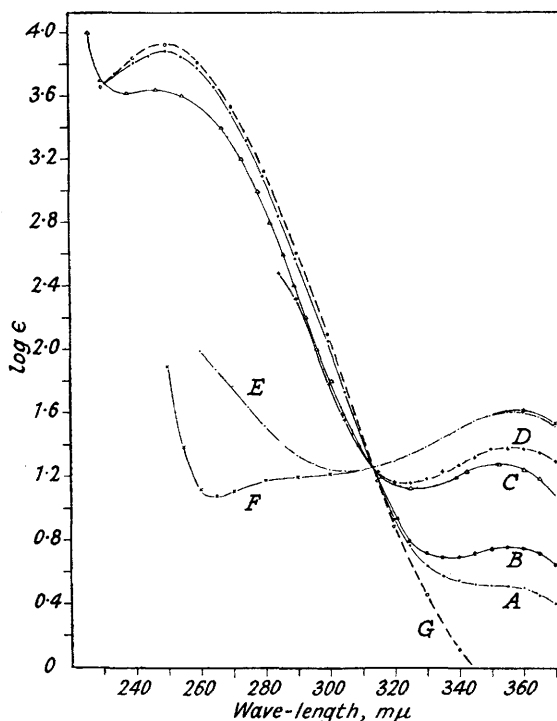
between the two curves, particularly in the pronounced peak through which Kortum and Finckh's values pass at 357 mμ. It was necessary in the present work to determine the true absorption curve for sodium α-oxyhyponitrite for two reasons : first, a knowledge of the true curve is essential for the qualitative and quantitative analysis of products of reaction with dinitrogen tetroxide; secondly, a peak in an absorption curve at 357 mμ is characteristic of the nitrite group, and its presence would have an important bearing on the structure of the α-oxyhyponitrite ion, which is still in doubt.

When the fresh solution (curve *A*) was kept in a stoppered vessel at room temperature and absorption curves were redetermined after 11 days and 12 weeks, curves *D* and *E*, respectively, were obtained. Aqueous solutions of sodium α-oxyhyponitrite are known to give nitrite on decomposition (Naik, Shah, and Patel, *J. Indian Chem. Soc.*, 1946, **23**, 284), and the increase in $\varepsilon_{max.}$ at 357 mμ with time was consistent with the progressive decomposition of the solution. It then appeared possible that the flat portion of curve *A* might not be a characteristic of the α-oxyhyponitrite ion but be due to a submerged maximum arising from the presence of nitrite in the original solution. However, chemical analysis (for both sodium and nitrogen content) had shown that the solid sodium α-oxy-

hyponitrite was pure; any nitrite present therefore must be formed during or after the preparation of the fresh solution. This could occur by the decomposition :

$$2Na_2N_2O_3 + H_2O = 2NaNO_2 + 2NaOH + N_2O \quad . \quad . \quad . \quad (1)$$
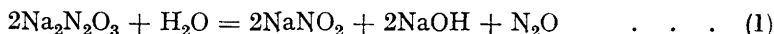
(Naik, Shah, and Patel, *loc. cit.*) or by the more rapid atmospheric oxidation noted by Angeli and Angelico (*Gazzetta*, 1900, **30**, 593) :

$$Na_2N_2O_3 + O = 2NaNO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The presence of any appreciable quantity of nitrite in the fresh solution favours reaction (2); this reaction would also be expected to lead to lack of reproducibility of the absorption curve, since ready atmospheric oxidation is difficult to control. A second determination, carried out under experimental conditions as nearly identical as possible with those employed for curve A, gave curve B; comparison shows that the curves are not reproducible. It appeared from the above that neither of the curves A or C was the true α-oxyhyponitrite absorption curve, but that each curve was obtained from solutions containing the nitrite ion also. This has been confirmed quantitatively as follows.

If it is assumed that the decomposition of sodium α-oxyhyponitrite in alkaline solution takes place according to equation (2), and if the molecular weight of sodium nitrite is used in the calculation of ε, the calculated curve for a completely decomposed solution is shown by F (Fig. 3). The experimental curve E is almost identical with F at the higher wave-lengths, and comparison of the two values at 365 mμ indicates a 99% decomposition of the α-oxyhyponitrite according to equation (2) after 12 weeks. The discrepancy between curves E and F at lower wave-lengths arises from the high extinction values of the remaining α-oxyhyponitrite in this region. The quantity of α-oxyhyponitrite was calculated from curve E at 260 mμ, at which ε for nitrite is near the minimum. Allowance being made for absorption due to nitrite, the apparent ε for α-oxyhyponitrite is 84; the value of ε interpolated from the true absorption curve (see below) is 6500, from which it follows that 1·3% of α-oxyhyponitrite remains undecomposed. This is in good agreement with the 99% decomposition to nitrite calculated at 365 mμ.

The present measurements indicate, more clearly than has hitherto been possible, the influence of added alkali on the mode of decomposition of sodium α-oxyhyponitrite. Naik, Shah, and Patel (*loc. cit.*) observed the stabilising influence of added alkalis, without reference to any change in mode of decomposition. In neutral or dilute acid solution, decomposition occurs in accordance with equation (1), and one molecule of sodium α-oxyhyponitrite yields one molecule of sodium nitrite (Angeli, *Gazzetta*, 1896, **26**, 17). However, in alkaline solution two molecules of sodium nitrite are produced [equation (2)]. The same influence of added alkali may be observed in oxidations by means of potassium permanganate. In neutral solution, oxidation takes place according to the equation $Na_2N_2O_3 + 3O = 2NaNO_3$ (*idem, ibid.*, 1904, **34**, 50), but in the presence of alkali (Naik, Shah, and Patel, *loc. cit.*) the quantity of permanganate required is decreased [probably to the amount required by equation (2)], and is only increased again on acidification of the solution.

The atmospheric oxidation of alkaline solutions of sodium α-oxyhyponitrite is an extremely rapid process. In preparing the solutions for curves A and B, about 0·1 g. of the pure salt was placed in a 100-ml. graduated flask, which was then filled with 0·1N-sodium hydroxide (prepared from recently distilled water) and stoppered, leaving not more than 10 ml. of air space. As soon as the solid had dissolved the solution was shaken, and poured immediately (through air) into the silica cell of the spectrophotometer. Nevertheless, the ε values for curves A and B at 365 mμ indicate that the sodium α-oxyhyponitrite in these solutions was oxidised to nitrite to the extent of 7·5 and 14·0%, respectively. The decomposition represented by curves D (60% after 11 days) and E (99% after 12 weeks) is not therefore a measure of the true rate of oxidation, but is determined by the extent to which air is admitted to contact with the solution during the withdrawal of samples.

It is of interest that each of the curves A, B, D, E, and F passes through an isosbestic point at 314 mμ, where $\varepsilon = 18\cdot4$. This is in accord with the presence, in each solution, of only two absorbing groups (α-oxyhyponitrite and nitrite). Curve C also passes through this point, so that the solutions used by Kortum and Finckh (*loc. cit.*) also contained these

two absorbing groups only.   The ε value for curve C at 365 mµ indicates 41·3% decomposition to nitrite.   A similar result is obtained by comparison of ε (curve C) at 260 mµ ($\varepsilon = 3550$) with the true value.   Kortum and Finckh (*loc. cit.*) make no reference to precautions taken in the preparation of solutions, and in view of the rapidity of atmospheric oxidation, it is quite possible that their solutions could contain this relatively high concentration of nitrite.

In order to obtain a true absorption curve for sodium α-oxyhyponitrite experimentally, it would be necessary to carry out the measurements in the complete absence of atmospheric or dissolved oxygen.   The experimental difficulties involved are considerable, and such measurements were not carried out since the true curve may be readily obtained by calculation.   For example, curve A was at this stage known to be a composite curve, obtained from a solution of known composition; ε values obtained after subtraction of the absorption due to the 7·5% decomposition to nitrite were then multiplied by 100/92·5 to give the curve corresponding to pure sodium α-oxyhyponitrite.   This is shown in Fig. 3 by the broken curve G, which has one peak at 250 mµ, and log $\varepsilon_{max.} = 3.92$.

Structural Implications.—The value of $\lambda_{max.}$ for sodium hyponitrite (248 mµ) is close to the value given by some other compounds having N:N bonds; *e.g.*, 252 mµ for ethyl diazoacetate (Hantzsch and Lifschitz, *Ber.*, 1912, **45**, 3011; Wolf, *Z. physikal. Chem.*, 1932, *B*, **17**, 46), and 245 mµ for azomethane (Morton, " Practical Aspects of Absorption Spectrophotometry," Royal Inst. of Chem. Lecture, 1938, p. 35).   Although other bonds in the molecule may modify the absorption, the curve suggests that the dominant absorption is due to the N:N bond.   This is in accord with the generally accepted structure HO·N:N·OH for the acid (see, *e.g.*, Partington, " General and Inorganic Chemistry," Macmillan, 1947, p. 586).

The true absorption curve for sodium α-oxyhyponitrite shows only one peak, and $\lambda_{max.}$ is identical with that for sodium hyponitrite.   This fact, together with the general similarity of the shape of the two curves, suggests that the N:N bond is also the dominant feature in the structure of the α-oxyhyponitrite ion, and that the structure is closely related to that of the hyponitrite ion.   There is at present no generally accepted structure for α-oxyhyponitrous acid.   Postulated structures are shown by (1)—(4).   Structures
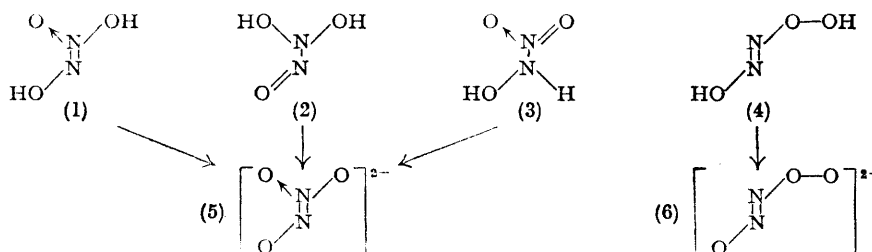
(1) and (2) are considered by Kortum and Finckh (*loc. cit.*).   Partington (*op. cit.*, p. 587) considers (3) (the nitrohydroxylamine formula) and (4) as possible alternatives.   Whatever the structure of the pure acid may be, structures (1), (2), and (3) each give rise to the bivalent ion (5), or to its resonance forms.   Of the three possible resonance forms, only one gives an ion having the N:N bond, and the absorption curve suggests that the probable structure for the ion is as shown in (5).   The ion (6), obtained from acid structure (4), also contains this bond; but the acidic character of a hydrogen atom attached to a peroxy-group [as in structure (4)] is generally much less that that of the hydrogen atom in :N·O·H, so that on structure (4) it is to be expected that the monobasic ion $(HN_2O_3)^-$ would be a common feature in the products of reaction of the acid with alkalis.   However, there appears to be little evidence of this, and reaction of the acid or its sodium salt with bivalent cations gives precipitates of the type BaN_2O_3.   On such evidence, the hydrogen atoms are regarded as combined in the acid molecule in a similar manner, which is the case in formulæ (1) and (2) only.   Atmospheric oxidation to two nitrite ions in alkaline solution is also more readily reconciled with ion (5) than with (6).   [The possibility that structure (6) represents the β-oxyhyponitrite ion is discussed in the following paper.]

EXPERIMENTAL

Absorption Curves.—The absorption spectra of solutions were measured by using a Unicam S.P. 500 spectrophotometer and 1-cm. silica cells. A hydrogen-discharge lamp, giving a continuous spectrum, was used as a light source. In each measurement the blank cell was filled with the same solution of " AnalaR " sodium hydroxide as was employed in the preparation of the test solutions.

Preparation of Sodium Hyponitrite.—Sodium hyponitrite was prepared by reduction of sodium nitrite in a modification of the method due to Divers (*J.*, 1899, **75**, 87) and Partington and Shah (*loc. cit.*). 25 G. of " AnalaR " sodium nitrite were dissolved in 40 ml. of water contained in a stout 1-l. flask. Sodium amalgam (prepared by dissolving 25 g. of clean sodium in 140 ml. of mercury) was added slowly with constant agitation of the flask and cooling in ice-water. The mixture was then transferred, in a stream of nitrogen gas to prevent absorption of carbon dioxide by the alkaline liquid, to a thick-walled separating funnel and shaken until gas evolution ceased. During the latter stage of the reduction process the aqueous phase changed from a voluminous foam to a suspension of fine crystals in a syrupy liquid which could readily be separated from the mercury layer. The liquor was run off into a beaker containing 800 ml. of ethyl alcohol, the tip of the funnel being held beneath the surface of the alcohol to avoid exposure to the atmosphere. Any liquor and crystals adhering to the walls of the funnel were quickly washed through with two 5-ml. portions of water. After being stirred vigorously for several minutes, the lower layer was transformed into a paste, which on trituration produced white sand-like crystals of hydrated sodium hyponitrite. The crystals were filtered off and dissolved in the minimum of water (about 8 ml.), and the solution was filtered to remove droplets of mercury, the product then being obtained from the filtrate by precipitation with alcohol as described above. The crystals were finally filtered into a sintered-glass crucible and washed with alcohol and ether, and the ether removed in a vacuum-desiccator. Anhydrous sodium hyponitrite (about 1 g.) was obtained by further drying for several days (over P_2O_5) and finally in an air-oven, the temperature of which was raised from 60° to 120° during several hours. The temperature of the oven was then kept at 120° (for about 2 hours) until the hyponitrite attained constant weight.

The above method comprises a refinement in the preparative techniques of earlier workers and combines the advantages of both rapidity and purity of product. Of the likely impurities due to this general method of preparation, sodium nitrite (from unchanged starting material) and sodium hydroxide are eliminated at the precipitation stage because of their solubility in alcohol. Sodium carbonate, arising from the absorption of atmospheric carbon dioxide by the alkaline liquor, is, however, not so readily eliminated and once formed it is precipitated together with the hyponitrite, and cannot be removed by recrystallisation. It is therefore essential to guard carefully against its formation at all stages of the preparation; the technique described above has been found to provide a product free from detectable carbonate. The treatment of the entire alkaline liquor with alcohol was found to be preferable to the method of Partington and Shah (*loc. cit.*) in which the crystals first formed are filtered off and dissolved in water, and the solution is concentrated in a vacuum-desiccator until the octahydrate is formed, before trituration with alcohol. By the present method, not only is the possible time of contact with the atmosphere reduced to the minimum, but the yield of sodium hyponitrite is increased and the preparation greatly expedited. It was found necessary to give the product a preliminary drying (P_2O_5) at room temperature for several days before finally drying it at 120°, for if attempts were made to dry the material too rapidly the hyponitrite partly melted in the remaining water of crystallisation and decomposed to sodium hydroxide. Although sodium carbonate impurity may arise from reaction of carbon dioxide with solid sodium hyponitrite as well as with alkaline solutions, the quantity of carbon dioxide in the atmosphere of the oven was insufficient to produce detectable carbonate over the period of several hours required. Provision of a soda-lime guard tube to the vessel containing the hyponitrite during the drying process is undesirable in that escape of water vapour is restricted and the salt again decomposes in the water of crystallisation.

Analysis of Sodium Hyponitrite.—(a) *Qualitative.* In view of the difficulties incurred in the quantitative analysis, it has been found that the most convenient assessment of batch purity of sodium hyponitrite is by means of qualitative tests for impurities likely to arise from materials used in the preparation. Nitrite may readily be detected in the presence of hyponitrite by liberation of iodine from potassium iodide solutions acidified with dilute sulphuric acid. In accordance with Oza's observations (*J. Indian Chem. Soc.*, 1945, **22**, 225), we have found that the hyponitrite ion does not liberate iodine immediately. Since hydrolysis of sodium

hyponitrite produces a highly alkaline solution, simple pH tests do not reveal the presence of sodium hydroxide impurity. The addition of silver nitrate solution, however, provides a means of detecting excess of alkalinity. Whereas pure sodium hyponitrite in aqueous solution reacts to provide the canary-yellow flocculent precipitate characteristic of silver hyponitrite, traces of sodium hydroxide impurity produce a marked difference in the colour and flocculation of the precipitate. Addition of small amounts of silver nitrate solution to a solution of sodium hyponitrite containing added alkali produced an instantaneous brown precipitate which rapidly changed on shaking to the yellow of silver hyponitrite, the colour reverting to brown only when excess of the reagent was added.

(b) *Quantitative.* The sodium content was determined as sulphate (Found : Na, 43·35. Calc. for $Na_2N_2O_2$: Na, 43·39%). Although the presence of either sodium nitrite (Na, 33·33%) or sodium hydroxide (Na, 57·49%) would be readily detected by their effect upon the sodium content, traces of sodium carbonate would not be detected in this way, since the sodium content and molecular weights of sodium hyponitrite and sodium carbonate are identical. Sodium content is not therefore sufficient in itself for the determination of purity, and a knowledge of the nitrogen or $N_2O_2{}^{2-}$ content is also desirable. Partington and Shah (*loc. cit.*) found the standard methods of nitrogen determination to be unsuitable and determined the hyponitrite content gravimetrically as $Ag_2N_2O_2$; this method has been employed in the present work. Somewhat low values are obtained owing to the slight solubility of silver hyponitrite in water (Mellor, " Treatise, etc.," Vol. VIII, p. 413). 0·1849 G. of the dried sodium salt was dissolved in 8 ml. of water, and silver nitrate solution added in slight excess. The flocculent yellow precipitate was filtered into a sintered-glass crucible (porosity 4), washed with two 5-ml. portions of cold water, and dried in a vacuum-desiccator to constant weight (0·4700 g.). This is equivalent to a $N_2O_2{}^{2-}$ content in the sodium salt of 55·4% (Calc. for $Na_2N_2O_2$: N_2O_2, 56·61%). Silver hyponitrite is not sufficiently stable to permit drying in an oven, and its solubility in organic liquids precludes alcohol–ether washing. The absence of silver nitrite in the precipitate was confirmed by conversion of 0·3443 g. of silver hyponitrite into 0·3570 g. of silver chloride (Found : Ag, 78·03. Calc. for $Ag_2N_2O_2$: Ag, 78·25%). The purity of sodium hyponitrite may also be determined satisfactorily by direct titration with standard hydrochloric acid (Oza, Dipali, and Oza, *loc. cit.*). By this method, with methyl-orange screened with xylene-cyanol F.F., and at room temperature, the prepared sodium hyponitrite was found to be 100% pure. This titration method does not reveal the presence of sodium carbonate as impurity, but it was not possible by any qualitative test to detect the presence of carbonate in the hyponitrite.

Preparation of Sodium α-Oxyhyponitrite.—Sodium α-oxyhyponitrite was prepared by Angeli's method (*loc. cit.*), involving the interaction of hydroxylamine, ethyl nitrate, and sodium ethoxide in ethanol solution. A concentrated solution of sodium ethoxide (9 g.) in ethanol was added to a saturated solution in ethanol of hydroxylamine hydrochloride (3 g.). The sodium chloride precipitated was filtered off, and 4 g. of ethyl nitrate were added to the filtrate at room temperature. A finely-divided suspension of sodium α-oxyhyponitrite was formed, the yield increasing as the liquid was cooled. After several hours, the crystals were filtered into a sintered-glass crucible (porosity 4) and washed with alcohol. They were then recrystallised twice by dissolving them in 2 ml. of water and adding a large excess of ethyl alcohol, as described above for the hyponitrite. The crystals (about 1 g.) were finally dried by washing them with ether, removing the ether in a vacuum-desiccator, and drying to constant wt. at 120°.

Sodium α-oxyhyponitrite so prepared was found to be free from impurities. Neither the mother-liquor nor the product absorbs or reacts with carbon dioxide, so that sodium carbonate does not interfere with this preparation. Any unchanged starting materials are eliminated on account of their solubility in ethanol. In view of the ready solubility of sodium α-oxy-hyponitrite in water, it was necessary to dry the alcohol and ethyl nitrate thoroughly. However, contrary to Angeli's observations (*loc. cit.*), the salt is not of such a hygroscopic nature as to preclude purification by recrystallisation, provided that a small volume of water and a large excess of dry alcohol are employed.

Analysis of Sodium α-Oxyhyponitrite.—The sodium content of the dry salt was determined as sodium sulphate (Found : Na, 37·85. Calc. for $Na_2N_2O_3$: Na, 37·70%). The radical $N_2O_3{}^{2-}$ cannot be determined as the silver salt on account of the almost instantaneous reduction to silver, and the rapid fading of the characteristic red colour produced with uranyl nitrate does not permit colorimetric estimation. The nitrogen content, however, can readily be determined by Dumas's method (Found : N, 22·8, 23·0. Calc. for $Na_2N_2O_3$: N, 22·95%).

THE UNIVERSITY, NOTTINGHAM.   [*Received, August 9th,* 1951.]