# 71. *The Oxidation of Sodium Hyponitrite and Sodium α-Oxyhyponitrite with Dinitrogen Tetroxide.*

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The paper describes the preparation, and some properties, of a series of compounds $Na_2N_2O_x$, where $x$ has values between 2 and 6.

Sodium hyponitrite ($Na_2N_2O_2$) is oxidised rapidly by liquid dinitrogen tetroxide to sodium β-oxyhyponitrite (β-$Na_2N_2O_3$), which differs in chemical properties from the α-compound prepared from hydroxylamine and ethyl nitrate.

Sodium α-oxyhyponitrite also undergoes rapid oxidation to the compound $Na_2N_2O_4$, which is readily distinguished from sodium nitrite. This compound undergoes slow secondary oxidation by liquid dinitrogen tetroxide to a compound having empirical formula $NaNO_3$. This may be the dimer $Na_2N_2O_6$, and a silver salt believed to have the formula $Ag_2N_2O_6$ has been prepared.

Sodium β-oxyhyponitrite undergoes slow oxidation with liquid dinitrogen tetroxide to the compound $Na_2N_2O_5$. The same product is formed rapidly by the action of nitrogen dioxide gas at 100° on sodium hyponitrite. The compound $Na_2N_2O_5$ is slowly oxidised by nitrogen dioxide gas at 100° to the $NaNO_3$ (or $Na_2N_2O_6$) stage.

The hydrolysis products of these compounds have been identified and estimated from measurements of the ultra-violet absorption spectra of their aqueous solutions. An attempt is made to correlate possible structures for the compounds with their mode of aqueous decomposition.

During many experiments involving liquid dinitrogen tetroxide (*J.*, 1949, S 211 *et seq.*), it was observed that both nitrate and nitrite ions are quite stable in liquid dinitrogen tetroxide. In view of the strongly oxidising character displayed by the tetroxide towards many organic compounds (Riebsomer, *Chem. Reviews*, 1945, **36**, 157) the stability of the nitrite ion is somewhat surprising. In order to determine whether stability towards dinitrogen tetroxide is a common property of the nitrogen oxyacid ions, the liquid tetroxide was added to dry samples of sodium α-oxyhyponitrite ($Na_2N_2O_3$) and sodium hyponitrite ($Na_2N_2O_2$), compounds in which the nitrogen atoms are in a lower state of oxidation. Preliminary experiments indicated that each compound was immediately oxidised to a product containing one additional atom of oxygen.

The product ($Na_2N_2O_4$) obtained by oxidation of sodium α-oxyhyponitrite had chemical properties quite different from those of sodium nitrite, and appeared therefore to be the sodium salt of a new nitrogen oxyacid of formula $H_2N_2O_4$. The product ($Na_2N_2O_3$) obtained by oxidation of sodium hyponitrite had chemical properties different from the sodium α-oxyhyponitrite prepared (as described in the preceding paper) from hydroxylamine and ethyl nitrate, from which it appeared that the ion $N_2O_3^{2-}$ might exist in two distinct forms. The products of each of these two rapid oxidations underwent slow secondary oxidation by dinitrogen tetroxide, to an extent which suggested the formation of other new compounds containing a higher proportion of oxygen.

With the exception of the sodium salt of nitroxylic acid, $H_2NO_2$, described by Maxted (*J.*, 1917, **111**, 1016), there has been no appreciable extension to the field of nitrogen oxyacids since before 1900. The possible existence of a new family of oxyacids of nitrogen gave added significance to the preliminary experiments outlined above. The oxidation of sodium hyponitrite and α-oxyhyponitrite has therefore been studied in greater detail. The existence of sodium salts of two new acids has been confirmed, and the existence of others is possible.

*Oxidation of Sodium Hyponitrite.*—In aqueous solution sodium hyponitrite is known to undergo oxidation to nitrate (*e.g.*, by potassium permanganate in acid solution) or to nitrite (by alkaline permanganate), but there is no evidence of any intermediate stages of oxidation under these conditions; *e.g.*, there is no reference in the literature to the oxidation of hyponitrite to oxyhyponitrite in aqueous solution. However, in liquid dinitrogen tetroxide the oxidation can be arrested at an intermediate stage corresponding to the formation of a compound $Na_2N_2O_3$. The reaction was found to proceed as follows: 5 ml. of liquid tetroxide were added rapidly, in a closed system, to about 0·1 g. of carefully dried sodium hyponitrite in the form of a finely crystalline white powder (prepared as described in the preceding paper). The reaction was strongly exothermic, sufficient heat being generated to cause rapid boiling of the tetroxide. Nitric oxide was evolved. When reaction ceased after 2—3 minutes, the liquid was decanted, and the tetroxide gas removed in a stream of dry nitrogen; the product remained as a free-flowing, finely divided, white powder, its weight corresponding to the addition of one atom of oxygen. When this experiment was repeated with the reaction tube immersed in a freezing mixture, reaction was still rapid; under these conditions the nitric oxide produced by reduction of the tetroxide was partly retained in the liquid, which developed the clear green-blue colour characteristic of dinitrogen trioxide–tetroxide mixtures. If only a few drops (instead of several ml.) of tetroxide were added to the sodium hyponitrite, the heat of reaction could not then be dissipated by vapourisation of the tetroxide, and sufficient heat was produced partly to fuse the solid. This initial reaction clearly involves the transfer of oxygen from the tetroxide to the sodium hyponitrite. The number of nitrogen atoms does not change during reaction, as shown by the fact that the ultimate product of oxidation (*i.e.*, on allowing the $Na_2N_2O_3$ to react further) is sodium nitrate in a quantity equivalent to the sodium and the nitrogen content of the sodium hyponitrite originally taken for reaction. The same reaction takes place between sodium hyponitrite and gaseous dinitrogen tetroxide, but measurements recorded below show that reaction with the gas is more rapid than with the liquid. In the case of the gaseous reaction, more than one atom of oxygen per molecule of hyponitrite is rapidly added, and it is only with the liquid tetroxide that the reaction can be arrested after the addition of a single atom of oxygen. For this reason, the addition of liquid tetroxide to the hyponitrite was carried out rapidly under conditions in which the amount of preliminary reaction between solid and gaseous dinitrogen tetroxide was negligible.

The oxidation process will be considered under two headings: (*a*) primary oxidation, involving the initial rapid oxidation by the liquid tetroxide, and the formation of the compound $Na_2N_2O_3$, and (*b*) secondary oxidation, involving the slow oxidation of the compound $Na_2N_2O_3$.

### PRIMARY OXIDATION: SODIUM β-OXYHYPONITRITE.

The liquid tetroxide was removed immediately following the completion of the initial reaction, and the increase in weight of the solid determined. Typical results are:

| Experiment | (1) | (2) | (3) | (4) | (5) | (6) | (7) |
|---|---|---|---|---|---|---|---|
| (A) $Na_2N_2O_2$ (g.) | 0·1038 | 0·1126 | 0·0851 | 0·0692 | 0·1584 | 0·1567 | 0·1627 |
| (B) Product (g.) | 0·1192 | 0·1291 | 0·0988 | 0·0794 | 0·1854 | 0·1812 | 0·1878 |
| Ratio (B)/(A) | 1·149 | 1·147 | 1·161 | 1·148 | 1·170 | 1·156 | 1·154 |

The theoretical ratio $Na_2N_2O_3/Na_2N_2O_2$ is 1·151, and the mean of the above results (1·155) is in close agreement with this ratio.

The possible nature of products which could give rise to this 1·151 ratio may be summarised by the following equations; each is consistent with the addition of one atom of oxygen per molecule of hyponitrite:

$$Na_2N_2O_2 + O = Na_2N_2O_3 \tag{1}$$

$$2Na_2N_2O_2 + 2O = Na_2N_2O_2 + 2NaNO_2 \tag{2}$$

$$3Na_2N_2O_2 + 3O = 2Na_2N_2O_2 + NaNO_2 + NaNO_3 \tag{3}$$

$$Na_2N_2O_2 + O = NaNO_2 + NaNO \tag{4}$$

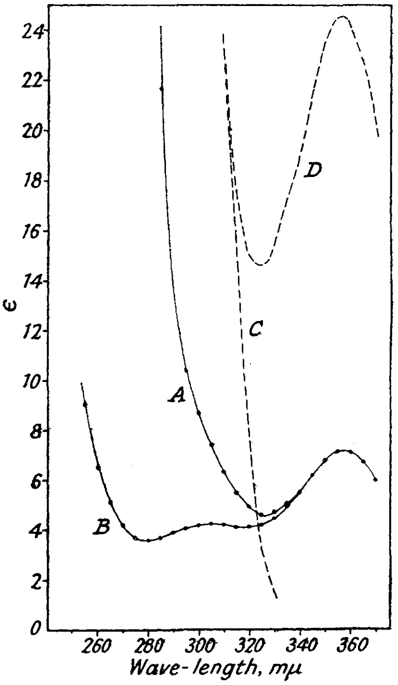
In order to distinguish between these various possibilities, the chemical reactions of the product (in particular its reactions with water) were studied. (As in the preceding paper, the compound $Na_2N_2O_3$ obtained by oxidation of sodium hyponitrite is termed sodium β-oxyhyponitrite, to distinguish it from the α-compound prepared from hydroxylamine and ethyl nitrate.)

*Properties of Sodium β-Oxyhyponitrite.*—The addition of water to this compound resulted in an immediate and considerable effervescence. The solid particles were readily wetted, and the mode of evolution of gas was similar to that of carbon dioxide in a carbonate–dilute acid reaction (cf. the compound $Na_2N_2O_4$). The evolved gas was colourless and appreciably soluble in water, indicating nitrous oxide (this is confirmed quantitatively below). Neutral solutions of sodium α-oxyhyponitrite undergo slow decomposition but there is no effervescence when the solid is added to water, and the decomposition proceeds over a period of weeks. Moreover, alkaline solutions of the α-oxyhyponitrite decompose to nitrite only ($Na_2N_2O_3 + O = 2NaNO_2$).

The vigorous effervescence with water enables equations (2) and (3) to be dismissed, since the aqueous decomposition of sodium hyponitrite is also slow. Again, sodium β-oxyhyponitrite is quite insoluble in absolute alcohol, whereas sodium nitrite is appreciably soluble. The insolubility in alcohol also dismisses equation (4), although the reaction with water is in some respects similar to that of sodium nitrosyl : $NaNO + H_2O = NaOH + N_2O$ (Joannis, *Ann. Chim. Phys.*, 1894, **118**, 713; Zintl and Harder, *Ber.*, 1933, **67**, 760). If equation (4) were correct, the hydrolysed compound should contain 56% of sodium nitrite, and this quantity should not decrease as a result of secondary oxidation; results discussed below show that this is not the case.

Sodium β-oxyhyponitrite is therefore to be regarded as a single compound. It can be further distinguished from the α-compound by the action of silver nitrate and of uranyl nitrate on the aqueous solutions. When silver nitrate solution is added to an aqueous solution of the α-compound, at room temperature, the transient yellow precipitate first formed changes almost immediately to a black precipitate of silver. (This change is accompanied by effervescence, and probably results from the auto-reduction of silver oxide by the α-oxyhyponitrite ion, with evolution of oxygen.) With the β-compound, a stable yellow precipitate of silver hyponitrite is obtained provided that the silver nitrate is not in excess. Addition of excess of silver nitrate results in a brown precipitate of silver oxide, produced by the sodium hydroxide which is one product of hydrolysis of sodium β-oxyhyponitrite. Uranyl nitrate solution produces, with solutions of the α-compound, a deep red colour which fades in dilute solution to pale yellow after several minutes. With the β-compound no colour is produced, but on storage a yellow precipitate of sodium diuranate is formed, owing again to the alkalinity of the β-oxyhyponitrite solutions.

FIG. 1.



*Products of Aqueous Decomposition.*—Curve *A* (Fig. 1) shows the ultra-violet absorption spectrum of the freshly prepared solution of sodium β-oxyhyponitrite in $0\cdot1$N-sodium hydroxide solution, and curve *B* is the spectrum obtained when the solution had been kept for 18 days. The solution was prepared under exactly the same experimental conditions as were employed for the preparation of solutions of the α-compound, the corresponding curves for which are superimposed for comparison in Fig. 1 : curve *C* was obtained with the freshly prepared solution and curve *D* with an 11-day old solution.

The curves (*A* and *C*) for the fresh solutions are clearly quite different and the aqueous solution of the β-oxyhyponitrite originally contains a greater quantity of nitrite than is present in the solution of the α-compound. Decomposition of the α-oxyhyponitrite solution on standing leads to a considerable increase in nitrite content, whereas the nitrite content of the solution of the β-compound remains unchanged. Curve *A* is consistent with the presence of sodium hyponitrite, nitrite, and nitrate in the solution, the change to curve *B* on standing arising from the decomposition of the hyponitrite to nitrous oxide and sodium hydroxide. Formation of the latter by this means does not influence the absorption curves, since the hydroxide ion does not absorb over this wave-length range (and the solutions are prepared in sodium hydroxide solution). Curve *B* reveals the presence of nitrate in the solution by the appearance of a peak at 302·5 mμ; no nitrate is obtained as a result of aqueous decomposition of the α-compound.

Analysis of the solution of sodium β-oxyhyponitrite by the methods outlined in the preceding paper gave the following results :

| | $Na_2N_2O_2$ | $NaNO_2$ | $NaNO_3$ |
|---|---|---|---|
| G.-mols. produced from 1 g.-mol. of β-$Na_2N_2O_3$ | 0·13 | 0·55 | 0·26 |
| N content (g.-atoms) of solution | 0·26 | 0·55 | 0·26 |

From these results it is clear that the nitrogen content of the solution (1·07 g.-atoms) is only about half of the nitrogen originally added as β-oxyhyponitrite; the remainder may be regarded as lost from the system in the form of nitrous oxide. In the decomposition of sodium salts of nitrogen oxyacids, the evolution of nitrous oxide must involve the formation of an equivalent quantity of sodium hydroxide in solution. This has been confirmed by direct titration of the solution. Oza, Dipali, and Oza (*J. Indian Chem. Soc.*, 1950, **27**, 409) have shown that sodium hyponitrite may be determined by titration with solutions of strong mineral acids; the quantity of acid required to titrate a solution of sodium β-oxyhyponitrite will therefore be the sum of that required for the hyponitrite and the sodium hydroxide produced on reaction with water. When 0·1 g. of sodium β-oxyhyponitrite was dissolved in water, 9·8 ml. of 0·1N-hydrochloric acid solution were required for titration. (The end-point is somewhat confused by the presence of nitrite in the solution, but is sufficiently accurate for present purposes.) By reference to the sodium hyponitrite content as determined from the absorption curves, it may be calculated that 2·1 ml. of this titre was due to the sodium hyponitrite. It is thus seen that the remaining 7·7 ml. of hydrochloric acid are equivalent to the production, in solution, of 0·94 g.-mol. of sodium hydroxide per g.-mol. of sodium β-oxyhyponitrite. From the results in the above table, it may also be calculated from the loss in nitrogen content that 0·47 g.-mol. of nitrous oxide is produced by reaction of 1 g.-mol. of sodium β-oxyhyponitrite with water.

The quantities recorded above are suitably related if we assume that hydrolysis proceeds primarily in accordance with the equation

$$\overset{(2)}{2Na_2N_2O_3} + H_2O = \overset{(1{\cdot}10)}{2NaNO_2} + \overset{(1{\cdot}88)}{2NaOH} + \overset{(0{\cdot}94)}{N_2O} \quad . \quad . \quad . \quad . \quad (5)$$

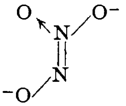
but that in addition during the rearrangement of the fragments of the β-oxyhyponitrite ion, some $NaNO_2$ fragments disproportionate to give nitrate and hyponitrite :

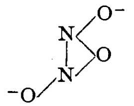
$$4NaNO_2 = \overset{(0{\cdot}26)}{Na_2N_2O_2} + \overset{(0{\cdot}52)}{2NaNO_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

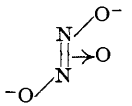
The numbers given in parentheses above the equations represent the number of g.-mols. of each compound produced from 2 g.-mols. of sodium β-oxyhyponitrite; the sodium hydroxide and nitrous oxide values are close to those required by equation (5), and the relative quantities of nitrate and hyponitrite bear the appropriate 2 : 1 ratio required by such a disproportionation. From equation (6), 1·04 g.-mols. of $NaNO_2$ fragments disproportionate, and the total nitrite obtained (2·14 g.-mols.) by adding this value to the nitrite observed to be present in the solution is close to the requirements of equation (5).

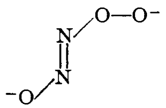
It is of interest that reaction (5) has been postulated by Naik, Shah, and Patel (*J. Indian Chem. Soc.*, 1946, **23**, 284) as a method of decomposition of neutral solutions of sodium α-oxyhyponitrite. Even so, the decomposition is slow, and in sharp contrast to the vigorous reaction of the β-compound in contact with water. Again, in the decomposition of the β-compound, sodium nitrate and hyponitrite are produced in a quantity equivalent to half the sodium nitrite required by equation (5); Angeli and Angelico (*Atti R. Accad. Lincei*, 1901, **10**, 249) postulate six ways in which the α-oxyhyponitrite could decompose under varying conditions, but none of the reactions involves the formation of nitrate as a reaction product.

*Structure, and Mechanism of Aqueous Decomposition.*—The major obstacle in the study of the mechanism of decomposition in water is the lack of conclusive evidence for the structure of the two forms of sodium oxyhyponitrite. In the preceding paper, structure (I) was considered to be the most suitable for the α-oxyhyponitrite ion. Structure (II) involves a three-membered ring which is unlikely to be stable, and by fission of either of the N–O ring bonds the structure reverts to (I). Structure (III), involving π-bonding of the additional oxygen atom, differs from (I) in electronic rather than atomic distribution, and both structures (II) and (III) are therefore so similar to (I) that their chemical properties would be unlikely to differ considerably from those of the α-oxyhyponitrite ion. It is possible, however, that an ion having structure (IV) might differ significantly in chemical behaviour from (I), and the aqueous decomposition of the sodium salts will be considered in the light of this structure.


(I)

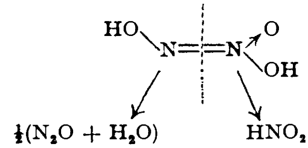

(II)


(III)

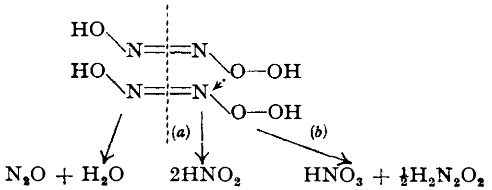

(IV)

In the acid corresponding to structure (IV), the :NO•OH group will be more weakly acidic than the :N•OH group. The acid corresponding to structure (I) contains only :N•OH groups, and in consequence the sodium salt of ion (IV) would be more readily hydrolysed than the salt of ion (I), to give rise to a less stable acid. This is in agreement with experimental observations.

The production of nitrite in solution indicates that fission of both the α- and the β-acid must occur at the •N:N• bond, and such hydrolytic fission may be represented diagrammatically as :



α-Oxyhyponitrous acid



β-Oxyhyponitrous acid

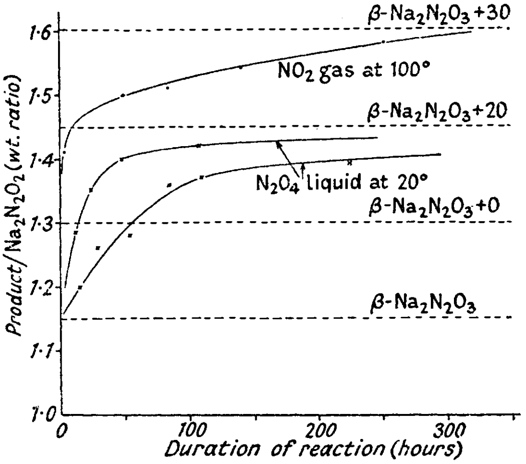
Of the two fragments resulting from fission of the α-acid, one fragment requires only an electronic rearrangement to give nitrous acid. This agrees with the observation that neither nitric nor hyponitrous acid is produced by this decomposition. The unstable NOH fragment, when produced under these conditions, may be regarded as giving rise directly to nitrous oxide. (The NOH group is probably also an intermediate in the aqueous decomposition of sodium nitrosyl.) The total decomposition is then represented by equation (5). The same fragment, in the same proportion, results from •N:N• fission of β-oxyhyponitrous acid. However, the second (NO•OH) fragment is required to undergo atomic rearrangement to give nitrous acid. During this rearrangement, it is possible that an atom of oxygen may be transferred from one fragment to another; if it is assumed that the intramolecular rearrangement (*a*) and the intermolecular rearrangement (*b*) proceed to equal extents, then nitrous, nitric, and hyponitrous acids are produced in the relative quantities required by equations (5) and (6).

It is to be inferred here that the suggested atomic rearrangements, or oxygen-atom transfers, take place more readily than those involving the release of oxygen as hydrogen peroxide, since the presence of hydrogen peroxide has not been detected in the solutions by qualitative tests, nor in spite of its appreciable absorption has it been detected during ultra-violet spectrophotometric analyses. It is difficult to formulate the compounds discussed here without resort to •O•O• linkages, yet it is a characteristic property of most per-acids and their salts that they release hydrogen peroxide in solution. However, in the case of perdisulphuric or perdiphosphoric acid, normal oxyacid ions are linked by peroxy-bridges; there is no direct bonding between atoms of the typical elements, and no atomic rearrangement occurs on release of hydrogen peroxide. With these higher oxyacids of nitrogen the fission of the •N:N• bond is considered to dominate their behaviour on hydrolysis, and the peroxy-properties are manifest in the transfer of oxygen atoms to other fission fragments rather than in the release of hydrogen peroxide.

### Secondary oxidation: the compounds $Na_2N_2O_5$ and $Na_2N_2O_6$.

Although sodium hyponitrite gains one atom of oxygen from dinitrogen tetroxide almost instantaneously, oxidation beyond this stage is slow. Fig. 2 shows the rate at which the sodium salt increases in weight. The two curves for secondary oxidation with liquid dinitrogen tetroxide were obtained with two samples of sodium hyponitrite separately prepared, but each sample was pure and dry. The curves illustrate the wide variation observed in the rates of secondary oxidation. This is attributed to such factors as the variation in particle size (*i.e.*, surface area) between different samples, and not to any difference in the nature of the reaction taking place, since the increase in weight has been found to be the only factor determining the chemical behaviour of the product. All such curves display the same features; beginning at the 1·15 ratio, the curves approach a ratio of 1·45, but no reaction involving the liquid tetroxide has been found to give rise to a weight ratio exceeding 1·45. The liquid reaction therefore produces ultimately a compound of empirical formula $Na_2N_2O_5$. The curves pass, without deflection, through the 1·3 ratio, and these experiments therefore suggest that the compound $Na_2N_2O_4$ is not significant in this reaction. The gaseous reaction (Fig. 2) provides additional support for the existence of the compound $Na_2N_2O_5$; when sodium hyponitrite is treated with the gaseous $NO_2$–$N_2O_4$ mixture, the solid rapidly gains three atoms of oxygen.

FIG. 2.



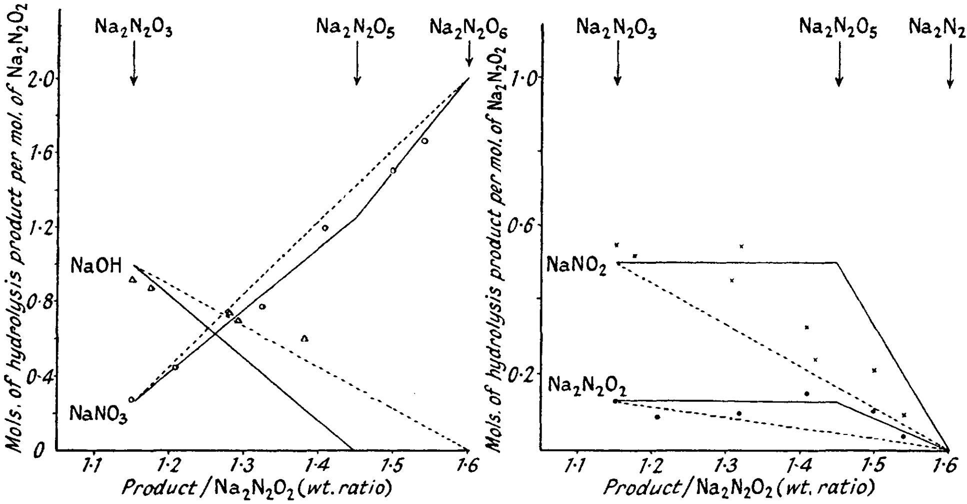
The curve shows a sharp break at a ratio of 1·45 (equivalent to $Na_2N_2O_5$) and the final atom of oxygen is taken up very slowly.

In order to obtain further evidence on the nature of the products formed during secondary oxidation, reactions of the products with water have been studied. A parallel series of oxidations was carried out, varying times being allowed for reaction. In each case the solid was freed from dinitrogen tetroxide, and the increase in weight determined. A portion of the solid was dissolved in water. and titrated with 0·1N-hydrochloric acid in order to determine total alkalinity. The remainder of the product was then dissolved in 0·1N-sodium hydroxide, and the ultra-violet absorption spectra of the solution were measured immediately, and again after several weeks. From these curves the nitrate, nitrite, and hyponitrite contents of the solution were calculated. The numbers of g.-mols. of each constituent thereby obtained from each g.-mol. of sodium hyponitrite originally taken are plotted in Fig. 3 against the increase in weight.

The results indicate that the same mechanism of oxidation probably applies to both the liquid and the gaseous reaction. The quantities of hydrolysis products recorded for Product/$Na_2N_2O_2$ ratios less than 1·45 were determined on solutions of oxidation products prepared by using liquid dinitrogen tetroxide. At ratios greater than 1·45, the product was prepared by using the gaseous reaction at 100°, and the experimental points for ratios above 1·45 are seen to represent a continuation of the trends shown by the values for lower ratios. This supports the belief that the mechanism of oxidation involves the $NO_2$, rather than the $N_2O_4$ molecule. The more rapid oxidation by gaseous than by liquid dinitrogen tetroxide is also explained thereby, since the degrees of dissociation to nitrogen dioxide are 90 and <1·0%, respectively.

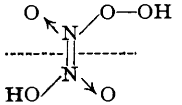
*The Compound* $Na_2N_2O_5$.—Three possible processes may take place during secondary oxidation : (1) The material produced by liquid tetroxide oxidation, empirical formula $Na_2N_2O_5$, could be an equimolecular mixture of sodium nitrate and sodium nitrite. (2) The liquid reaction may produce a single compound $Na_2N_2O_5$ which could then undergo further oxidation to $Na_2N_2O_6$ (or $NaNO_3$). (3) Secondary oxidation may involve only the direct oxidation of sodium β-oxyhyponitrite to nitrate. The first possibility may be dismissed, since analysis of the aqueous solution of the 1·45 ratio material (Fig. 3) shows nitrate and nitrite to be present in the molar ratio 1·3 : 0·25, rather than 1 : 1. Again, the product is insoluble in absolute alcohol, and separate experiments have shown that sodium nitrite is not oxidised by nitrogen dioxide at 100°.

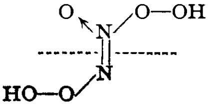
FIG. 3.



The results in Fig. 3 afford some help in distinguishing between possibilities (2) and (3). Alternative structures for the acid $H_2N_2O_5$ are (V) and (VI). Structure (5) should

(V)





(VI)

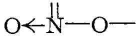
give rise to nitrate and nitrite in solution in equimolecular quantities; this is not the case. With structure (VI) (if we assume that disproportionation of the :NO·OH group proceeds to give 50% of $HNO_2$, as with β-oxyhyponitrous acid), the decomposition of the compound $Na_2N_2O_5$ in water should take place according to the equation

$$8Na_2N_2O_5 = 10NaNO_3 + 4NaNO_2 + Na_2N_2O_2 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is to be compared with the equation

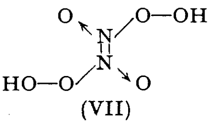
$$8\ \beta\text{-}Na_2N_2O_3 + 4H_2O = 2NaNO_3 + 4NaNO_2 + Na_2N_2O_2 + 8NaOH + 4N_2O \quad . \quad (8)$$

which represents the summation of equations (5) and (6).

The full lines in Fig. 3 represent the change in hydroxide and nitrate content [Fig. 3(*a*)] and in nitrite and hyponitrite content [Fig. 3(*b*)] of the aqueous solution obtained from a product considered to consist of a mixture of the compounds β-$Na_2N_2O_3$ and $Na_2N_2O_5$ in the ratio range 1·15—1·45, and a mixture of the compounds $Na_2N_2O_5$ and $NaNO_3$ in the ratio range 1·45—1·60. The broken lines represent the corresponding changes to be expected if sodium β-oxyhyponitrite undergoes secondary oxidation directly to sodium nitrate. The experimental values in Fig. 3 are somewhat scattered; this is probably an inevitable feature in experiments of this type, since it is not possible to reproduce exactly the conditions of the vigorous reaction between the solid product and water, and the speed of solution will depend to some extent on the particle size of the powder. Nevertheless, attention should be directed to the following points concerning the position of the experimental values with respect to the full and the broken lines. (*a*) All nitrate values [Fig. 3(*a*)] lie below the broken line, and are close to the full line. This agrees with the formation of a  $\mathrm{O{\leftarrow}\overset{\|}{N}{-}O{-}OH}$ fragment on hydrolysis. (*b*) The hydroxide content falls with increasing ratio. As the titration decreases, the end-point error due to the presence of nitrite becomes considerable, so the hydroxide values recorded should not be regarded as serving to differentiate between the full and the broken lines; for this reason, hydroxide contents are not recorded beyond the 1·4 ratio. Although the quantity of nitrous oxide evolved on dissolution of the product was not measured directly, it was observed that effervescence markedly decreased as the weight ratio of the product increased. (*c*) With one exception, the hyponitrite values [Fig. 3(*b*)] fall above the broken line, and favour the full line. (*d*) All nitrite values lie above the broken line, but do not reach the full line. The latter was calculated on the assumption that during decomposition, half of the :NO·OH fragments give rise to $HNO_2$ molecules. This quantitative analogy with the decomposition of sodium β-oxyhyponitrite may not be justified. During the decomposition of the acid $H_2N_2O_5$ a smaller proportion of the :NO·OH fragments may yield $HNO_2$ molecules; this could bring the full line closer to the experimental values.

The evidence obtained from the study of aqueous solutions of the products of secondary oxidation, together with the more direct evidence in Fig. 2, may therefore be regarded as supporting (though inconclusively) the existence of a distinct compound of formula $Na_2N_2O_5$ which is the salt of an acid having structure (VI).

*The Compound of Type* $M_2N_2O_6$.—In view of the probable existence of the compound $Na_2N_2O_5$ (as well as the compound $Na_2N_2O_4$ discussed below) it is reasonable to consider the possibility that the ultimate oxidation of sodium hyponitrite with nitrogen dioxide is the compound $Na_2N_2O_6$, rather than sodium nitrate. This compound, whose acid we would formulate as (VII) by analogy with compounds in a lower state of oxidation, would be expected to give two molecules of $NaNO_3$ as a result of ·N:N· fission in water, since no other groups are present to which atoms of oxygen may be transferred. Acids $H_2N_2O_5$ and $H_2N_2O_6$ are suggested by Oddo (*Gazzetta*, 1915, **45**, 414) as being present in mixtures of liquid dinitrogen tetroxide and water, but are considered only as loose addition compounds of the component nitrous and nitric acids. Reference is made by Yost and Russell ("Systematic Inorganic Chemistry," Oxford Univ. Press, 1946, p. 65) to the ion $N_2O_6^{2-}$.



(VII)

Although no evidence for the existence of the dimeric form $M_2N_2O_6$ is available from a study of the sodium salt, it is possible to prepare a silver salt believed to have this formula.

Silver hyponitrite was prepared, as a yellow precipitate, by the action of silver nitrate on a 5% solution of sodium hyponitrite. The precipitate was dried to constant wt. over phosphoric oxide in a vacuum-desiccator, which was kept in the dark, since silver hyponitrite is photosensitive. Owing to its instability to heat, the compound could not be dried in an oven, and at least ten days' drying at room temperature was required; on addition of liquid dinitrogen tetroxide to dry silver hyponitrite, nitric oxide was evolved, the colour of the liquid changing to blue-green; the yellow colour of the solid became paler, without any other noticeable change in physical condition. The reaction was complete within a few minutes, and the increase in weight of the solid was then determined :

| Expt. | $Ag_2N_2O_2$ (g.) | Product (g.) | Product/$Ag_2N_2O_2$ (by wt.)* |
|---|---|---|---|
| 1 | 0·1211 | 0·1453 | 1·200 |
| 2 | 0·2209 | 0·2696 | 1·221 |

* Theoretical ratios : $Ag_2N_2O_3/Ag_2N_2O_2 = 1{\cdot}058$; $Ag_2N_2O_6/Ag_2N_2O_2 = 1{\cdot}228$.

The silver content of the reaction product in Expt. (1) was found to be 64·6% ($Ag_2N_2O_6$ requires Ag, 63·5%). This is consistent with the fact that oxidation is not quite complete (Calc. for $Ag_2N_2O_2$ : Ag, 78·4%). Oxidation of the silver salt therefore proceeds almost immediately to the $Ag_2N_2O_6$ stage, whereas corresponding oxidation of the sodium salt required 300 hours at 100°. The yellow colour, and solubility in organic solvents, of silver hyponitrite suggest that the parent compound may be predominantly covalent in character. If this is so, oxidation of the covalent molecule rather than of the hyponitrite ion may well follow a different course, and may account for the striking difference in the rates of oxidation of the silver and the sodium salt. The reaction product was insoluble in cold water, and appeared to undergo no decomposition. In boiling water decomposition occurred to give soluble silver salts, leaving a black residue. This residue readily dissolved with effervescence in dilute nitric acid solution and was presumably silver and silver oxide. From this behaviour it is clear that the reaction product is not silver nitrate, but its properties are those expected of a compound $Ag_2N_2O_6$ having some covalent character. Unlike the behaviour of the corresponding sodium salt, treatment with water does not immediately give rise to the liberation and decomposition of the acid $H_2N_2O_6$. However, when the compound $Ag_2N_2O_6$ is dissolved directly in dilute sulphuric acid, the free acid is presumably produced; hydrolytic fission can then take place as with the sodium salts and analysis of the resulting solution showed the presence of no oxyacid ion of nitrogen other than nitrate.

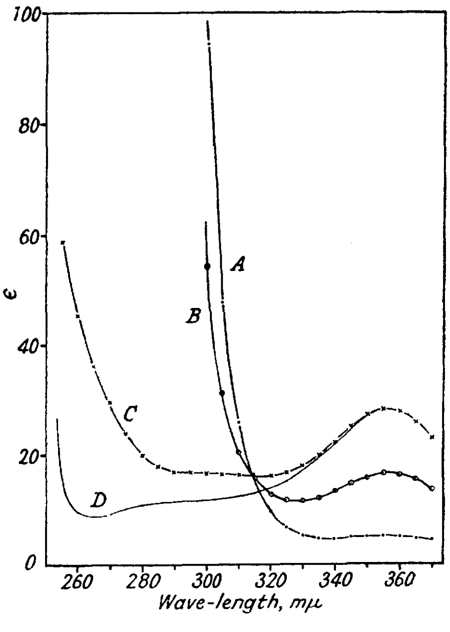
## PRIMARY OXIDATION OF SODIUM α-OXYHYPONITRITE.

Some examples of the difference in chemical properties between sodium α- and β-oxyhyponitrites have already been given. In addition, their behaviour towards liquid dinitrogen tetroxide is quite different. Although the β-compound undergoes the slow secondary oxidation considered above, yet the α-compound reacts immediately. When several ml. of the tetroxide were added to about 0·1 g. of sodium α-oxyhyponitrite, the colour of the liquid changed to blue-green; the reaction, which was strongly exothermic, was complete within a few minutes. On removal of the dinitrogen trioxide–tetroxide mixture, the solid was found to have increased in weight in a ratio of **1·13** ($Na_2N_2O_4/Na_2N_2O_3 = 1{\cdot}131$). This ratio was readily reproducible, and the reaction may be represented by the equation : α-$Na_2N_2O_3 + N_2O_4 = Na_2N_2O_4 + N_2O_3$.

It is of interest that, although the oxidation of sodium β-oxyhyponitrite passes through the $Na_2N_2O_4$ stage without hesitation, yet the reaction is readily arrested at this stage by oxidation of the α-compound.

Its chemical properties confirm that the compound is not sodium nitrite. The solid is not readily wetted by water. When water is added to a sample of the compound in a test-tube, the powder remains at the bottom; as the particles are wetted there is an evolution of gas. The small bubbles coalesce to one large one, which remains attached to the dissolving solid until it becomes large enough to break away. The effect is in marked contrast to the effervescence which occurs with sodium β-oxyhyponitrite. The gas was found to be nitrous oxide, and about 1 ml. of gas was liberated from 0·1 g. of solid during solution. The aqueous solution gave an instantaneous black precipitate with silver nitrate solution; treatment with uranyl nitrate solution produced the same deep red colour as was obtained with sodium α-hyponitrite.

FIG. 4.

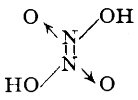


*Products of Hydrolysis of the Compound* $Na_2N_2O_4$.—The salt was dissolved in 0·1N-sodium hydroxide. Curve *A* (Fig. 4) shows the ultra-violet absorption spectrum obtained immediately after preparation of the solution, and curves *B* and *C* were obtained after the solution had been kept for 11 days and 3 months, respectively. The curves indicate the presence, in the original solution, of sodium α-oxyhyponitrite, sodium nitrate, and sodium nitrite. Applied quantitatively, it may be calculated from curve *A* that in the original solution 10·6% of the compound $Na_2N_2O_4$ has been converted into sodium nitrite. It has been shown in the preceding paper that the formation of quantities of sodium nitrite of this order is almost unavoidable in the preparation of solutions of sodium α-oxyhyponitrite. Since the fresh solution of the compound $Na_2N_2O_4$ contains much α-oxyhyponitrite, the major portion of the sodium nitrite present in the original solution is regarded as arising from this cause. When the solution is kept, the α-oxyhyponitrite decomposes to nitrite only; the difference between the curve obtained on complete decomposition (curve *C*) and the pure sodium nitrite curve *D* is due to the nitrate contained in the solution.

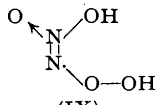
The decomposition of the compound $Na_2N_2O_4$ in aqueous solution has been found to proceed as follows :

$$3Na_2N_2O_4 = \overset{(1\cdot95)}{2NaNO_3} + \overset{(1\cdot8)}{2Na_2N_2O_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

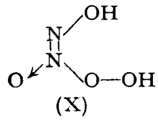
The figures in parentheses over equation (9) are the molar quantities of the compounds observed to be present in the original solution. The alternative structures for the acid



(VIII)



(IX)

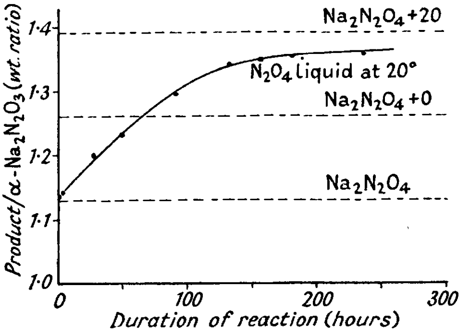


(X)

$H_2N_2O_4$ are (VIII), (IX), and (X). The fragments formed by fission of acids (VIII) and (IX) would give two and at least one molecules of nitrous acid, respectively, whereas nitrite is not a major constituent of the solutions; structures (X) is therefore considered to be more appropriate.

The fission of the $N{:}N$ bond in one out of three $H_2N_2O_4$ molecules, with transfer of oxygen atoms, is in accord with equation (9). It is to be expected, as observed, that the product of this decomposition would produce α-, rather than β-, oxyhyponitrous acid. However, if we assume that the small quantity (0·2 mol.) by which the fresh solution is found to be deficient in α-oxyhyponitrite content represents the formation of β-oxyhyponitrite, it is possible to account for the evolution of nitrous oxide on aqueous decomposition of the compound $Na_2N_2O_4$. Since sodium β-oxyhyponitrite decomposes immediately in water according to equation (5), its presence would not be detected in the fresh solution, and calculation shows that the quantity of nitrous oxide evolved is approximately equivalent to 0·2 mol. of sodium β-oxyhyponitrite (equation 9).

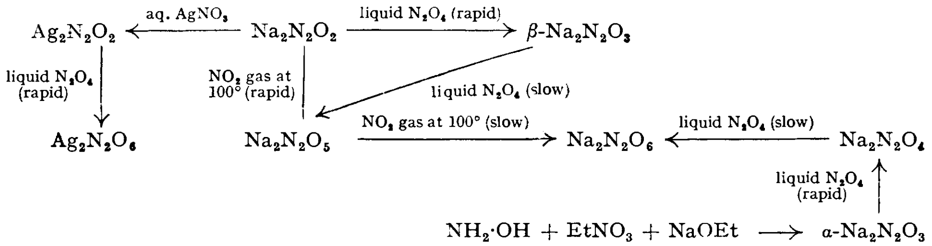
FIG. 5.



### SECONDARY OXIDATION OF SODIUM α-OXYHYPONITRITE.

Oxidation by liquid dinitrogen tetroxide beyond the $Na_2N_2O_4$ stage is very slow; the fact that it does occur is further clear evidence that the compound $Na_2N_2O_4$ differs from sodium nitrite. Fig. 5 shows a typical curve relating weight ratio to time. The curve shows no break at the $Na_2N_2O_5$ stage (cf. the secondary oxidation of sodium β-oxyhyponitrite) but smoothly approaches the state of complete oxidation represented by $NaNO_3$ (or $Na_2N_2O_6$). Analyses of the reaction product at various stages in the ratio range 1·13—1·393 have been carried out by study of the ultra-violet absorption spectra of the aqueous solutions. They indicate that the nitrate content of the solutions increases, and the α-oxyhyponitrite content diminishes, almost linearly with increasing ratio, so that oxidation of the compound $Na_2N_2O_4$ involves the slow addition of two further atoms of oxygen.

*Conclusions.*—The reactions and products described in this paper are summarised in the following scheme.



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