Hyponitrites

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Hyponitrous acid, HON=NOH, and its salts have been known for some time. Almost a hundred years have gone by since Divers[1] first identified hyponitrites among the reduction products of sodium amalgam on nitrite, but comparatively little attention has been paid to these compounds. Recently, however, aspects of hyponitrous acid chemistry have been re-investigated and have demonstrated the potential interest of this area of chemistry.

Preparation and General Properties

Hyponitrous Acid.—Aqueous solutions are usually obtained by acidifying sodium hyponitrite solutions. Dilute solutions, with excess of mineral acid, are fairly stable, but decomposition to nitrous oxide does occur under certain conditions of pH. Nitrous oxide is not normally regarded as the anhydride, however, as a pressure of 10^{27} atmospheres of nitrous oxide would be necessary to produce 0·001M-hyponitrous acid in water.[2] Oxygen-18 labelling[3] also suggests that the reaction of nitrous oxide with water is extremely slow.

Solid hyponitrous acid is prepared from the silver salt by treatment with hydrogen chloride in ether, removal of the precipitated silver chloride, and evaporation of the ethereal solution. The solid forms white, deliquescent plates, which are explosively unstable. It is soluble in a number of solvents, including the alcohols, ethers, benzene, and chloroform. Hussain[4] has determined partition coefficients for hyponitrous acid between an aqueous solution and various solvents; thus values of $K = [H_2N_2O_2]_S/[H_2N_2O_2]_{aq}$ for benzene, diethyl ether, and di-n-butyl ether are $3{\cdot}6 \times 10^{-4}$, 1·14, and $7{\cdot}7 \times 10^{-2}$ respectively.

Hyponitrites.—The sodium salt is usually isolated, but purification procedures often involve conversion into the sparingly soluble silver salt. Preparative methods can be classified under the following headings.

(i) *Reduction processes.* The most frequently used method involves essentially Divers[1] reduction of sodium nitrite with sodium amalgam. A number of products are obtained, and the yield of hyponitrite is low. Divers'[1] method has been

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[1] E. Divers, *Proc. Roy. Soc.*, 1871, **19**, 425.

[2] D. M. Yost and H. Russell, 'Systematic Inorganic Chemistry of the Fifth and Sixth Groups', Prentice Hall, New York, 1944.

[3] L. Friedmann and J. Bigeleisen, *J. Chem. Phys.*, 1950, **18**, 1325; F. Bonner and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1952, **74**, 4944.

[4] M. A. Hussain, Ph.D. Thesis, Wales, 1966.

modified by Addison, Gamlen, and Thompson,[5] but still tends to give a carbonate- and nitrite-contaminated product. Polydoropoulos[6] claimed an 18% yield by this method and purified it by precipitation as the silver salt, which was reconverted into the sodium salt by treatment with sodium iodide. Recently[7] he has described an electrolytic cell, in which sodium amalgam is continuously formed electrolytically and then swirled into another compartment containing concentrated aqueous sodium nitrite, which is reduced to hyponitrite.

(ii) *Condensation reactions.* These involve the reaction between nitrous acid and hydroxylamine or its derivatives. Jones and Scott[8] obtained a 13% yield by treating hydroxylamine with sodium ethoxide and ethyl nitrite in ethanol. They suggested that the reaction involved the intermediate formation of an *N*-nitroso-species which rearranges to give hyponitrous acid. The hydroxylamine–nitrous acid reaction[9] in aqueous solution also gives small yields of hyponitrous acid. Hussain[4] has studied the yield of hyponitrous acid produced in this reaction under various conditions and found that it depends upon the actual nitrosating agent. These results show that there is not a common product-determining step in this reaction such as the breakdown of $ON\cdot{}^{+}NH_2OH$.

(iii) *Other reactions.* Several other reactions involving the oxidation[10] and disproportionation[11] of hydroxylamine in alkaline solutions lead to the production of hyponitrite, as also does the decomposition[12] of *N*-hydroxysulphamate ion, again in alkali [reaction (1)]

$$2HONHSO_3^- + 4OH^- \longrightarrow 2SO_3^{2-} + N_2O_2^{2-} + 4H_2O \qquad (1)$$

The sodium hyponitrite obtained from these reactions contains water of crystallisation. This can be removed by controlled drying.[5] The solid hyponitrites are decomposed by carbon dioxide to sodium carbonate and nitrous oxide, and so must be stored in tightly sealed containers.

The Stability and Mechanism of Decomposition of Aqueous Solutions of Hyponitrous Acid

A number of decomposition pathways for hyponitrous acid in aqueous solution have been established, their relative importance depending upon the experimental conditions. It is convenient to consider these under two headings, in solutions over and under pH 4.

A. The pH Range 4–14.—Hyponitrous acid is a weak dibasic acid and ionises according to (2). Latimer and Zimmerman[13] by colorimetric measurements give

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[5] C. C. Addison, G. A. Gamlen, and R. Thompson, *J. Chem. Soc.*, 1952, 338.
[6] C. N. Polydoropoulos, *Chimika Chronika*, 1959, **24**, *A*, 147.
[7] C. N. Polydoropoulos, *Chem. and Ind.*, 1963, 1686.
[8] L. W. Jones and A. W. Scott, *J. Amer. Chem. Soc.*, 1924, **46**, 2174.
[9] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 2824.
[10] M. N. Hughes and H. G. Nicklin, unpublished observations.
[11] R. Nast and I. Foppl, *Z. anorg. Chem.*, 1950, **263**, 310.
[12] E. Divers and T. Haga, *J. Chem. Soc.*, 1889, 760.
[13] W. M. Latimer and H. W. Zimmerman, *J. Amer. Chem. Soc.*, 1939, **61**, 1550.

$$H_2N_2O_2 \underset{K_1}{\rightleftharpoons} HN_2O_2^- + H^+ \underset{K_2}{\rightleftharpoons} N_2O_2^{2-} + 2H^+ \qquad (2)$$

$pK_1 = 7$ and $pK_2 = 11$, while Polydoropoulos quotes 6·92 and 11·58 respectively. At pH values higher than 12, between 7 and 11, and in more acid solutions, the important species are $N_2O_2^{2-}$,$HN_2O_2^-$, and $H_2N_2O_2$ respectively. It is often thought that the unstable species is the undissociated acid $H_2N_2O_2$. In fact the unstable species is the hydrogen hyponitrite ion, $HN_2O_2^-$, so in the pH range 4–14 hyponitrous acid decomposes through (3).

$$HN_2O_2^- \longrightarrow OH^- + N_2O \qquad (3)$$

This confusion arose out of some erroneous conclusions reached by Abel and Proisl[14] who studied the decomposition of hyponitrous acid in sodium hydroxide solutions, and found the rate equation to be (4), where $[N_2O_2^{2-}]$ = total hyponitrite and k,β are constants. They explained this in terms of the rate-determining decomposition of hyponitrous acid, $H_2N_2O_2$. However, these results suggest that hyponitrous acid in dilute acid should have a half-life of the order of 0·1 seconds, and also that $pK_2 = 13$, a value that differs appreciably from that obtained by Latimer and Zimmerman. This, coupled with the fact that hyponitrous acid is much more stable than is suggested by Abel and Proisl, has led to a re-examination of the decomposition reaction by a number of workers.[15] It has been shown that the unstable species is the hydrogen hyponitrite ion. The variation in rate of decomposition with pH parallels the variation in concentration of $HN_2O_2^-$ with pH. Thus the maximum rate of decomposition at 25° occurs at pH 9, where the concentration of $HN_2O_2^-$ is also a maximum. These results have allowed further estimations of the pK values; thus Hughes and Stedman give 7·18 and 11·54 for pK_1 and pK_2 respectively. These have been confirmed by Hussain's more recent work. The agreement with the values determined by the non-kinetic methods confirms the suggested mechanism. The spurious rate equation observed by Abel and Proisl was due to a failure to keep the ionic strength constant, and the resultant negative ionic strength effect superimposed on the expected first-order dependence on $[OH^-]^{-1}$ resulted in the rate varying inversely with $[OH^-]$ to a power appreciably greater than unity.

$$d(N_2O)/dt = k[N_2O_2^{2-}] / \{[OH^-](1 + \beta[OH^-])\} \qquad (4)$$

A study[3,15a,d] of the temperature-variation of both dissociation constants has allowed an estimation of the first and second heats of ionisation of hyponitrous acid. The mean of the available values are 3·7 and 6·1 kcal. mole^{-1} for $\triangle H_1$ and $\triangle H_2$ respectively. The sum, $\triangle H_1 + \triangle H_2$, equals 9·8 kcal. mole^{-1} which is lower than the value obtained calorimetrically by Latimer and Zimmerman (11·1 kcal. mole^{-1}), but is probably not outside the total error involved in all these sets of measurements.

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[14] E. Abel and J. Proisl, *Monatsh.*, 1938, **72**, 1.

[15] (*a*) M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 1239; (*b*) J. R. Buccholz and R. E. Powell, *J. Amer. Chem. Soc.*, 1963, **85**, 509; (*c*) J. H. Anderson, *Analyst*, 1963, **88**, 494; (*d*) C. N. Polydoropoulos and M. Pippinis, *Z. phys. Chem.*, 1964, **40**, 322.

B. Decomposition at Higher Acidities.—Partington and Shah[16] have shown that the decomposition of hyponitrites in strong acid solutions at high temperature gives a mixture of gaseous products including nitrogen, nitric oxide, and nitrous oxide. Buccholz and Powell[15b,17] have shown that under such conditions a chain-reaction mechanism can operate resulting in a fast erratic decomposition to nitrous oxide and other products. This probably accounts for the decomposition observed by Partington and Shah. This decomposition will not take place in the absence of certain ions and is eliminated by the addition of small amounts of ethanol, probably by removing hydroxyl radicals which act as chain carriers. The following discussion refers only to solutions to which ethanol has been added[17] or from which the catalysing ions are absent.[18]

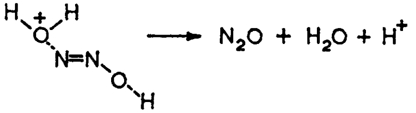
The decomposition of hyponitrous acid in aqueous acid solution can be represented by the rate law (5). In the acid range pH 4 → $H_0 = -1$ only the

$$\text{Rate} = (k^1 + k^{11}h_0)\,[H_2N_2O_2] \qquad (5)$$

non-acid-catalysed decomposition is important. This is very slow at room temperature, so solutions of hyponitrous acid are reasonably stable ($k^1 \simeq 10^{-6}\text{sec.}^{-1}$). The actual mechanism of decomposition probably involves[18] a slow isomerisation of the normal *trans*-hyponitrous acid molecule to the *cis* isomer which then decomposes to nitrous oxide and water in a fast step. This is consistent with the fact that '*cis*'-sodium hyponitrite[19] decomposes immediately on solution in acid, whereas the normal *trans* compound dissolves without appreciable reaction.

At higher acidities the acid-catalysed reaction becomes increasingly important, probably involving the fast pre-equilibrium protonation (6) of hyponitrous acid, followed by a slow decomposition step (7), the addition of the proton to the one end of the molecule facilitating the loss of a proton from the other.

$$\overset{+}{H} + H_2N_2O_2 \rightleftharpoons H_3\overset{+}{N}_2O_2 \qquad \text{Fast} \qquad (6)$$



Slow (7)

The Table gives details of the half-lives of hyponitrous acid solutions under conditions where decomposition is taking place essentially through only one of the above-mentioned mechanisms and also under other conditions of pH to show how the different mechanisms make varying relative contributions to the decomposition.

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[16] J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 1931, 2071.

[17] J. R. Buccholz and R. E. Powell, *J. Amer. Chem. Soc.*, 1965, **87**, 2350.

[18] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1964, 163.

[19] (*a*) N. Gee, D. Nicholls, and V. Vincent, *J. Chem. Soc.*, 1964, 5897; (*b*) J. Goubeau and K. Laitenberger, *Z. anorg. Chem.*, 1963, **78**, 320.

Table *Stability of hyponitrous acid solutions*

Reacting species	*Temp.*	*Acidity*	$t_{\frac{1}{2}}$
$HN_2O_2^-$	25°	pH 12·38	220 min.
,,	,,	pH 11·00	32 ,,
,,	,,	pH 8·80	16 ,,
,,	,,	pH 6·64	97 ,,
$H_2N_2O_2$	,,	pH 1—3	16 days
$HN_2O_2^-$	70°	pH 8·80	5 sec.
$H_2N_2O_2$	,,	pH 1—3	90 min.
$H_2N_2O_2 + H_3^+N_2O_2$	,,	$[H^+] = 1{\cdot}24$M	70 ,,
,,	,,	$[H^+] = 2{\cdot}30$M	42 ,,
,,	,,	$[H^+] = 3{\cdot}36$M	26 ,,
,,	,,	$[H^+] = 4{\cdot}49$M	12 ,,

C. Decomposition through the Chain Reaction.—Buccholz and Powell[17] have shown that this only occurs in the presence of certain ions and involves an induction period of erratic length. The presence of radical intermediates is confirmed by the fact that decomposing hyponitrous acid solutions cause polymerisation of added acrylonitrile. Further, nitrophenols are formed when benzene is added to such a decomposing solution, suggesting that OH and NO_2 are intermediates. It is suggested that the first step in this decomposition involves disproportionation to nitrous acid and that this is only important in the presence of certain cations and anions that can be oxidised to higher oxidation states. It is assumed that these are oxidised initially by traces of OH radicals which either arise adventitiously from traces of other reactants or by homolytic fission of hyponitrous acid. The oxidised species act as oxidation transfer agents in the oxidative decomposition of hyponitrous acid to nitrous acid, as OH itself is ineffective for this [reactions (8)—(12)].

$$X + OH \rightarrow X^+ + OH^- \qquad (8)$$
$$X^+ + H_2N_2O_2 \rightarrow X + HO{\cdot}N{:}NO + H^+ \qquad (9)$$
$$HO{\cdot}N{:}NO \rightarrow N_2O + OH \qquad (10)$$
$$HO{\cdot}N{:}NO + H_2N_2O_2 \rightarrow 2NO + N_2 + H_2O + OH \qquad (11)$$
$$NO + H_2N_2O_2 \rightarrow HNO_2 + N_2 + OH \qquad (12)$$

The nitrous acid produced in this way then *O*-nitrosates hyponitrous acid to give, as the final products, nitrate and nitrogen gas, as in reactions (13)—(16).

$$HNO_2 + H_2N_2O_2 \rightarrow ON.O{\cdot}N{:}NOH \rightarrow NO_2 + N_2 + OH \qquad (13)$$
$$NO_2 + H_2N_2O_2 \rightarrow H^+ + NO_3^- + N_2 + OH \qquad (14)$$
$$OH + HNO_2 \rightarrow H_2O + NO_2 \qquad (15)$$
$$OH + NO_2 \rightarrow N^+ + NO_3^- \qquad (16)$$

Obviously once the reaction has been initiated by trace OH radicals, further reaction produces OH radicals and so the reaction proceeds autocatalytically.

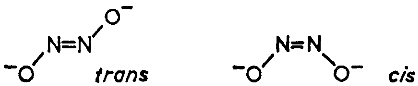
The reaction between nitrous acid and hyponitrous acid has been studied[20] independently of the hyponitrous acid decomposition. At $[H_2N_2O_2] \rightarrow 10^{-3}$M the stoicheiometry is as in (17), but at higher concentrations the consumption

$$HNO_2 + H_2N_2O_2 \rightarrow HNO_3 + N_2 + H_2O \qquad (17)$$

of hyponitrous acid is increased relative to that of nitrous acid and is shown in the formation of nitrous oxide as an additional product. As the hyponitrous acid concentration is raised[4] so the dependence of rate on hyponitrous acid decreases from unity. This is probably a result of the formation of nitrous acid from hyponitrous acid as suggested by Buccholz and Powell. The nitrosation of hyponitrous acid is then regarded as an *O*-nitrosation by the nitrous acidium ion giving ON-O·N:NOH which decomposes as outlined above. The formation of N_2O is accounted for by the decomposition of HO·N:NO. The reaction has also been studied in acetate buffers[21,22] and although the nitrosating agent is now dinitrogen trioxide, N_2O_3, the same general mechanism seems to hold.

Structure of Hyponitrous Acid and the Hyponitrite Anion

The physical and chemical properties of hyponitrites suggest the presence of an N=N double bond; thus the ultraviolet spectrum[5] of the anion shows a maximum absorption at 248 mμ (ϵ = 3980); a value which is characteristic for compounds containing an N=N bond. The structure can be written either with



cis or *trans* configuration. It has been shown by Raman[23–25] and infrared studies[23,26,27] that the product obtained in the usual preparative reactions is the *trans* isomer. Such a planar *trans* centrosymmetric structure belongs to the C_{2h} point group and should therefore show three infrared-active and three Raman-active fundamentals. These have been satisfactorily assigned and other details of the infrared spectrum interpreted in terms of combination bands.

It has always been assumed that the acid formed by acidifying sodium hyponitrite also has the *trans* structure. McGraw, Bernitt, and Hisatsune[27] have recently shown from infrared studies on solid $H_2{}^{14}N_2O_2$ and $H_2{}^{15}N_2O_2$ that this assumption is correct. Nuclear magnetic resonance studies[28] on the acid in ether also suggest a symmetric structure, but Ray and Ogg[29] claim on the basis of isotopic

[20] M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 2824.
[21] M. N. Hughes, Ph.D. Thesis, Wales, 1962.
[22] C. N. Polydoropoulos and M. Pippinis, *Chimika Chronika*, 1965, **30**, *A*, 43.
[23] D. J. Millen, C. N. Polydoropoulos, and D. Watson, *J. Chem. Soc.*, 1960, 687.
[24] L. Kuhn and E. R. Lippincott, *J. Amer. Chem. Soc.*, 1956, **78**, 1820.
[25] J. E. Rauch and J. C. Decius, *Spectrochim. Acta.*, 1966, **22**, 1963.
[26] M. N. Hughes, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1376.
[27] G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta*, 1967, **23**, *A*, 25.
[28] D. P. Hollis, Ph.D. Thesis, Stanford University, California, 1961.
[29] J. D. Ray and R. A. Ogg, cited in ref. 27.

exchange reactions that the acid may have a non-symmetrical structure in the aqueous phase. An attempt[21] has been made to measure the Raman spectrum in aqueous acid solution, but, although such solutions are normally stable, decomposition was rapid, presumably owing to a photochemical reaction.

The possibility of the existence of the *cis* isomer has attracted some attention. At one time it was thought that the compound nitramide was the *cis* acid since it has the same molecular formula, but it is now known that its structure can be best represented as NH_2NO_2. Recent attention has been focused on the so-called alkali-metal 'nitrosyls', MNO. These can be prepared by the action of nitric oxide on sodium in liquid ammonia[19] or directly on sodium metal.[30] These compounds have been formulated as M^+NO^-, but this is not in accord with infrared evidence.[19] They differ from the normal *trans*-hyponitrites in *X*-ray powder photographs,[31] thermal stability and decomposition, and their reaction with water. Sodium 'nitrosyl' effervesces on dissolution in water, giving nitrous oxide, and slowly decomposes in a vacuum above 150° giving N_2O and Na_2O, while sodium hyponitrite dissolves in water without appreciable reaction and decomposes explosively at 260° giving nitrite, oxide, and nitrogen. A reasonable alternative, although not conclusively proved, is that the metal nitrosyls are dimeric, but have the *cis* configuration. This is in accord with infrared evidence.[19b]

Some evidence for the existence of *cis*-hyponitrous acid as an unstable reaction intermediate has been presented by Hughes and Stedman[9] on the basis of a study of the hydroxylamine–nitrous acid reaction. Oxygen-18 and nitrogen-15 studies suggest[32] the formation of a symmetrical intermediate. Hyponitrous acid is stable under the conditions of this reaction (apart from a little reaction with nitrous acid) and is in fact produced by the reaction, and so cannot be the intermediate. It is suggested, therefore, that the stereochemical rearrangements during the reaction were such that both *cis* and *trans* acids were produced, but that the *cis* form rapidly decomposes to nitrous oxide and water, leaving the *trans* acid in solution. Fraser, Lee, and Hayden have recently suggested that *cis*-$H_2N_2O_2$ may be an intermediate in the reduction of nitrous acid by europium(II).[32a]

The Oxidation and Reduction of Hyponitrites

Hyponitrites are supposed to undergo both oxidation and reduction. The number of confirmed reduction reactions are rather limited. Much of the earlier work[33] is contradictory and reports of successful reductions have not been confirmed. von Brackel[34] claimed to have isolated hydrazine by reduction with zinc in

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[30] E. Nachbaur, *Monatsh*, 1962, **93**, 129.

[31] R. W. Asmussen, *Acta Chem. Scand.*, 1957, 1435.

[32] L. Friedmann and A. A. Bothner-By, *J. Chem. Phys.*, 1952, **20**, 459.

[32a] R. T. M. Fraser, R. N. Lee, and K. Hayden, *J. Chem. Soc.* (*A*), 1967, 741.

[33] See Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longmans, 1928, vol. VII, p. 404.

[34] F. von Brackel, *Ber.*, 1900, **33**, 2115.

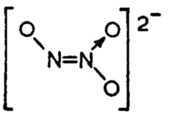
glacial acetic acid, but later workers have not been able to repeat this result and have shown that hyponitrites are relatively stable to reduction. Partington and Shah[16] showed, for example, that hyponitrites are not reduced by amalgams, stannous chloride, titanous chloride, zinc in glacial acetic acid, or Devarda's alloy in alkali. Coblens and Bernstein,[35] however, claim to have reduced silver hyponitrite to ammonia by successive treatment with stannous and titanous chloride. Kirschner[36] has quantitatively reduced a number of metal hyponitrites to nitrogen by treatment with copper powder.

Oxidation of hyponitrites to nitrites and nitrates takes place readily. Thus oxidation to nitrate is effected by acid permanganate, ferricyanide, and hypochlorite, whereas alkaline permanganate oxidises to nitrite only. Iodine oxidises hyponitrous acid to nitrite and nitrate. This reaction (18) is used in the colorimetric determination of hyponitrite.[37]

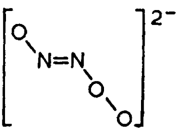
$$3H_2O + H_2N_2O_2 + 3I_2 \rightarrow HNO_3 + HNO_2 + 6HI \qquad (18)$$

Addison, Gamlen, and Thompson[5] have shown that the oxidation with liquid dinitrogen tetroxide can be stopped at a stage corresponding to the formation of $Na_2N_2O_3$, although normally the reaction goes further, though slowly, to give $Na_2N_2O_5$ and $Na_2N_2O_6$. Alternatively the product $Na_2N_2O_5$ can be formed rapidly by the action of nitrogen dioxide gas on sodium hyponitrite, suggesting that the actual oxidising agent in liquid N_2O_4 is also NO_2, the slow rate reflecting the low equilibrium concentration of NO_2. The NO_2 is reduced to nitric oxide.

The compound $Na_2N_2O_3$ has the same molecular formula as Angeli's salt (sodium nitrohydroxylamate) but differs from it in chemical behaviour. Angeli first prepared his salt by the reaction of hydroxylamine, ethyl nitrate, and sodium ethoxide in ethanol solution, but this method has been improved[38] to give a much higher yield. Addison has renamed Angeli's salt sodium α-oxyhyponitrite, and the compound obtained by liquid N_2O_4 oxidation, sodium β-oxyhyponitrite, and has suggested the structures as shown.



α-Oxyhyponitrite



β-Oxyhyponitrite

Addison assigned these structures on the basis of ultraviolet spectra and hydrolysis products. The α-oxyhyponitrite structure has now been confirmed by infrared[39] and calorimetric evidence.[38] Sodium α-oxyhyponitrite is also of interest as it is regarded as a source of nitroxyl NOH. Its aqueous solutions

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[35] M. Coblens and J. K. Bernstein, *J. Phys. Chem.*, 1925, **29**, 780.

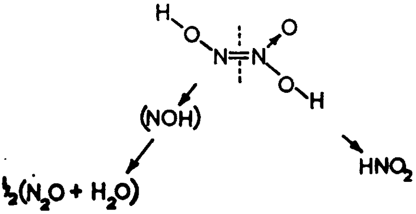
[36] A. Kirschner, *Z. anorg. Chem.*, 1898, **16**, 424.

[37] G. Ferrani, *Ann. Chim. (Italy)*, 1958, **48**, 322.

[38] H. R. Hunt, J. R. Cox, and J. D. Ray, *Inorg. Chem.*, 1962, 938.

[39] R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 900.

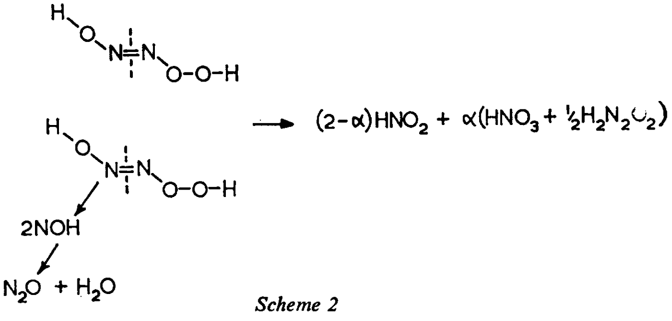
undergo atmospheric oxidation to nitrite, but provided oxygen is eliminated, then these solutions are stabilised by alkali. In dilute acid solution decomposition occurs, through the acid form, giving nitrous oxide and nitrous acid. It is assumed that fission occurs at the N=N bond giving a nitrite fragment and nitroxyl, which decomposes to give nitrous oxide and water (Scheme 1).



Scheme 1

In more concentrated acid solution, an alternative decomposition pathway,[3] to nitric oxide, is favoured.

The β-oxyhyponitrite ion, formed by N_2O_4 oxidation of hyponitrite, differs appreciably from the α salt. Thus, it reacts immediately with water with effervescence of nitrous oxide. Addison has suggested Scheme 2.



Scheme 2

Further oxidation of β-$Na_2N_2O_3$. Further oxidation with N_2O_4 or direct oxidation of hyponitrite with NO_2 gas leads to the formation of $Na_2N_2O_5$, which is oxidised further to $Na_2N_2O_6$. Silver hyponitrite is oxidised almost immediately to a pale yellow compound $Ag_2N_2O_6$ with evolution of nitric oxide. Addison has considered the structures of these compounds in terms of their hydrolysis products. He considers them to be salts of the acids (1) and (2).

The Oxidation and Reduction of Hyponitrites in Biological Systems. Nitrification and Denitrification Reactions.—Hyponitrites and related species have often been suggested as possible intermediates[40] in the Nitrogen Cycle. Nitrogen is

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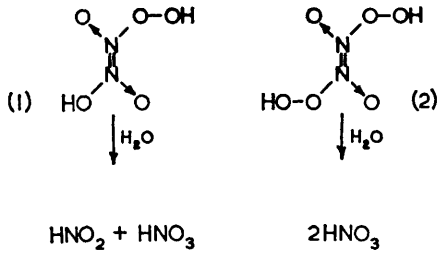
[40] See for example, *Sci. Progr.*, 1966, **54**, No. 213, 93.



fixed by conversion into ammonia (for example, by *Azotobacter*), the ammonia is then oxidised to nitrite by several species of micro-organism, mainly *Nitrosomonas*, and the nitrite is finally oxidised to nitrate. The main problem in nitrification lies in deciding the chemical pathway from ammonia to nitrite. It is generally thought that the reaction proceeds through hydroxylamine (N^{-I} species) and hyponitrous acid (N^{+I} species) although appreciable build-up of intermediates is not to be expected as experiments[41] with *Nitrosomonas* have shown that the rate of appearance of nitrite practically equals the rate of loss of ammonia. It has also been shown that hydroxylamine is oxidised almost as rapidly as ammonia under these conditions and so its postulation as an intermediate is reasonable. The anaerobic oxidation of hydroxylamine by *Nitrosomonas* results in the production of some nitrous and nitric oxides and it is thought that the nitrous oxide arises from the decomposition of hyponitrite. However hyponitrite is not oxidised under these conditions, and it has been argued that it cannot lie on the main reaction pathway, but rather occurs as the result of some side reaction, possibly the dimerisation of nitroxyl NOH (which would then be the N^{+I} intermediate). The presence of hyponitrite has been confirmed by colorimetric methods.[42]

There is also uncertainty regarding the pathway of nitrite reduction in micro-organisms and higher plants. Hyponitrous acid (with N_2O as a side product) and hydroxylamine have been isolated and the use of isotopic techniques has suggested the formation of ammonia. Medina and Nicholas[43] have, however, identified a hyponitrite reductase in *Neurospora*, supporting the view that the N^{+I} intermediate is probably hyponitrite. Again, as in nitrification, the compound nitroxyl is suggested as an alternative intermediate.

In view of this interest in the intermediates of the Nitrogen Cycle, it would probably be helpful to study the reactions of hyponitrites and related species under pH conditions that correspond more closely to those of biochemical interest.

Nitroxyl

Nitroxyl (NOH or HNO) is often postulated as an intermediate in various re-

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[41] T. Hofmann and H. Lees, *Biochem. J.*, 1954, **54**, 579.
[42] A. S. Corbet, *Biochem. J.*, 1928, **28**, 1575.
[43] A. Medina and D. J. Nicholas, *Nature*, 1957, **179**, 533; *Biochim. Biophys. Acta*, 1957, **25**, 138.

or nitrous oxide is produced. This is based on the assumption that nitroxyl dimerises to hyponitrous acid, which in turn decomposes to nitrous oxide. Nitroxyl is well known in the gas phase and has a bent structure[44] with a HNO bond angle of 109°. Gas-phase sources[45] usually involve the direct reaction between nitric oxide and hydrogen atoms, or the abstraction of a hydrogen atom by nitric oxide from hydrogen iodide or ethoxyl radicals. The end product is nitrous oxide.

The situation regarding solution studies is not so clear. Reactions that were once thought to give nitroxyl as an intermediate are now known[32] not to do so. Nast, Nyul, and Grziwok[46] have shown, however, that the formation of actions involving nitrogen compounds, mainly those in which hyponitrous acid $K_2[Ni(CN)_3NO]$ from $K_2[Ni(CN)_4]$ is a sensitive test for nitroxyl and have demonstrated that nitroxyl appears immediately in the hydrolysis of *N*-hydroxysulphamate (and then dimerises to hyponitrite). Ackermann and Powell[47] have confirmed the presence of nitroxyl by kinetic methods. Yagil and Anbar[48] have claimed that nitroxyl is formed in the oxidative decomposition of alkaline solutions of hydroxylamine (which explains how metal nitrosyl complexes can be prepared by this method) and suggest that nitroxyl reacts with oxygen to give pernitrite ($ONOO^-$). Thus when oxygen is bubbled through alkaline solutions of Angeli's salt the yellow colour of pernitrite is seen.

Nitroxyl is known to be formed by the decomposition of Angeli's salt and also Piloty's salt $C_6H_5\cdot SO_2\cdot NHOH$, but Smith and Hein[49] have shown that the formation of aldoximes by the reaction of primary alkyl halides with either of these two compounds does not involve the reaction of nitroxyl, but rather arises through direct reaction of the compound with the alkyl halide. Similarly, the Angeli–Rimini test for aldehydes, in which a hydroxamic acid is formed from the reaction of an aldehyde with Piloty's acid, does not involve the formation of nitroxyl.

Hyponitrous Esters

Esters of hyponitrous acid, $RON{=}NOR$, are known, the most studied ones being the ethyl and benzyl compounds. Hunter and Partington[50] prepared these by the reaction of the alkyl or aryl halide with silver hyponitrite. This method is probably the most useful, but alternative routes are available, involving the oxidation of alkoxyamines with oxidising agents such as peroxide and hypobromite.[51] Diethyl hyponitrite occurs as an oil which explodes at temperatures above 80°, while the dibenzyl ester is a colourless crystalline solid, m.p.

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[44] H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, 1958, **29**, 883.

[45] F. C. Kohout and F. W. Lampe, *J. Amer. Chem. Soc.*, 1965, **87**, 5795; J. L. Holmes, *Proc. Chem. Soc.*, 1962, 75; E. A. Arden and L. Phillips, *J. Chem. Soc.*, 1964, 5118.

[46] R. Nast, K. Nyul, and E. Grziwok, *Z. anorg. Chem.*, 1952, **267**, 304.

[47] M. N. Ackermann and R. E. Powell, *Inorg. Chem.*, 1966, **5**, 1334.

[48] G. Yagil and M. Anbar, *J. Inorg. Nuclear Chem.*, 1964, **26**, 453.

[49] P. A. S. Smith and G. E. Hein, *J. Amer. Chem. Soc.*, 1960, **82**, 5731.

[50] E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 1932, 2593.

[51] L. Seed, B.P., 795,824; (*Chem. Abs.*, 1959, **53**, 219f).

48°. Both decompose on slight warming to give nitrogen, an alchol, and an aldehyde. This is accounted for by the initial rupture of the two O–N bonds with the elimination of nitrogen and the formation of two alkoxyl radicals, which decompose (19) to the aldehyde and alcohol.

$$C_2H_5ON = NOC_2H_5 \rightarrow N_2 + 2[C_2H_5O] \rightarrow C_2H_5OH + CH_3{\cdot}CHO \qquad (19)$$

The formation of free radicals in these decompositions is confirmed by recent interest in these compounds as polymerisation catalysts.[52] Thus Marshall, Harris, and Garrett[53] have shown that 0·1% dibenzyl hyponitrite at 25° gave a polymerisation rate for methyl methacrylate that was 34 times as great as that produced by dibenzoyl peroxide. The decomposition of dibenzyl hyponitrite is rapid[54] (*e.g.*, $t_{\frac{1}{2}}$ = 13 sec. at 89°) but di-t-butyl hyponitrite[55] is much more stable and has no tendency to explode. It has recently been suggested that it would make an excellent initiator.

Metal Hyponitrites

Earlier workers[33] have claimed to isolate the hyponitrites, hydrogen hyponitrites, and, in some cases, the basic salts of the alkali and alkaline-earth metals, and of copper, silver, zinc, cadmium, mercury, aluminium, lead, bismuth, nickel, and cobalt. Partington and Shah[56] were able to prepare many of these by adding excess of metal nitrate to an aqueous solution of sodium hyponitrite, but were unable to repeat the preparation of the basic salts. Polydoropoulos and Yannakopoulos[57] prepared several heavy-metal hyponitrites by gradually neutralising a solution of hyponitrous acid and the metal salt with alkali.

Very little work has been carried out on the metal hyponitrites. Oza[58] and his co-workers have studied their thermal decomposition and claim to have established several decomposition pathways. Thus lead(II) and copper(II) hyponitrites decompose to the oxide and nitrous oxide, while the decomposition of calcium, strontium, and barium hyponitrites goes by three possible pathways giving (*a*) nitrate, oxide, and nitrogen, (*b*) oxide, nitric oxide, and nitrogen, and (*c*) oxide and nitrous oxide. A thermogravimetric study of these decomposition reactions would probably be very helpful.

The infrared spectra of lead, barium, cobalt, and magnesium hyponitrites have been reported.[59] Kuhn and Lippincott[24] have shown that the silver and mercury hyponitrites have a *trans* configuration.

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[52] J. W. Batty, A. Lambert, G. Scott, F. Bebbington, and L. Seed, B.P., 814,688; (*Chem. Abs.*, 1960, **54**, 6196d).

[53] G. Scott, B.P., 823,103; (*Chem. Abs.*, 1960, **54**, 6549a); I. Marshall, I. Harris, K. B. Garrett, and Imperial Chemical Industries Limited, B.P., 618,168; (*Chem. Abs.*, 1949, **43**, 5641b).

[54] S. K. Ho and J. B. de Sousa, *J. Chem. Soc.*, 1961, 1788; N. H. Ray, *Ibid.* 1960, 4023.

[55] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.

[56] J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 1932, 2589.

[57] C. N. Polydoropoulos and T. Yannakopoulos, *Chimika Chronika*, 1961, **26**, 70.

[58] See for example, T. M. Oza, and V. T. Oza, *J. Chem. Soc.*, 1953, 909.

[59] R. J. W. LeFèvre, W. T. Oh, J. H. Reece, and R. L. Werner, *Austral. J. Chem.*, 1957, **10**, 361.

Transition-metal Complexes with Bridging Hyponitrite Groups.—Raynor[60] has suggested that metal nitrosyl complexes with ν(NO) in the region 1195—1040 cm.$^{-1}$ can best be regarded as dimers with bridging hyponitrito-groups. One example is the red nitrosylpentammine cobalt(III) species {while the black isomer is regarded as a Co^{I} species, $[Co(NH_3)_5NO]^{2+}$ with a NO^+ group}. Feltham[61] has shown that the red species is a 4 : 1 electrolyte, while ion-exchange measurements[62] also confirm the bridged structure. Other examples cited by Raynor include potassium μ-hyponitritobis[pentacyanocobaltate(III)] and iron and ruthenium nitrosyls $[(NO)_3M.N_2O_2.M(NO)_3]$.

Gans has considered[63] the configuration of the bridging hyponitrito-ligand in the red nitrosylpentammine cobalt(III) isomer and suggests that it has a *cis* or skew configuration rather than a *trans* one.

[60] J. B. Raynor, *J. Chem. Soc.* (*A*), 1966, 997.
[61] R. D. Feltham, *Inorg. Chem.*, 1964, 3, 1038.
[62] M. Ardon, *Israel. J. Chem.*, 1964, 2, 181.
[63] P. Gans, *J. Chem. Soc.* (*A*), 1967, 943.