525. *Kinetics and Mechanism of the Reaction between Nitrous Acid and Hydroxylamine. Part I.*

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The kinetics of the reaction between nitrous acid and hydroxylamine have been examined over a wide range of acidity. At low acidities reaction occurs by attack of dinitrogen trioxide on free hydroxylamine, while at high acidities the nitrous acidium ion attacks the hydroxylammonium ion. The reaction is catalysed by bromide and thiocyanate ions, an equilibrium concentration of the nitrosyl compound attacking free hydroxylamine. A small amount of *trans*-hyponitrous acid is formed as one of the products, the yield being greater when reaction occurs through free hydroxylamine than when it occurs through the hydroxylammonium ion. The mechanism of the initial nitrosation is discussed, together with the subsequent rearrangements leading to the final product.

Nitrous acid and hydroxylamine react readily in aqueous solution at room temperature according to the stoicheiometric equation: $HNO_2 + NH_2{\cdot}OH \longrightarrow N_2O + 2H_2O$. The present work was begun as part of a general study of the mechanism of reaction of nitrous acid with various inorganic nitrogen compounds. The reaction with hydroxylamine seemed particularly interesting for two reasons; there have been two tracer studies of the reaction, in which nitrogen-15 and oxygen-18 were used, and there was evidence that one of the likely intermediates, hyponitrous acid, could be isolated in measurable amounts. Friedman and Bothner-By [1] studied the reaction with sodium [^{15}N]nitrite and isotopically normal hydroxylamine hydrochloride, with [^{18}O]water as solvent. They found that the nitrous oxide contained only a small amount of $^{15}N^{15}NO$, showing that the nitroxyl radical was not an intermediate in the reaction. They investigated the composition of the nitrous oxide molecules containing one nitrogen-15 atom and found that at pH 7 the gas contained equal amounts of $^{15}N^{14}NO$ and $^{14}N^{15}NO$, while at pH 1 there was 34% of $^{15}N^{14}NO$ and 66% of $^{14}N^{15}NO$. They concluded that in neutral solution a symmetrical intermediate was involved, while at pH 1 an unsymmetrical species was present. They also concluded that the oxygen originally on the hydroxylamine did not exchange with the solvent under acid conditions. The oxygen-18 data show that, at pH 1, 60% of the oxygen in the nitrous oxide comes from the nitrous acid or the solvent. Within the experimental error estimated by Friedman and Bothner-By, this agrees with the figure of 66% based on the nitrogen-15 data. Clusius and Effenberger [2] confirmed the result at pH 7. Friedman and Bothner-By suggested that the symmetrical species was hyponitrous acid, $HO{\cdot}N{:}N{\cdot}OH$, while the unsymmetrical species was *N*-nitrosohydroxylamine, $ON{\cdot}NH{\cdot}OH$. In support of their ideas they pointed out that Audrieth [3] had isolated small amounts of silver hyponitrite from decomposing solutions of hydroxylammonium nitrite. These results needed to be supplemented by a kinetic study before detailed conclusions could be drawn about the mechanism. Montemartini,[4] in an early investigation, found that the rate was of first order in nitrous acid and in hydroxylamine. More recent work by Holzapfel [5] is consistent with this result. Neither study is sufficiently detailed to provide much information about the mechanism. After the present work was largely complete, Doering and Gehlen [6] published a kinetic study of the reaction in acetate buffers. They found evidence for three mechanisms, involving nitrosation of free hydroxylamine by the nitrous acidium ion, nitrosyl acetate, and dinitrogen trioxide, but they did not extend

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[1] Friedman and Bothner-By, *J. Chem. Phys.*, 1952, **20**, 459.
[2] Clusius and Effenberger, *Helv. Chim. Acta*, 1955, **38**, 1834.
[3] Audrieth, *J. Phys. Chem.*, 1930, **34**, 538.
[4] Montemartini, *Gazzetta*, 1892, **22**, 304.
[5] Holzapfel, *Wiss. Z. Univ. Leipzig, Math.-Natur. Reiche*, No. 2, 1951/2, **4**, 30.
[6] Doering and Gehlen, *Z. anorg. Chem.*, 1961, **312**, 32.

their work to the more acid conditions where the isotopic results suggested the presence of an unsymmetrical intermediate.

RESULTS

(1) *The Rate Equation in the Range* $[H^+] = 0{\cdot}005$—$0{\cdot}1$M.—The reaction was run in perchloric acid solution at 0°, with a large excess of hydroxylamine over nitrous acid. The first experiments were carried out with hydroxylammonium perchlorate to avoid possible complications due to nitrosation by nitrosyl chloride. Later work showed that added chloride ion had no effect and that the results with the hydrochloride were identical with those obtained with the perchlorate. The reaction was of first order in nitrous acid. In a typical run with $[HNO_2] = 2{\cdot}5 \times 10^{-3}$M, $[NH_3OH^+] = 2{\cdot}5 \times 10^{-2}$M, $[H^+] = 0{\cdot}1$M, successive half-lives were 18·5, 18·5, and 20 min. By varying the hydroxylamine and perchloric acid concentrations it was shown that the rate equation was:

$$v = k_3[H^+][HNO_2][NH_3{\cdot}OH^+]. \qquad (1)$$

Measurements at other temperatures confirmed this rate equation and gave an Arrhenius activation energy of 14·7 kcal. mole^{-1}. Some of the results on which these conclusions are based are given in Table 1.

TABLE 1.

Rate constants for reaction in an excess of perchloric acid at 0°.

$[H^+]$ (M)	$[NH_3{\cdot}OH^+]$ (10^{-2}M)	$[HNO_2]$ (10^{-3}M)	10^4k_1 (sec.$^{-1}$)	$10k_3$ (mole^{-2} l.^{2} sec.$^{-1}$)
0·10	3·75	2·5	8·64	2·30
0·10	2·5	5·0	6·25	2·48
0·10	2·5	1·25	6·20	2·47
0·10	1·25	1·25	3·07	2·36
0·075	2·5	1·25	4·61	2·45
0·05	5·00	5·00	6·90	2·76
0·05	1·25	1·25	1·62	2·60
0·025	3·75	1·25	2·81	3·00
0·010	3·75	0·625	1·54	4·1
0·005	3·75	0·313	1·11	6·0
0·005	2·50	0·313	0·80	6·4

Although equation (1) represents the results down to 0·025M-H^+ quite well, there were two complications. When the nitrous acid concentration was increased, there was a small but definite increase in the first-order rate constant k_1. This effect was very small in 0·1M-perchloric acid but much more marked in 0·01M-solution. At low acidities the order in nitrous acid rose well above 1 and in extreme cases approached 2. Results in Table 2 illustrate this point. By analogy with other reactions of nitrous acid we suspected that this was due to the incursion into the rate equation of a term of the form

$$v = k_a[HNO_2]^2[NH_2{\cdot}OH] = k_b[HNO_2]^2[NH_3{\cdot}OH^+]/[H^+], \qquad (2)$$

due to a rate-determining nitrosation of free hydroxylamine by an equilibrium concentration of dinitrogen trioxide. The second complication is that if the values of k_1 (for constant $[NH_3OH^+]$) are plotted against $[H^+]$ there is an intercept on the $[H^+] = 0$ axis. This corresponds to the drift in the k_3 values in Table 1. This could be due to a contribution by reaction (2) to the rate equation, but it might be partly due to an additional term of the form

$$v = k_c[H^+][HNO_2][NH_2{\cdot}OH] = k_d[HNO_2][NH_3{\cdot}OH^+], \qquad (3)$$

which is what would be expected for a rate-determining nitrosation of free hydroxylamine by the nitrous acidium ion.

To clear up these points a series of runs were carried out at low acidities, and with very low concentrations of nitrous acid (10^{-4}M). These are summarised in Table 3.

With nitrous acid concentrations of 10^{-4}M there is no sign of a component in the rate equation that is of second order in nitrous acid, and the apparent intercept on the $[H^+] = 0$

axis disappears. This is shown by the constancy of the k_3 values in Table 3, especially when compared with those in Table 2.

(2) *The Rate Equation in Acetate Buffers at* 0°.—It was suspected that the second-order component of the rate equation discussed above was due to nitrosation by dinitrogen trioxide. An attempt was made to isolate this mechanism by studying the kinetics in acetate buffers at pH 4 and 4·6. The rate equation was found to be

TABLE 2.

Effect of nitrous acid concentration on the order of reaction with respect to nitrous acid.

$[H^+]$ (M)	$[NH_3{\cdot}OH^+]$ (10^{-2}M)	$[HNO_2]$ (10^{-3}M)	1st $t_{½}$ (min.)	2nd $t_{½}$ (min.)	" Order " *
0·10	2·5	0·63	18·5	18·5	1·0
0·10	2·5	5·0	17·5	18·0	1·0
0·025	2·5	0·63	65	65	1·0
0·025	2·5	5·0	38	51	1·4
0·010	2·5	0·63	100	100	1·0
0·010	2·5	2·5	50	74	1·6
0·010	10·0	7·5	7·25	14·5	2·0

* The " order " with respect to nitrous acid has been calculated from the first and second half-lives.

TABLE 3.

Runs at low nitrous acid concentration.

$[NH_3{\cdot}OH^+] = 0{\cdot}025$M. $[HNO_2]_0 = 0{\cdot}0001$M.

$[H^+]$ (M)	0·100	0·05	0·025	0·0175	0·010
$10k_3$ (mole^{-2} l.^{2} sec.$^{-1}$)	2·50	2·29	2·24	2·51	2·68

$$v = k_4[HNO_2]^2 + k_5[HNO_2]^2[OAc^-]. \qquad (4)$$

This is the familiar rate equation for a rate-determining formation of dinitrogen trioxide. Doering and Gehlen [6] have already published results establishing this mechanism, and therefore we do not include our own.

(3) *Anion-catalysis.*—Halide ions catalyse the nitrosation of aromatic amines through the formation of the corresponding nitrosyl compounds. In the present work it was found that added chloride ion had no effect, but added bromide ion (0·01—0·04M) produced a marked catalytic effect, while thiocyanate ion was a very powerful catalyst. The reaction rate remained of first order in nitrous acid under all conditions. By subtracting the first-order rate constant in the absence of added halide (k_6) from the total first-order rate constant (k_1), the contribution due to the catalysing halide (k_7) was evaluated. It was found that k_7 was independent of acidity and was proportional to $[NH_3{\cdot}OH^+]$. Thus for the halide catalysis the rate equation is:

$$v = k_7[HNO_2] = k_8[H^+][HNO_2][X^-][NH_2{\cdot}OH]. \qquad (5)$$

The values of k_8 at 0°, and 0·15 ionic strength, are $6{\cdot}36 \times 10^5$ and $1{\cdot}39 \times 10^8$ mole^{-3} l.^{3} sec.$^{-1}$ for bromide and thiocyanate ion, respectively. The measurements were extended to 15° and 25°. The Arrhenius activation energy was found to be 11·6 kcal. mole^{-1} for the bromide-ion reaction. Typical results are in Table 4.

Isotopic Measurements.—The results of Friedman and Bothner-By [1] were obtained at only two acidities, pH 7 and pH 1. In the second case the pH was not known accurately. It seemed desirable to extend these measurements over a wide range of acidity, in conditions where the rate equation was known. The experiments were carried out with normal hydroxylamine and water enriched in oxygen-18. The nitrous acid was in isotopic equilibrium with the solvent. At low acidities, up to pH 4, it was found that N'_{N_2O}/N'_{H_2O} was 0·50 as found by previous workers. On increasing the acidity the ratio rose to 0·60, but it did not rise above this value, even in 5M-perchloric acid. N'_X represents the atom % excess over normal of oxygen-18 in compound X. Thus the figure of 66% found by Friedman and Bothner-By is a limiting value for high acidities. (We think that the difference between the two figures of

60% and 66% is within the combined experimental errors of the two sets of measurements.) The accuracy of our mass-spectrometric analyses was about 1—2%, so the values of N'_{N_2O}/N'_{H_2O} are accurate to about ±0·02. As the ratio changes only from 0·5 to 0·6 it was not possible accurately to follow the change in this ratio with acidity.

Another point of interest bearing on the nature of the intermediates in the reaction is the yield of *trans*-hyponitrous acid. For reaction when the rate equation was $v = k_3[H^+][HNO_2][NH_3{\cdot}OH^+]$ a yield of between 2% and 3% was obtained. It is difficult to be more precise because the solutions contained some other species whose ultraviolet light absorption overlapped that of the hyponitrite anion and a correction had to be made for this. For reaction when the rate equation was $v = k_8[H^+][HNO_2][NCS^-][NH_2{\cdot}OH]$ this overlapping absorption was considerably weaker and the yield of hyponitrite was 5%.

TABLE 4.

Rate constants for halide ion catalysis at 0°.

$[H^+]$ (M)	$[NH_3OH^+]$ (10^{-2}M)	$[X^-]$ (10^{-2}M)	k_1 (sec.$^{-1}$)	k_6 (sec.$^{-1}$)	k_7 (sec.$^{-1}$)	k_8 (mole^{-3} l.^{3} sec.$^{-1}$)
			Chloride ion			
0·1	2·5	2·5	5·83			
0·1	2·5	14·75	5·84			
			Bromide ion			
0·1	2·5	1	7·04	5·60	2·04	0·66
0·04	2·5	4	10·1	2·46	3·87	0·62
0·04	2·5	1	4·45	2·46	1·99	0·64
0·04	1·25	2	3·18	1·23	1·95	0·62
			Thiocyanate ion			
0·1	1·25	1	221	3	218	1·40
0·1	0·63	1	111	1	110	1·46
0·1	1·25	1·25	58	3	55	1·41
0·1	1·25	2	456	3	453	1·45
0·07	1·25	2	474	1	473	1·51
0·07	1·25	0·25	62	1	61	1·57
0·04	1·25	1	197	1	196	1·42
0·04	1·25	0·5	111	1	110	1·42

DISCUSSION

(1) *Reaction in Acetate Buffers.*—Rate equation (4) has the form expected for a rate-determining formation of dinitrogen trioxide in acetate buffers. This does not tell us whether free hydroxylamine or its conjugate acid is being attacked. Normally there would be little reason to doubt that the free base was involved, but the discussion later in this paper will show that nitrosation of the hydroxylammonium ion can be involved even in mildly acid conditions (pH 2). The last run in Table 2 at pH 2 is of the second order in nitrous acid. The second-order rate constant, $v/[HNO_2]^2$ is 0·32 mole^{-1} l. sec.$^{-1}$. This is about a third of the rate constant for the formation of dinitrogen trioxide at pH 4, although the concentration of hydroxylammonium ion is the same. There seems little doubt that reaction proceeds through the free base. This explains the results at pH 4 and 4·6. In more acid solutions the concentration of free hydroxylamine falls, reaction (9) becomes the rate-determining step and (8) is then a fast reversible reaction.

$$H_2NO_2^+ + CH_3{\cdot}CO_2^- \rightleftharpoons CH_3{\cdot}CO{\cdot}O{\cdot}NO + H_2O \quad \text{Fast} \qquad (6)$$

$$CH_3{\cdot}CO{\cdot}O{\cdot}NO + NO_2^- \longrightarrow N_2O_3 + CH_3{\cdot}CO_2^- \quad \text{Slow} \qquad (7)$$

$$H_2NO_2^+ + NO_2^- \longrightarrow N_2O_3 + H_2O \quad \text{Slow} \qquad (8)$$

$$N_2O_3 + NH_2{\cdot}OH \longrightarrow ON{\cdot}NH_2{\cdot}OH^+ + NO_2^- \quad \text{Fast} \qquad (9)$$

It appears from a comparison of our results with those for diazotisation that hydroxylamine is substantially less reactive towards dinitrogen trioxide than is aniline. This reaction scheme agrees well with the work of Doering and Gehlen [6] and does not seem to call for further comment. We did not observe the reaction paths involving nitrosation, by nitrosyl acetate and the nitrous acidium ion, of free hydroxylamine that they reported. The likely reason is that at the concentration of nitrous acid used by us the rate of reaction by steps (6)—(9), being of second order in nitrous acid, was much larger than the rate of the other two processes which were of first order in nitrous acid. Had our measurements been extended to much lower nitrous acid concentrations we should have been able to observe these other two mechanisms reported by Doering and Gehlen.

(2) *Anion-catalysed Reaction.*—The relative catalytic effect of halide and pseudohalide ions, $NCS^- > Br^- > Cl^-$, is the same as has been observed in diazotisation. Rate equation (5) has the form characteristic of attack by an equilibrium concentration of the nitrosyl halide on free hydroxylamine. Again, by analogy with diazotisation and deamination,[7] the mechanism can be written:

$$H_2NO_2^+ + Br^- \rightleftharpoons NOBr + H_2O \qquad \text{Fast} \qquad (10)$$

$$NOBr + NH_2{\cdot}OH \longrightarrow ON{\cdot}NH_2{\cdot}OH^+ + Br^- \qquad \text{Slow} \qquad (11)$$

From the value of k_8 at 0°, thiocyanate ion is 219 times as powerful a catalyst as bromide ion, while chloride ion shows no observable catalytic activity at all. Now k_8 is a composite constant made up from the equilibrium constant for (10) and the rate constant for (11). Schmid and Fouad[8] found that for the bromide ion the equilibrium constant for reaction (10) is 0·0225 at 0°, and Whincup[9] found that the corresponding value for the thiocyanate ion is 46. Thus the equilibrium concentration of nitrosyl thiocyanate should be 2040 times that of nitrosyl bromide, when neither is the bulk component of nitrous acid. The greater catalytic effect of thiocyanate ion is therefore due to the greater equilibrium concentration of the nitrosyl compound, which is intrinsically a less reactive nitrosating agent. Nitrosyl chloride should be still more reactive, but the equilibrium constant for its formation is much smaller than that for bromide (0·00055), and from the results above it seems that the overall catalytic effect is governed largely by the size of the equilibrium concentration of nitrosyl halide rather than by its reactivity. Hence chloride ions have very little catalytic effect. The nitrosation of aniline and of several other aromatic amines by nitrosyl chloride and bromide appears to be a collision-controlled process,[10] and thus the rate constant for reactions of type (11) do not vary much from one nitrosyl halide to another. In the present case the rate of reaction is substantially less than the encounter rate between hydroxylamine and nitrosyl halide, but it can readily be seen that there may not be a great spread in the rate constants for reaction (11) and the corresponding reaction with thiocyanate, and hence that the overall catalytic effect may be governed by the size of the equilibrium constant for reaction (10). These results also confirm the tentative conclusion from the results with acetate buffers that hydroxylamine is less reactive towards nitrosating agents than is aniline, despite the fact that it is more basic. The activation energy for reaction (11), calculated from Schmid and Fouad's data and the present results, is 11·6 kcal. mole^{-1}, *i.e.*, about 7 kcal. mole^{-1} more than for aniline.[10]

(3) *Reaction in an Excess of Perchloric Acid.*—The rate equation $v = k_3[H^+][HNO_2] \times [NH_3{\cdot}OH^+]$ can be interpreted as a rate-determining attack by the nitrous acidium ion on protonated hydroxylamine. There are two conjugate acids of hydroxylamine that might be involved, $^+NH_3{\cdot}OH$ (I) and $NH_2{\cdot}OH_2^+$ (II).

The fact that nitrous oxide and hyponitrous acid are the products of reaction strongly suggests *N*-nitrosation, and as only form (II) has a lone pair of electrons on the nitrogen atom, analogy with diazotisation and deamination points to (II) as the reactive form.

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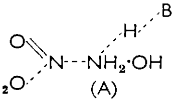
[7] Hughes, Ingold, and Ridd, *J.*, 1958, 58.
[8] Schmid and Fouad, *Monatsh.*, 1957, **88**, 631.
[9] Whincup, personal communication.
[10] Ridd, *Quart. Rev.*, 1961, **15**, 418.

However, there are difficulties. One can attempt to calculate the concentration of form (II) by estimating pK_a from values for similar molecules, though such a procedure is fraught with uncertainties. The following values have been obtained from the literature: $NH_3{\cdot}NH_3^{2+}$ $-1{\cdot}05$; $NH_2{\cdot}NH_3^+$ $7{\cdot}9$; $HO{\cdot}NH_3^+$ $5{\cdot}8$; NH_4^+ $9{\cdot}8$. Wynne-Jones and Mitchell[11] reported that " hydrogen peroxide is more than a million times less basic than water." On these figures we estimate the pK_a of form (II) to be at most -2. If this is accepted, then $[^+NH_3{\cdot}OH]/[NH_2{\cdot}OH_2^+]$ is more than 6×10^7. Values of the same order of magnitude can be calculated from the basicities of ammonia and water, and of methylamine and methanol. If the rate equation is written as $v = k_9[H^+][HNO_2][NH_2{\cdot}OH_2^+]$, then $k_9 = 6 \times 10^7 k_3 = 1{\cdot}6 \times 10^7$ mole^{-2} l.^{2} sec.$^{-1}$. It has plausibly been suggested[10] that the limiting rate constants observed for such substitutions at the nitrous acidium ion represent a collision-controlled process. These limiting rate constants are about 3000 for singly charged anions and about 200 for neutral molecules. The limiting rate for attack on a positively charged species should be lower still. Thus the value of k_9 calculated above is many powers of ten greater than the expected limit. This argument may be criticised on the grounds that the value chosen for the pK_a of form (II) is too low, but to get acceptable agreement between k_9 and a limiting rate constant of 20 the pK_a of form (II) would have to be about 4. This would make the nitrogen in hydroxylamine only about 60 times as basic as the oxygen. General experience of the relative basicities of amino and hydroxyl groups would lead one to expect a value several powers of ten greater. Then, if form (II) is rejected, the mechanism appears to be electrophilic attack by the nitrous acidium ion on the ammonium group of form (I). This is unusual because there is no lone pair of electrons available for addition of the nitrosonium group. There is a precedent for this type of mechanism; Ridd and Challis[12] have observed electrophilic attack by the nitrous acidium ion on the conjugate acid of aniline, and of *p*-toluidine in moderately concentrated perchloric acid (up to 3M). The rate constants, k_3, when corrected for ionic-strength effects, are $0{\cdot}0049$ for aniline and $0{\cdot}028$ mole^{-2} l.^{2} sec.$^{-1}$ for *p*-toluidine.[13] It seems likely that similar mechanisms are involved. In an attempt

$$H_2NO_2^+ + NH_3{\cdot}OH^+ \longrightarrow \text{Transition state} \qquad (12)$$

to obtain further information about the structure of the transition state the deuterium solvent isotope effect was studied. It was found that at 5·2° the ratio $k_3(H_2O)/k_3(D_2O)$ was $1{\cdot}4$. Studies of the rate of formation of nitrosyl iodide in H_2O and D_2O indicate[13] that the equilibrium concentration of $D_2NO_2^+$ in D_2O is about twice the concentration of $H_2NO_2^+$ in H_2O at equal concentrations of D_3O^+ and H_3O^+. Thus in the formation of the transition state the replacement of protium by deuterium decreases the rate a factor of 3·8. This suggests that one of the bonds to hydrogen is substantially stretched in the transition state relative to the initial state. We suggest (A) for the structure of the transition state. The hydrogen atoms of the ammonium group in the hydroxylammonium ion will normally be bonded to adjacent water molecules. One of these will accept the proton that is expelled by the incoming nitrosonium group. In the diagram this is represented as B. The stereochemistry of the substitution is not known.



(A)

Rearrangements Leading to the Final Products.—So far the discussion has been concerned with the initial nitrosation, which presumably leads to the formation of $ON{\cdot}NH_2{\cdot}OH^+$ Subsequent rearrangements lead to the formation of nitrous oxide and small amounts of hyponitrous acid. There are not sufficient results available to permit detailed conclusions about the rearrangements, but it seems to be worth attempting a tentative explanation. The isotope results make it clear that a symmetrical intermediate is involved at low acidity.

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[11] Wynne-Jones and Mitchell, *Trans. Faraday Soc.*, 1956, **52**, 824.
[12] Ridd and Challis, *Proc. Chem. Soc.*, 1961, 173.
[13] Ridd, personal communication.

This cannot be *trans*-hyponitrous acid, which is stable under these conditions. The only likely alternative species appears to be *cis*-hyponitrous acid. This could be formed from $ON{\cdot}NH_2{\cdot}OH^+$ by a series of proton transfers $ON{\cdot}NH_2{\cdot}OH^+ \longrightarrow ON{\cdot}NH{\cdot}OH \longrightarrow ON{:}N{\cdot}OH^- \longrightarrow HO{\cdot}N{:}N{\cdot}OH$. We suggest that the hyponitrous acid formed is largely the *cis*-form which rapidly breaks down to nitrous oxide and water, leaving a small amount of the stable *trans*-form.

At higher acidities it seems an unsymmetrical species is involved, because the value of N'_{N_2O}/N'_{H_2O} rises from 0·50 to 0·60. This might be due to the change in mechanism from (6—9) to (12). Alternatively, if both involve the common intermediate $ON{\cdot}NH_2{\cdot}OH^+$, the change might be due to the effect of acidity on the rearrangements of this species. If the latter were the case, then as all nitrosating agents might reasonably be expected to yield $ON{\cdot}NH_2{\cdot}OH^+$, the isotopic results at a given acidity should be independent of the nitrosating agent. Work is in progress to check this point. The preliminary results on the yield of *trans*-hyponitrous acid provide further evidence. Nitrosation of free hydroxylamine by nitrosyl thiocyanate gives about 5% of *trans*-hyponitrous acid, while nitrosation by the nitrous acidium ion on the hydroxylammonium ion gives 2—3% together with some other product that absorbs ultraviolet light. It thus seems that the products are a function of mechanism and this suggests that the isotopic results may be so too.

EXPERIMENTAL

Materials.—" AnalaR " chemicals were used throughout.

Analytical Methods.—The nitrous acid concentration was measured colorimetrically by Ridd and Halevi's method.[14] It was found that hydroxylamine interfered at high concentrations; apparently free hydroxylamine attacked the diazonium ion during the coupling stage. This was overcome by carrying out the coupling with α-naphthylamine in an acetate buffer at pH 5·4 instead of in borax solution. At this pH the hydroxylamine remains mainly in the protonated form which does not react with the diazonium ion, while the naphthylamine remains as the free base and couples readily. The azo-dye is then in the acid form and may be gradually precipitated. This can be avoided by adding a saturated solution of borax, converting the dye into its conjugate base.

Hyponitrous acid was estimated by extracting the aqueous solution with ether and then re-extracting the ether solution with sodium hydroxide solution. The ultraviolet spectrum of the alkaline extract was measured on a Unicam S.P. 500 spectrophotometer and the concentration estimated from the intensity of the $N_2O_2^{2-}$ band at 2480 Å. These solutions also contained some other component or components that absorbed lower in the ultraviolet region. The tail of this absorption overlapped the hyponitrite peak, and reduced the accuracy.

Isotope analyses were carried out by Dr. C. A. Bunton of University College, London.

Kinetic Runs.—These were followed by conventional methods. Most of the runs were carried out at 0°, with an ice–water thermostat bath. Samples were taken at suitable time intervals, and the nitrous acid concentration estimated by the colorimetric method described above. It is well established that one mole of hydroxylamine is consumed for each mole of nitrous acid, and the 1 : 1 stoicheiometry was checked and confirmed several times during the present work.

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[14] Burton, Halevi, and Llewellyn, *J.*, 1952, 4913.