591. *Mechanism of the Azide–Nitrite Reaction. Part II.*[1]

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Reaction between nitrous acid and hydrazoic acid in the presence of a large excess of sodium azide–hydrazoic acid buffer at 0° occurred by a rate-determining nucleophilic attack by the azide ion on the nitrous acidium ion to form nitrosyl azide. This decomposed in a subsequent fast step to nitrogen and nitrous oxide. Added chloride, bromide, and thiocyanate ions catalysed the reaction, *via* the formation of the corresponding nitrosyl compounds. Each of these nitrosyl compounds was formed in a rate-determining step, and then reacted rapidly with the azide buffer to form nitrosyl azide, which then decomposed in a further fast step to nitrogen and nitrous oxide. Perchlorate and nitrate ions did not affect the rate of reaction, other than by a small salt effect. The relative nucleophilic reactivities of chloride, bromide, thiocyanate, and azide ions towards the nitrous acidium ion were 1 : 1·2 : 1·5 : 2·4. The results are compared with other investigations of the kinetics of reactions of nitrous acid and their significance is discussed.

It has been shown[1] that there are two mechanisms whereby the azide–nitrite reaction occurred in the presence of excess of perchloric acid:

$$NO_2^- + H_2NO_2^+ \xrightarrow[\text{slow}]{} N_2O_3 + H_2O \xrightarrow[\text{fast}]{N_3^-} N_3{\cdot}NO + NO_2^- \xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \; . \; . \quad (1)$$

$$HN_3 + H_2NO_2^+ \xrightarrow[\text{slow}]{} N_3{\cdot}NO + H_3O^+ \xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \; . \; . \; . \; . \; . \quad (2)$$

No sign was found of a mechanism that might have been expected to occur, *viz.*, nucleophilic attack by the azide ion directly on the nitrous acidium ion to form nitrosyl azide, followed by decomposition to nitrogen and nitrous oxide:

$$N_3^- + H_2NO_2^+ \xrightarrow[\text{slow}]{} N_3{\cdot}NO + H_2O \xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \; . \; . \; . \; . \quad (3)$$

The reason is that the reactivities of various anions as nucleophilic reagents towards the nitrous acidium ion cover only a small range. Chloride, bromide, thiocyanate, iodide, and

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[1] Stedman, Part I, preceding paper.

nitrite ions differ in reactivity by a factor of less than two.[2,3] It is, therefore, unlikely that the reactivity of the azide ion towards the nitrous acidium ion will be much greater. The dissociation constant of hydrazoic acid is about thirty-two times smaller than that of nitrous acid [4-6] at 0°. For equimolar amounts of the two acids, and in the presence of an appreciable excess of perchloric acid, the concentration of the azide ion will be thirty-two times lower than that of the nitrite ion. Hence the rate of reaction by (1) will be much greater than the rate of reaction by (3) in the region where $[H^+] < 0{\cdot}04\text{M}$. Above this acidity, reaction by mechanism (1) is unimportant,[1] but reaction by mechanism (2) becomes sufficiently important to give a much greater rate than (3). The present work was carried out with a large excess of sodium azide–hydrazoic acid buffer over nitrous acid. This ensured that $[N_3^-] \gg [NO_2^-]$, and hence that the rate of mechanism (3) > rate of mechanism (1). The low acidity of the buffer used, pH *ca.* 5, ensured that reaction by mechanism (2) was negligible.

Results.—Reaction was of first order in nitrite in all the runs carried out. All other species were present in a large and constant excess in any one run. The dependence of rate on acidity, concentration of added salts, ionic strength, etc., was found by comparing the first-order rate constants for various runs in which these quantities were varied. The results are given in Table 1.

TABLE 1. *Dependence of rate on azide buffer concentration and composition.*

Run No.	55	64	65	66	56
$10^2[HN_3]$ (M)	6·19	2·48	4·03	7·87	2·48
$10^2[N_3^-]$ (M)	3·81	7·52	5·73	2·29	1·52
$10^5[H^+]$ * (M)	1·65	0·334	0·71	3·47	1·65
$10^5 k_1$ † (sec.$^{-1}$)	8·09	0·70	2·25	21·6	3·15
$10^{-6} k_1/[H^+]^2[N_3^-]$ (sec.$^{-1}$ mole^{-3} l.^{3})	7·80	8·35	7·79	7·84	7·63

* Calculated from $[H^+][N_3^-]/[HN_3] = 1{\cdot}0 \times 10^{-5}$ mole l.$^{-1}$ (Hantzsch, *Ber.*, 1899, **32**, 3073; Seel and Schwaebel, *Z. anorg. Chem.*, 1953, **274**, 169). † Corrected for ionisation of nitrous acid.

Buffer of Sodium Azide and Perchloric Acid.—The rate was proportional to the buffer concentration at constant composition, and the results fitted the rate equation $v = k[H^+]^2[NO_2^-][N_3^-]$ as can be seen from the last line of Table 1. This equation can be rearranged to the form $v = k_3^{N_3^-}[H^+][HNO_2][N_3^-]$, with $k_3^{N_3^-} = 2500$ sec.$^{-1}$ mole^{-2} l.^{2}. This rate equation is consistent with two possible mechanisms. One is a rate-determining nucleophilic attack by the azide ion on the nitrous acidium ion to form nitrosyl azide, as in mechanism (3). The other is a rate-determining reaction between azide ions and an equilibrium concentration of nitrosonium ions to form nitrosyl azide (4):

$$H_2NO_2^+ \underset{\text{fast}}{\rightleftharpoons} NO^+ + H_2O \xrightarrow[\text{slow}]{N_3^-} N_3{\cdot}NO \xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \; . \; . \; . \quad (4)$$

These two possibilities cannot be distinguished on the basis of the evidence presented above. A distinction can be drawn by carrying out the reaction in water enriched in oxygen-18, and determining the isotopic composition of the evolved nitrous oxide. These experiments will be described in the later paper.[7] They show that isotopic abundance of the oxygen-18 tracer in the nitrous oxide is always much less than that of the water. This excludes the nitrosonium ion as a reaction intermediate. If reaction occurred as shown in equation (4) then nitrous acid would exchange oxygen atoms with water by the formation and rehydration of the nitrosonium ion much more rapidly than nitrous oxide was formed.

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[2] Hughes, Ingold, and Ridd, *J.*, 1959, 58.

[3] Seel, Wölfle, and Zwarg, *Z. Naturforsch.*, 1958, **13*b***, 136.

[4] Seel and Schwaebel, *Z. anorg. Chem.*, 1953, **274**, 169.

[5] Klemmenc and Hayeck, *Monatsh.*, 1929, **54**—**55**, 407.

[6] Hantzsch, *Ber.*, 1899, **32**, 3073.

[7] Bunton and Stedman, *J.*, to be published.

Thus, nitrous acid would come into isotopic equilibrium with the solvent much more rapidly than reaction with azide ions occurred, and hence the isotopic composition of the evolved nitrous oxide would be the same as that of the solvent.

TABLE 2. *Effect of added salts on the rate of the azide–nitrite reaction at* 0°.

Run No.	55	56	60	62	58	61	59	63
[Buffer] (M)	0·10	0·04	0·04	0·08	0·04	0·08	0·04	0·08
Salt added	—	—	$NaNO_3$	$NaNO_3$	NaBr	NaBr	NaCl	NaCl
[Salt] (M)	—	—	0·06	0·06	0·06	0·06	0·06	0·06
10^5k_1 (sec.$^{-1}$)	8·1	3·2	3·6	7·7	10·6	14·5	9·1	14·0
$10^5(k_1 - k_1{}^*)$ ...	—	—	—	—	7·0	6·8	5·5	6·3

$k_1{}^*$ is the value of k_1 for the same concentration of sodium nitrate, and at the same buffer concentration. For runs 58 and 59 $k_1{}^* = k_1$ for run 60. For runs 61 and 63 $k_1{}^* = k_1$ for run 62. $[HN_3]/[N_3^-] = 1{\cdot}63$ for all runs.

Hughes, Ingold, and Ridd[2] concluded that nitrosyl halides are formed in aqueous solution by nucleophilic attack of the halide ion on the nitrous acidium ion, and not on the nitrosonium ion. Their conclusion was based on a comparison of rates of diazotisation and oxygen exchange between nitrous acid and water, which were necessarily measured under very different conditions.[8] The present work provides direct support for their view; in this case the kinetic and isotopic results were obtained under very similar conditions.

Effect of Added Salts.—The effect of adding sodium perchlorate, nitrate, bromide, and chloride, and of potassium thiocyanate was investigated. The results are in Tables 2 and 3.

Buffer of Sodium Azide and Perchloric Acid.—The results in Table 2 show that sodium nitrate has only a small effect on the rate. This is what would be expected in view of its low nucleophilic power towards the nitrous acidium ion.[2,9] The small increase in rate due to addition of sodium nitrate is probably a salt effect.

Sodium bromide and sodium chloride produce much larger increases in rate. When the rate of uncatalysed reaction is subtracted from the total rate observed in the presence of bromide and chloride ions, the rate constant for the catalysed reaction alone is obtained. These values are in the fifth row of Table 2. (The rate of uncatalysed reaction has been taken as the rate observed for an equal concentration of added sodium nitrate, in order to allow for ionic strength effects.) It can be seen that for bromide ions the rate of catalysed reaction is independent of buffer concentration, while for chloride ions the rate of catalysed reaction is almost independent of buffer concentration. The bromide and chloride catalysis is due to a rate-determining formation of the corresponding nitrosyl compound, which reacts with azide buffer in a subsequent fast step to form nitrosyl azide which then decomposes to nitrogen and nitrous oxide:

$$Br^- + H_2NO_2^- \xrightarrow[\text{slow}]{} NO{\cdot}Br + H_2O \xrightarrow[\text{fast}]{\text{azide}} N_3{\cdot}NO + Br^- \xrightarrow[\text{fast}]{} N_2 + N_2O \quad . \quad . \quad . \quad (5)$$

It is not known whether the nitrosyl bromide reacts with azide ions or with hydrazoic acid. By analogy with dinitrogen trioxide,[1] one would expect the azide ion to be the reactive species. As, however, nitrosyl bromide is much more reactive than dinitrogen trioxide, hydrazoic acid may also act as a nucleophilic agent towards it. When the bromide- and chloride-catalysed reactions are carried out in water enriched in oxygen-18, the nitrous oxide evolved is only slightly isotopically enriched.[7] This again shows that reaction is not occurring between the nucleophilic anion and an equilibrium concentration of nitrosonium ions. A similar set of experiments to those summarised in Table 2 was carried out with use of a buffer of sodium azide and nitric acid. Nitric acid was used instead of perchloric acid because it was desired to study the effect of added potassium

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[8] Bunton, Llewellyn, and Stedman, *J.*, in the press.

[9] Bunton, Halevi, and Llewellyn, *J.*, 1953, 2653; Stedman, Thesis, London, 1955.

thiocyanate on the rate of reaction, and this avoided difficulties due to the low solubility of potassium perchlorate. The results are given in Table **3**.

TABLE **3**. *Effect of added salts on the rate of the azide–nitrite reaction at* 0°.

Run No.	[Buffer] (M)	[Added salts]	$10^5 k_1$ (sec.$^{-1}$)	$10^5(k_1 - k_1^*)$ (sec.$^{-1}$)
75	0·0615	—	5·7	—
79	0·0615	0·0615M-$NaNO_3$	6·3	—
80	0·0615	0·0615M-$NaClO_4$	6·1	—
76	0·0615	0·0615M-KNCS	16·6	10·4
84	0·0615	0·0615M-KNCS	16·5	10·3
77	0·0615	0·0615M-NaBr	14·1	7·9
78	0·0615	0·0308M-NaBr + 0·0308M-$NaClO_4$	10·3	4·1
83	0·0308	0·0923M-$NaClO_4$	3·2	—
85	0·0308	0·0308M-$NaClO_4$ + 0·0615M-KNCS	12·3	9·1
86 †	0·0615	0·0615M-$NaClO_4$	8·3	—
87 †	0·0615	—	7·6	—
82 †	0·0615	0·0615M-NaBr	13·3	—
90	0·117	—	12·1	—

k_1^* is the first-order rate constant observed for reaction when the catalysing salt, NaBr or KNCS, is replaced by an equal concentration of $NaNO_3$ or $NaClO_4$. For runs 76, 77, 78, and 84, k_1^* is the mean of k_1 for runs 79 and 80, *i.e.* 6·2 × 10^{-5} sec.$^{-1}$. For run 85, k_1^* is k_1 for run 83, *i.e.* 3·2 × 10^{-5} sec.$^{-1}$. In runs 82, 86, and 87, $[HN_3]/[N_3^-] = 2·23$. For all other runs $[HN_3]/[N_3^-] = 1·63$.

Comparison of runs 79 and 80 with run 75 shows that addition of 0·06M-sodium nitrate and sodium perchlorate has no large effect on the rate. There is a small increase in rate, *ca.* 10%, which is due to a salt effect. Addition of 0·06M-potassium thiocyanate produces a very much larger increase in rate. If the rate of the thiocyanate-catalysed reaction is obtained by subtracting from the value of k_1, for the total reaction, the value of k_1^*, for reaction in the presence of an equal concentration of added sodium perchlorate or nitrate, it is found that the rate of the thiocyanate-catalysed reaction is almost independent of buffer concentration. In runs 77 and 78 all factors were kept constant except the bromide-ion concentration, which was varied by a factor of two. The results in Table **3** show that the rate of the bromide-catalysed reaction is proportional to the bromide-ion concentration.

There is little doubt that the chloride, bromide, and thiocyanate catalysis of the azide–nitrite reaction is due to a rate-determining formation of the nitrosyl compound, followed by a rapid reaction with the azide buffer to give nitrosyl azide; this breaks down in a subsequent fast step to form nitrogen and nitrous oxide. This is shown in equation (5). The exact value of the rate constant for the nitrosyl compounds depends on the value taken for the dissociation constant of hydrazoic acid (in order to calculate the pH of the buffer), and the value of the dissociation constant of nitrous acid (in these buffers most of the nitrite is present as nitrite ion, whereas the value of $[HNO_2]$ is required for insertion into the rate equation). As most of these results were obtained in buffers of constant composition it is possible to obtain the relative nucleophilic reactivities of the various catalysing anions by dividing the rate constant for the catalysed reaction alone by the concentration of the catalysing anion. This gives the ratio

$$k_3^{Cl^-} : k_3^{Br^-} : k_3^{NCS^-} : k_3^{N_3^-} :: 1 : 1·2 : 1·5 : 2·4$$

These values are in good agreement with those obtained [2,8] from studies of diazotisation, $k_3^{Br^-} : k_3^{NCS^-} :: 1·2 : 1·55$. The actual values of the rate constants are $k_3^{Br^-} = 1250$ sec.$^{-1}$ mole^{-2} l.^{2} and $k_3^{NCS^-} = 1560$ sec.$^{-1}$ mole^{-2} l.^{2}, and these are in good agreement with the values obtained [2,8] from diazotisation, 1170 and 1500 sec.$^{-1}$ mole^2 l.$^{-2}$, respectively. One should not attach too much significance to the numerical agreement, because the rate constants obtained in the present work depend for their absolute values on the square of the dissociation constant of hydrazoic acid, and on the reciprocal of the dissociation constant of nitrous acid. These dissociation constants are subject to considerable possible error, and hence the absolute values of the rate constants are also subject to this error.

The relative values should be unaffected. If the relative reactivities of chloride, bromide, thiocyanate, and azide ions are taken as accurate, and if the value for $k_3^{\mathrm{Br}^-}$ is taken [2] as 1170 sec.$^{-1}$ mole^{-2} l.^{2}, then the values of $k_3^{\mathrm{Cl}^-}$, $k_3^{\mathrm{NCS}^-}$, and $k_3^{\mathrm{N}_3^-}$ are 975, 1460, and 2340 sec.$^{-1}$ mole^{-2} l.^{2} at 0°.

The small difference in nucleophilic reactivity of the azide and chloride ions furnishes strong evidence for the high reactivity and low selectivity of the nitrous acidium ion and it would seem that the breaking of the nitrogen–oxygen bond is much more important than the formation of the new bond with the incoming nucleophilic reagent. The very low reactivity of the nitrate ion may be due to there being no free lone pair of electrons on the nitrogen atom, the *p* electrons forming a double bond with the more electronegative oxygen atoms, and resonating among the three possible positions.

The value of $k_3^{\mathrm{Cl}^-}$ is of some interest, as kinetic investigations of the mechanism of diazotisation were not able to provide data on the rate of substitution of this ion at the nitrous acidium ion to form nitrosyl chloride. Previous work had shown that chloride ions had a much lower catalytic effect on the rate of diazotisation than had an equal concentration of bromide ions. The present results show that this is not due to a much lower rate of formation of nitrosyl chloride than of nitrosyl bromide, and that the different catalytic effects must be due to different ratios of the reactivity of the nitrosyl halides towards water and the amine being diazotised. The results are in interesting contrast to those of Allen,[10] who studied the halide-catalysed hydrolysis of alkyl nitrites in aqueous dioxan. He found that for reaction (6):

$$\mathrm{X^- + Pr^nO{\cdot}N{\cdot}OH^+ \longrightarrow NO{\cdot}X + Pr^n{\cdot}OH + H^+ \ (X = Cl\ or\ Br)} \quad . \ . \ . \ . \ . \quad (6)$$

the relative reactivities of chloride and bromide ions were 1 : 0·7. Bunton and Masui [11] studied the same reaction in water, and found that the relative reactivities are chloride ion : bromide ion :: 1 : 1·2, as in the present work. The reason for this reversal in relative reactivities between water and aqueous dioxan is not clear.

Seel and his co-workers [3] have studied the effect of adding salts on the rate of the azide–nitrite reaction.[4] Their results for chloride and bromide are in agreement with those of the present work, but they claim that the nitrate ion has a nucleophilic reactivity of one half that of the bromide ion. This is at variance with Abel's work on the decomposition of nitrous acid,[12] and with the present work. The discrepancy may be due to the fact that Seel and his co-workers worked at an ionic strength of 1·2M where specific salt effects may vary by amounts similar to the small differences in nucleophilic reactivity of various anions.

EXPERIMENTAL

Materials.—The materials used were the same as those described in the previous paper.[1]

Kinetic Measurements.—The procedure was similar to that described earlier,[1] except that reaction was started by adding ice-cold sodium nitrite solution to the cooled azide buffer, instead of acidifying an azide–nitrite solution. Reaction was stopped by adding the sample to an excess of concentrated sodium hydroxide solution, and the amount of reaction determined by measuring the light absorption due to the nitrite ion, at 3520 Å, a Unicam spectrophotometer with 4-cm. silica cells being used. A slight background absorption due to the nitrate ion was corrected for by use of a blank solution.

Calculations.—In order to calculate the values of the rate constants $k_3^{\mathrm{N}_3^-}$, $k_3^{\mathrm{Br}^-}$, etc., it is necessary to know the values of [H$^+$] and of [HNO$_2$]. The values of [H$^+$] were calculated from the known composition of the buffer, and from the value for the dissociation constant of hydrazoic acid of $1{\cdot}0 \times 10^{-5}$M at 0°. This is an old value due to Hantzsch [6] but is believed to be reliable. Hantzsch measured the dissociation constants conductometrically and obtained values of $1{\cdot}0 \times 10^{-5}$ at 0° and $1{\cdot}9 \times 10^{-5}$ at 25°. The latter is in good agreement with the

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[10] Allen, *J.*, 1954, 1968.

[11] Bunton and Masui, personal communication.

[12] Bray, *Chem. Rev.*, 1932, **10**, 161.

modern values 2·04 × 10^{-5} at 25° (ref. 4), and 2·1, 2·2, and 1·9 × 10^{-5} at 25° (ref. 13). West [14] obtained a value 1·7 × 10^{-5} at 25°, again conductometrically, and Hantzsch's value at 0° can be compared with another conductometric value at 0°, 0·8 × 10^{-5}, due to Oliveri-Mandala'.[15]

These results underline the reliability of the value of 1·0 × 10^{-5} for the dissociation constant of hydrazoic acid at 0°, even though it is an early one. It is important to establish this value, as it is desirable to compare the values of $k_3^{\mathrm{Br}^-}$ and $k_3^{\mathrm{NCS}^-}$ obtained in this work with those obtained in other investigations.

First-order rate constants, k_1, were obtained from the slopes of conventional plots of $\log_{10}$ [nitrite] against time.

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[13] Tui, *Bull. Inst. Phys. Chem. Res., Tokyo*, 1941, **20**, 390.

[14] West, *J.*, 1900, 705.

[15] Oliveri-Mandala', *Gazzetta*, 1916, **46**, I, 298.